Quality Assurance Report
National Atmospheric Deposition Program
2010

Laboratory Operations
Central Analytical Laboratory

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Acknowledgments

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Tables and Figures

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^-), 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 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. In 2010, the same Flow Injection Analysis (FIA) used for NTN and AIRMoN ammonium quantification was also used for AMoN.

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
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 2010

- Stacey Henson qualified for back-up filtering duties (April 2010).
- Kim Attig qualified as an ICP-OES operator (April 2010).
- Tracy Dombek assumed duties as a CAL Quality Assurance and Data Specialist (May 2010).
- Tanya Grandt qualified for pH/conductivity measurements (June 2010).
- Tanya Grandt qualified for back-up filtering duties (June 2010).
- Tanya Grandt qualified for supply cleaning (October 2010).
- New FIA was received and an evaluation has commenced (August 2010).
- Tanya Grandt qualified as a back-up IC operator (November 2010).
- Buckets and bottles were sprayed with hydrogen peroxide before they were placed in the dishwasher (September 2010).
- NTN filters were condition-rinsed with 10 mL of sample (November 2010, sample TI0802SW).
- Bromide continued evaluation as a new IC analyte (June 2009–present).

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, blind samples, and split samples. For split samples, approximately 1 percent of samples are saved in their original 1 L shipping bottle and resubmitted with a new laboratory number one week after the original submission. The two samples are compared for reproducibility.

Accuracy is a measure of correctness and how closely the data represent the true value. Accuracy is evaluated through the use of verified standards 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/duplicate samples, 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 and new supplies 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 internal verification standards termed "faux rain" (FR) as dedicated matrix spike solutions with target concentrations that represent the 10^{th} , 25^{th}, 75^{th}, and 95^{th} percentile levels of analytes measured in NTN rain water samples (designated as FR10, FR25, FR75, and FR95, respectively). These solutions contain all CAL analytes except for orthophosphate, and are used for quality control. Orthophosphate standards are purchased from the Environmental Resource Association[1] and diluted as necessary. The target concentrations are shown in Table 2 for orthophosphate and Table 3 for all other analytes. A high calibration standard control solution is targeted for the 99^{th} percentile level, and the lowest calibration standard for each analyte is monitored daily on control charts.

To set annual control chart limits, solutions are measured at least seven times, and the average of these results becomes the target value for the control chart. Control limits are calculated using two times the standard deviation (2σ) for the warning limits and 3σ for the control limits. Control chart limits are monitored daily using FR solutions. When results for daily control solutions fall outside of control limits, analysis of the affected samples is repeated.

Control limits are used by the QA chemist to evaluate the instruments and analysts' performance when analyzing internal blind samples. Four different solutions are used for the internal blind study: deionized water (DI), two of the internally prepared simulated rain solutions targeted for the $10^{th}$and 95^{th} percentile concentration levels of all analytes, except for orthophosphate (FR10 and FR95), and an external certified reference sample AES-05 purchased from the RTC[2].

For NTN, internal blind samples are submitted weekly at an interval of approximately one set per every 75 samples and include all four internal blind solutions. For AIRMoN, one internal blind sample is analyzed per week and that solution is always the FR95 solution. Blind samples are given a unique laboratory identification number. Internal blind filtered samples were submitted in standard 1 L bottles used for NADP sites, and thus the samples are considered blind to all analysts.

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[1] Environmental Resource Association, 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 or project sponsors.

Table 2. Orthophosphate control solutions concentrations

	Low standard	High standard
Orthophosphate (ppm)	0.027	0.143

Table 3. Target Concentrations for Control and Internal Blind Solutions

	10th percentile Target concentration	25th percentile Target concentration	75th percentile Target concentration	95th percentile Target concentration	AES-05 Target concentration
CAL Designation	FR10	FR25	FR75	FR95	AES-05
pH	5.16	4.94	4.70	4.09	4.89
Specific Conductance (µS/cm)	3.7	6.4	16.1	63.1	10.8
Calcium (ppm)	0.026	0.047	0.237	0.564	0.186
Magnesium (ppm)	0.004	0.008	0.044	0.189	0.037
Sodium (ppm)	0.008	0.017	0.136	1.506	0.181
Potassium (ppm)	0.004	0.008	0.034	0.105	0.027
Chloride (ppm)	0.026	0.047	0.240	2.595	0.226
Sulfate (ppm)	0.210	0.468	1.691	5.524	1.28
Nitrate (ppm)	0.263	0.515	1.653	4.904	1.15
Ammonium (ppm)	0.037	0.096	0.465	1.187	0.311

A second batch of FR25 is prepared for the exclusive use of supply checks (labeled as FR25B). In addition, checks are made weekly of the DI water used to wash the supplies and the polisher water used to prepare reagents and for sample dilutions. The maximum allowable levels for weekly blank checks shown in Table 4 were determined using historic measurements of DI and FR10 internal blind solutions. When measured concentrations exceed the limits listed in Table 4, the sample is reanalyzed. If the limits are exceeded again, the supply in question is rewashed and rechecked. If the supply is a new supply such as a bag, another bag from the same lot number is checked. A summary of the weekly supply checks is shown in Table 5. There are two sets of target values for FR25B for 2010 because additional solution was needed to test supplies. Table 4 also includes the 5th percentile concentrations measured in NTN precipitation samples.

Table 4. Target Concentrations for Weekly Supply Checks

Analyte	Target DI Blanks	5th percentile Concentration for all analytes	FR25B Target Concentration Week 1-43	Limits for FR25B Week 1-43	FR25B Target Concentration Week 44-51	Limits for FR25B Week 44-51
pH	5.35-5.95	4.27	4.97	4.79-5.15	4.99	4.81-5.17
Specific Conductance (µS/cm)	<2.0	3.1	6.8	6.0-7.6	7.3	6.5-8.1
Calcium (ppm)	<0.009	0.021	0.048	0.039-0.057	0.048	0.039-0.057
Magnesium (ppm)	<0.003	0.003	0.009	0.006-0.010	0.009	0.007-0.011
Sodium (ppm)	<0.003	0.006	0.017	0.014-0.020	0.017	0.013-0.020
Potassium (ppm)	<0.003	0.004	0.008	0.005-0.011	0.008	0.005-0.011
Chloride (ppm)	<0.008	0.020	0.049	0.040-0.057	0.048	0.039-0.056
Sulfate (ppm)	<0.008	0.1271	0.471	0.437-0.505	0.486	0.452-0.520
Nitrate (ppm)	<0.010	0.156	0.522	0.480-0.564	0.533	0.491-0.575
Ammonium (ppm)	<0.020	0.010	0.097	0.077-0.117	0.099	0.079-0.119
Orthophosphate (ppm)	<0.008	NA	NA	NA	NA	NA

Table 5. Summary of Supply Check Frequencies

Description of blank sample	Volume and solution	Frequency
RO	Supply preparations laboratory	Weekly
Polisher DI	FIA laboratory	Monthly
	ICP-OES laboratory	
	IC laboratory	
	Sample Preparations laboratory	
Washed Buckets	50 mL DI water x2	Weekly
	50 mL FR25B solution x2	
	150 mL FR25B solution x2	
	300 mL DI water x2	
Washed NTN 1 L Bottles	50 mL DI water x2	Weekly
	150 mL DI water	
	50 mL FR25B solution x2	
	150 mL FR25B solution	
Filters	50 mL DI water	Weekly
	50 mL FR25B solution	
Lids	50 mL DI water	Weekly
	50 mL FR25B solution	
Lid Bags	50 mL DI water	Bi-weekly
	50 mL FR25B solution	
Bucket Bags	50 mL DI water	Bi-weekly
	50 mL FR25B solution	
New AIRMoN 250 mL Bottles	50 mL FR25B solution	Monthly
	150 mL FR25B solution	

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. The CAL uses the FR10 standard to determine MDLs for sodium, calcium, magnesium, potassium, ammonium, conductivity, and pH. (Conductivity and pH do not have defined MDLs; instead, the value is calculated based on a measure of long-term variability.) All FR10 samples used to determine MDLs are blind to the analyst, except for pH and conductivity. The MDL study for the Ion Chromatograph utilizes the lowest calibration standard for sulfate, nitrate, and chloride. That sample is given a unique label and is analyzed bimonthly by the IC analyst.

The FIA analyst prepares a check solution for orthophosphate and analyzes this sample bimonthly. The FIA analyst continued to experience problems with the instrument during 2009 and 2010. The instrument detection limit (IDL), calculated using a blank solution, was reported to be higher than the MDL for both orthophosphate and ammonium. A special study was completed on the FIA to determine new detection limits in 2010. The MDLs for the FIA were found to be higher than the reported values in 2009; the new values listed in Table 6 now exceed instrument detection limits as would be expected.

The results for all MDL study samples are compiled for an entire year and used to compute the method detection limit for the upcoming year. The solutions measured during 2009 were used to calculate MDLs for 2010. Standard deviations for the MDL samples are multiplied by Student's t value for the 99 percent confidence interval to compute the MDLs. The MDLs for 2010 are shown in Table 6 and were provided to the NADP Program office.

Table 6. MDLs for 2010

Analyte	MDL (ppm)
Calcium	0.004
Potassium	0.001
Magnesium	0.001
Sodium	0.001
Chloride	0.003
Nitrate	0.005
Sulfate	0.004
Ammonium	0.010
Orthophosphate	0.008

Control Charts

In 2010, control charts met all Data Quality Objectives (DQOs) as defined in the CAL QAP.

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 25th percentile solution. Box and whisker plots, as shown in Figure 1, identify outliers. The box identifies the 1st, 2nd, and 3rd quartiles of the data. The whisker illustrates 1.5 times the box. "X" designates points that statistically are outliers. When shaded areas are all gray, there is no difference between the 1st quartile and median. When shaded areas are all blue, there is no difference between the 3rd quartile and median.

Polisher and RO DI Blanks

The polisher and RO DI water blanks met all acceptance criteria for 2010 (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 2010

Parameter	Polisher DI N=52	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 FR25B

Low levels of sodium and chloride were detected in DI water eluent from NTN sample filter supply tests. The concentrations of sodium and chloride (Table 8) were typically less than the 5th percentile of NTN sample concentrations. This is not a new issue. In 2009 sodium and chloride were

detected in DI water eluent from NTN sample filters. The median concentration of sodium found on filters was 0.001 ppm, and the median concentration of chloride found on filters was 0.007 ppm. Box and whisker plots for sodium and chloride are shown below in Figure 1. Box and whisker plots for calcium sodium and chloride measured in FR25B solutions are show in Figure 2.

Calcium was detected on some filters; calcium has also been detected on filters in previous years. The target limits were exceeded with the FR25B tests only (Table 8). The FR25B filter blanks indicated losses exceeding the set target limits for magnesium (Table 8), but the losses are small in magnitude, ≤ 1 ppb and within the noise of the instrument.

The levels of sodium, chloride, and calcium found when leaching filters with both DI and FR25B are relatively small. Whenever sample volume allows, filters are condition rinsed with sample prior to sample collection. (See SOP PR-1055.14 for details.) The CAL started this as a precautionary measure. The CAL began rinsing the filters with excess sample during November 2010. Initially, filters were rinsed with 10 to 20 mL of sample. Results indicated small differences for calcium, sodium, and chloride so the rinse was increased to 50 mL for samples with volumes greater than 200 mL. For samples with volumes greater than 100 mL, but less than 200 mL, the rinse consists of approximately 20 mL of sample in order to have an adequate amount of sample for analyses. It is likely that lower volume samples generally have higher concentrations of analytes and therefore mask any filter contamination.

Table 8. Number of Results Outside of Target Limits in 2010 for Filter Blanks

Parameter	DI N=52	FR25B N=52
pH	0	0
Specific Conductance	0	0
Calcium	0	5
Potassium	1	0
Magnesium	0	2
Sodium	14	0
Chloride	19	0
Sulfate	0	2
Nitrate	0	0
Ammonium	0	0
Orthophosphate	0	NA

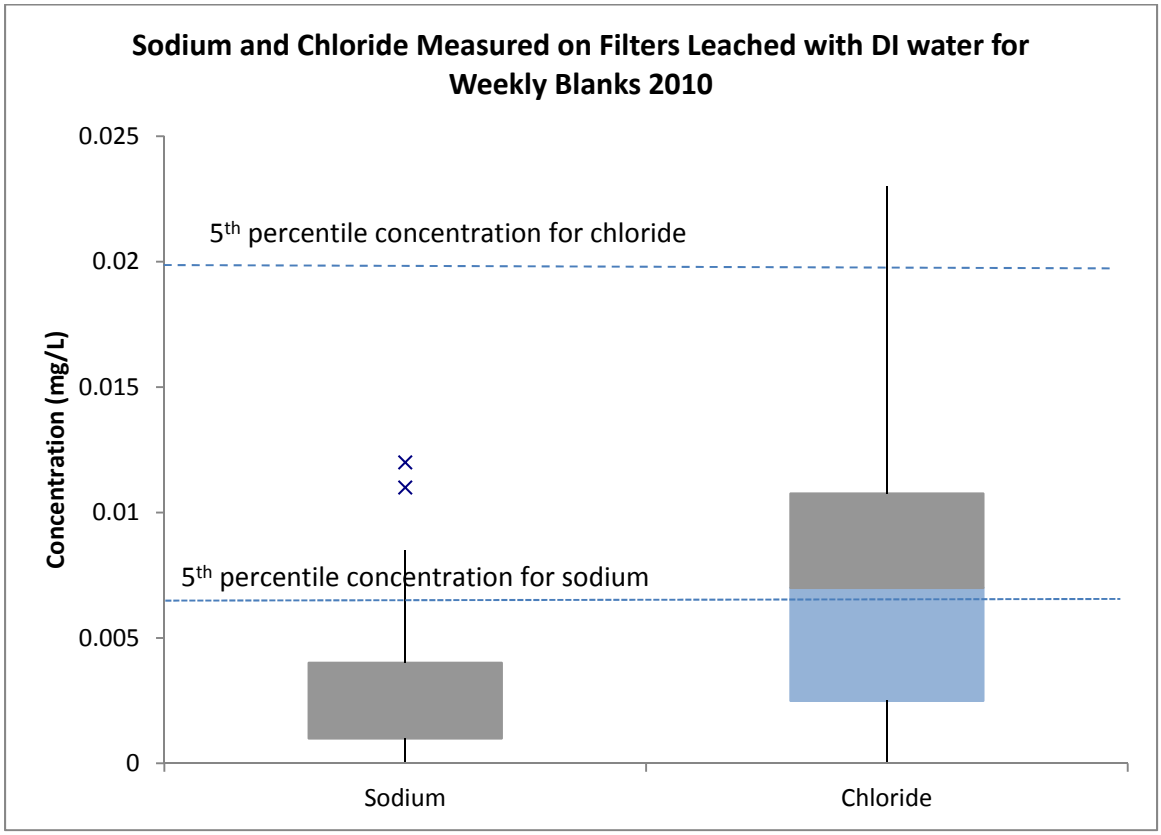

Figure 1. Box and whisker plot of sodium and chloride measured in filters leached with DI water for weekly blanks in 2010

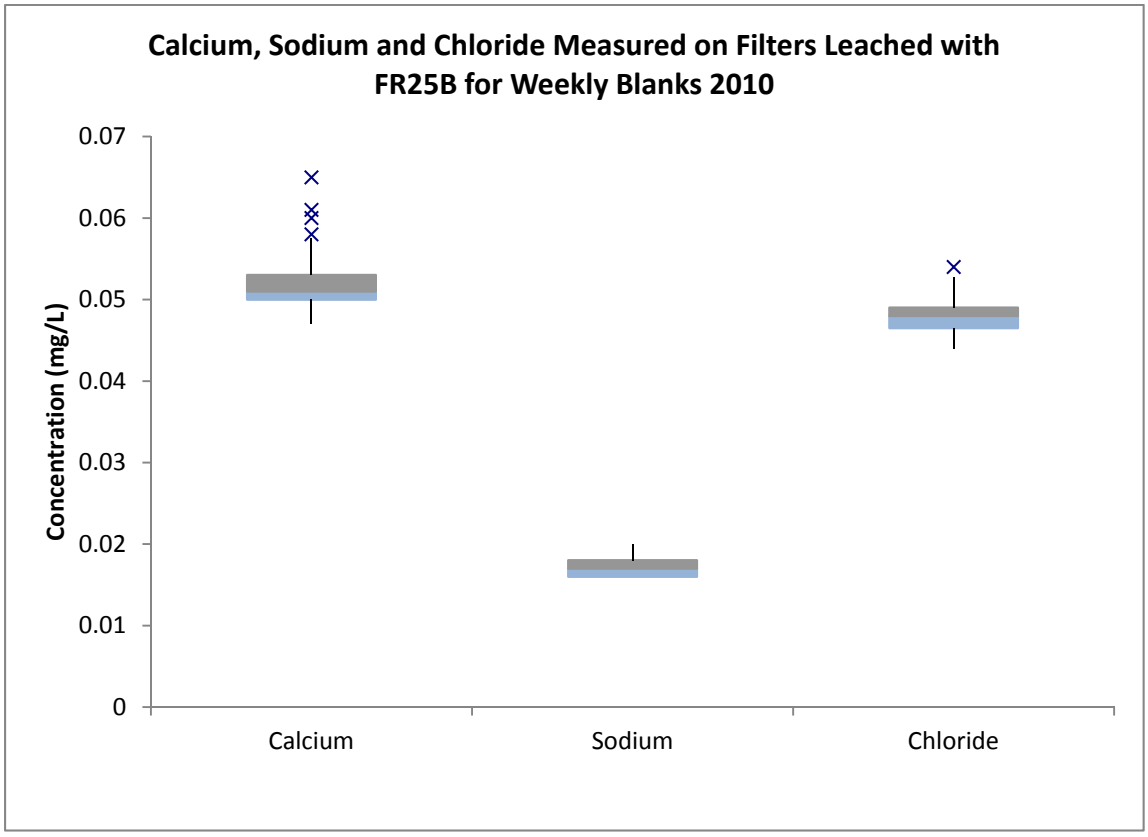

Figure 2. Box and whisker plot of calcium, sodium, and chloride measured in filters leached with FR25B for weekly blanks in 2010. See Table 4 for FR25B concentrations

Buckets, Bottles, and Lids

When the analyte concentration for supplies that are washed and reused (eg., buckets, lids, and standard NTN 1 L bottles) exceed the target levels, they are rewashed and rechecked. If the supply does not pass the second check, it is discarded.

The same buckets are used for both NTN and AIRMoN for sample collection. In 2009, primarily 50 mL and 150 mL of solution were used to test blanks. Since approximately 5 percent of NTN samples and 15 percent of AIRMoN samples have a volume of 50 mL, an additional volume of 300 mL was added in 2010. As anticipated, the background concentration for some analytes for the 50 mL DI bucket blanks were higher than the 300 mL bucket blanks. The number of samples exceeding the expected control limits is shown in Table 9. The results for analytes with the largest differences are shown in Figures 3 & 4. The number of outliers was significant for conductivity, chloride, and ammonium. About one-half of the buckets tested had conductivity readings that exceeded acceptance limits; however, all of the results were below the 5th percentile concentration measured in NTN samples. For ammonium and

chloride, about one-third of the samples had outliers. The chloride background observed was always below the median concentration measured in 5 percent of NTN samples. The ammonium background observed in 50 mL samples was sometimes higher than the 5th percentile concentration measured in NTN samples. Outliers in Figure 4 were identified by the month that the samples were measured to look for a seasonal tendency. Elevated ammonium can be found at different times throughout the year and is not specific to a season. The number of outliers identified with FR25B bucket blanks for ammonium (Table 9) is consistent with the number found for ammonium in the 50 mL DI samples. Only seven of these outliers were found to be higher than the control limits. The remaining outliers were lower than the control limits.

Table 9. Number of Results Outside of Target Limits in 2010 for Bucket Blanks

Parameter	50 mL DI N=104	300 mL DI N=104	50 mL FR25B N=104	150 mL FR25B N=104
pH	0	0	0	0
Specific Conductance	46	0	2	1
Calcium	3	0	2	0
Potassium	0	0	1	2
Magnesium	1	1	1	2
Sodium	1	0	2	0
Chloride	27	1	3	1
Sulfate	1	0	6	1
Nitrate	4	0	7	1
Ammonium	21	3	23	10
Orthophosphate	1	0	NA	NA

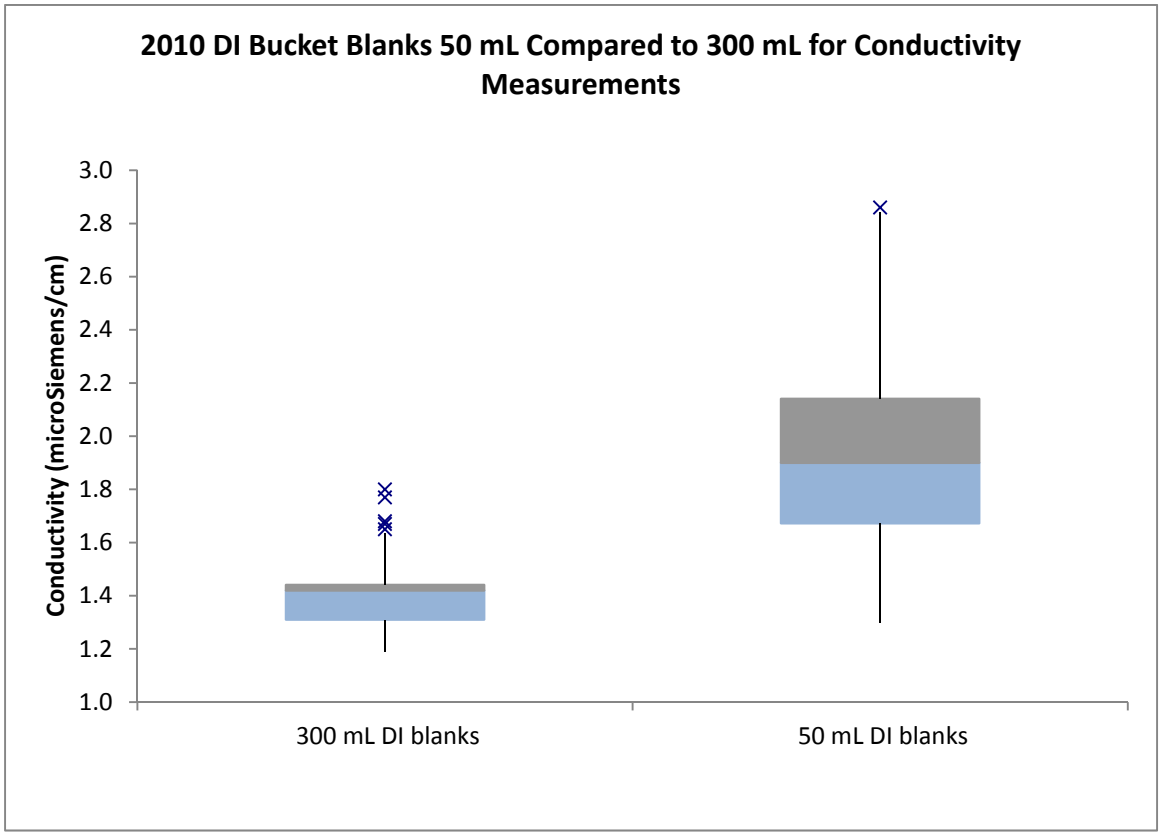

Figure 3. Box and whisker plot comparing the differences for conductivity measurements between 50 mL and 300 mL DI bucket blanks

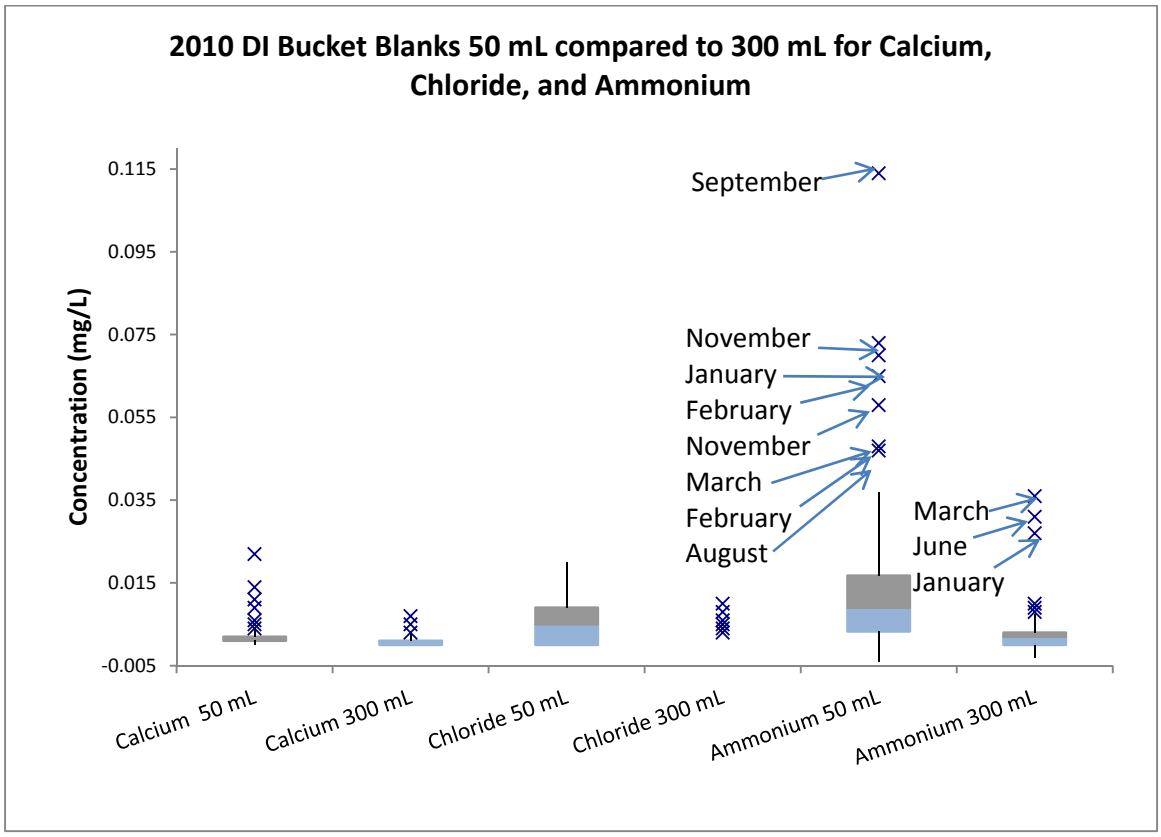

Figure 4. Box and whisker plot of calcium, chloride, and ammonium concentrations measured in 50 mL DI bucket blanks and 300 mL DI bucket blanks. Ammonium outliers were identified by the month to evaluate for a possible temporal influence.

Results were compared between buckets checked with 50 mL FR25B and 150 mL FR25B (Figure 5). All of the outliers were outside of the low control limits for the 150 mL samples. It was speculated that this may be due to a bacterial component that is surviving the wash cycle. Beginning in September 2010, buckets were soaked with hydrogen peroxide (H_2O_2). The H_2O_2 was applied using a spray bottle. The concentration as well as exposure time of the H_2O_2 solution was adjusted as ammonium losses continued to be observed with FR25B bucket blanks. In December, the decision was made to spray buckets with 3% H_2O_2 and allow them to sit at least 10 minutes prior to loading them into the dishwashers. Since that time, no significant losses of ammonium have been observed in the bucket blanks. Statistical results in the box and whisker plots are reflective of buckets prior to the addition of H_2O_2 and after the addition of H_2O_2. Given that samples may not have the elevated levels of contamination during the winter months, the effectiveness of the H_2O_2 spray will continue to be monitored and adjusted as necessary, particularly during periods when the potential for contamination in samples is higher.

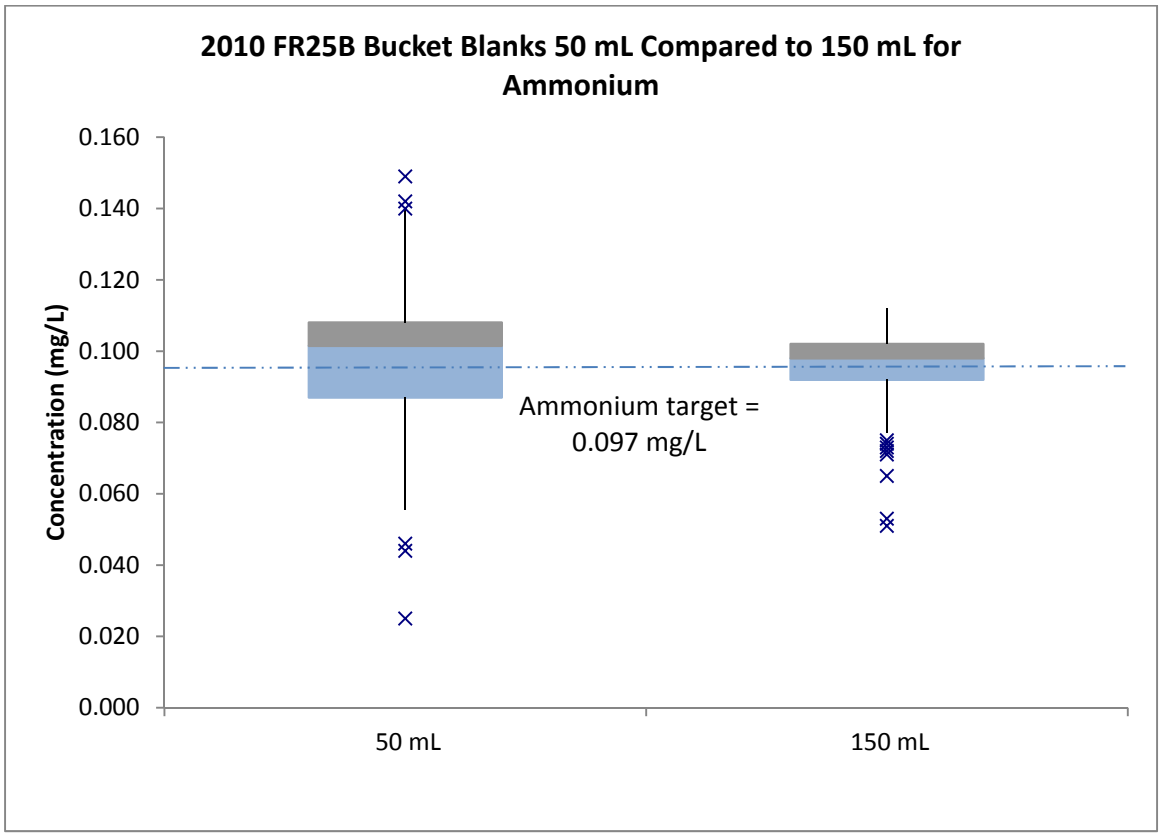

Figure 5. Box and whisker plot comparing ammonium measurements with 50 mL and 150 mL FR25B bucket blanks during 2010

A few outliers were observed for both sulfate and nitrate recovery in FR25B bucket blanks (Figure 6). It was a greater problem with the 50 mL blanks than the 150 mL blanks. These buckets were rewashed and rechecked and discarded as necessary.

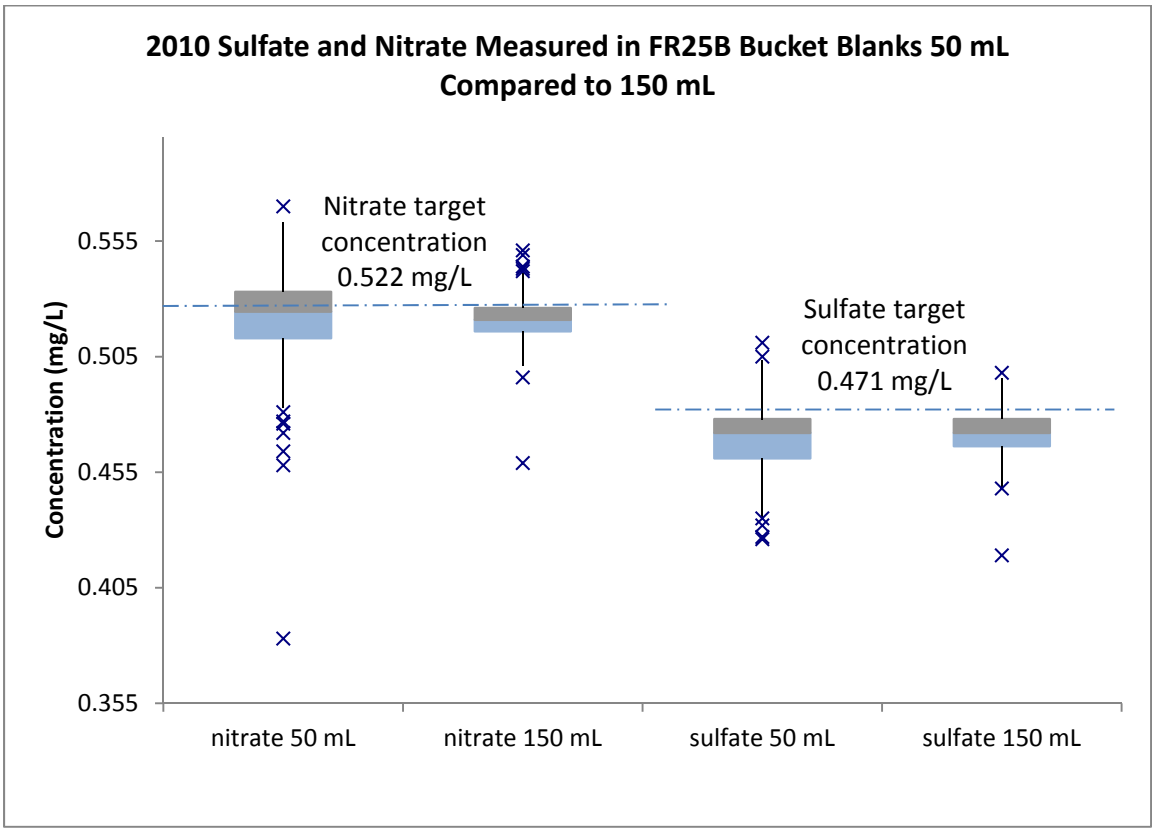

Figure 6. Box and whisker plot comparing sulfate and nitrate measured in FR25B bucket blanks during 2010

Small amounts of sodium and chloride were detected in lid blanks (Table 10). It is possible that the sodium found on the lids is from the lid bags. In further bag testing, sodium is present at concentrations which randomly exceed control limits. There is no counter ion that the CAL measures associated with this sodium observed in the samples. Lids stored in the bags were also found to have elevated levels of sodium which exceed control limits randomly. There is no counter ion that the CAL measures associated with the sodium observed in lid blanks. This suggests that the sodium found on the lids originates from its storage in the bags. The outliers observed in Figure 7 are within a few ppb of the control limits. As a precaution, new lid bags are being evaluated.

Table 10. Number of Results Outside of Target Limits in 2010 for Bucket Lids

Parameter	DI N=52	FR25B N=52
pH	0	1
Specific Conductance	0	0
Calcium	0	0
Potassium	1	2
Magnesium	0	0
Sodium	3	6
Chloride	3	0
Sulfate	1	0
Nitrate	0	0
Ammonium	1	2
Orthophosphate	0	NA

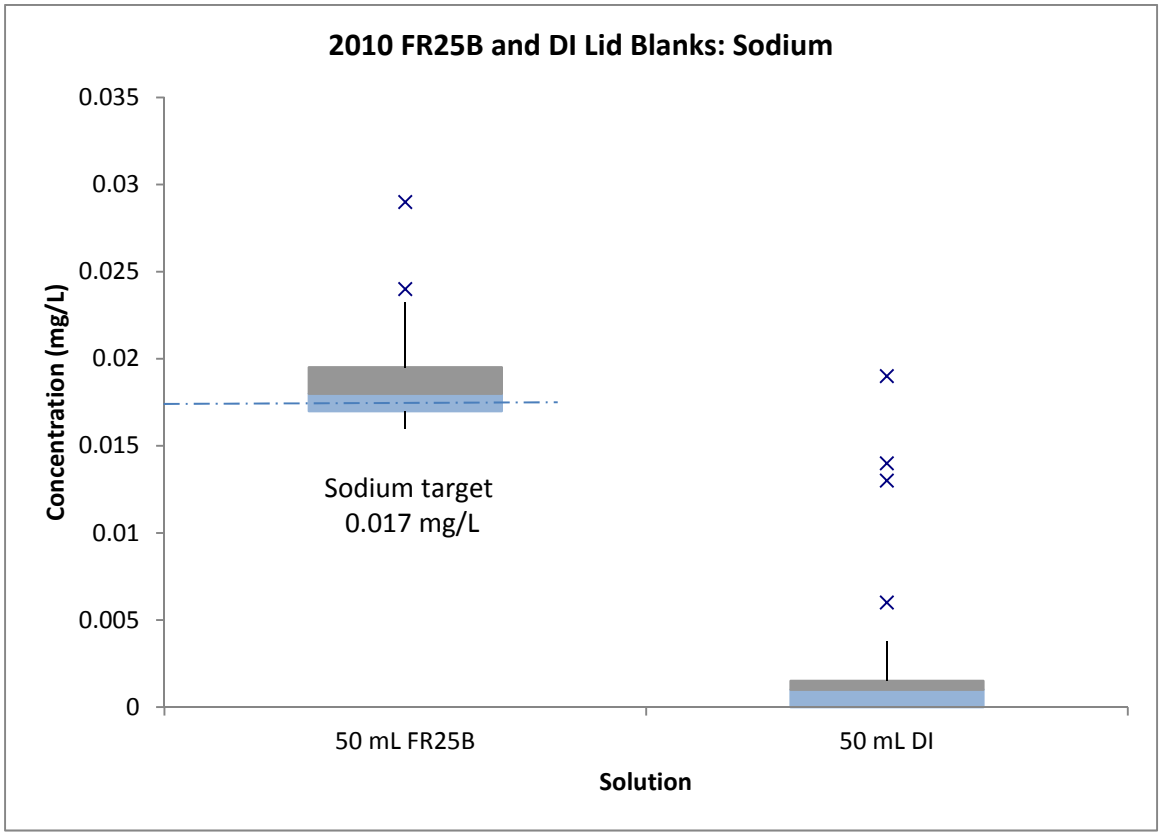

Figure 7. Box and whisker plot comparing sodium measured in FR25B and DI 50 mL lid blanks during 2010

During 2010, 1 L bottle blanks (Table 11) were found to have problems with ammonium. This was observed primarily with the 50 mL solution. Most of the problems were with loses of ammonium. When a loss of ammonium was observed in a 1 L bottle, there was also a small but measurable loss of potassium. This suggests that there may be a bacterial component that is not being removed during the wash cycle. Figure 8 illustrates the differences between 50 mL and 150 mL bottle blanks. The same H_2O_2 treatment was also added to the bottles in 2010. (See SOP PR-0009.13 for details.) Two samples were found with excessive ammonium, and it was thought that the contamination was due to carry-over from the previous sample. One of the samples also contained orthophosphate. These bottles were discarded.

Table 11. Number of Results Outside of Target Limits for Standard NTN 1 Liter Bottles to which 50 mL and 150 mL aliquots of DI and FR25B were added

Parameter	DI 50 mL N=102	DI 150 mL N=51	FR25B 50 mL N=102	FR25B 150 mL N=51
pH	0	0	1	0
Specific Conductance	2	0	1	0
Calcium	0	0	1	0
Potassium	1	0	3	0
Magnesium	0	0	2	0
Sodium	0	0	0	0
Chloride	5	0	0	0
Sulfate	4	0	0	0
Nitrate	0	0	0	0
Ammonium	1	0	23	1
Orthophosphate	0	0	1	NA

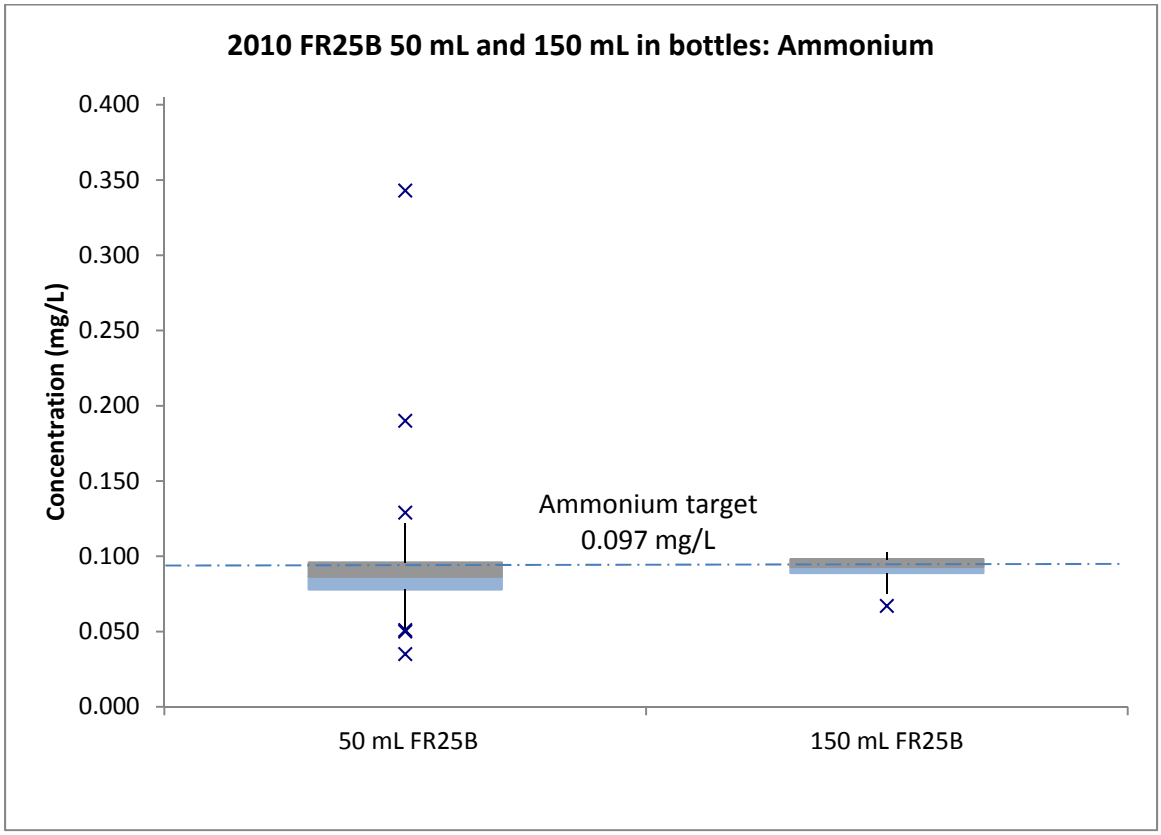

Figure 8. Box and whisker plot comparing ammonium measured in 50 mL and 150 mL FR25B 1 Liter bottle blanks during 2010

AIRMoN bottles are not rewashed or reused. All of the results for AIRMoN bottles (Table 12) were within acceptable limits.

Table 12. Number of Results Outside of Target Limits for AIRMoN 250 mL Bottles

Parameter	FR25B 50 mL N=12	FR25B 150 mL N=13
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	NA

Lid Bags

New lid bags are acceptance tested as shipments of bags are received. If a bag fails the acceptance test, 1 to 2 bags from the same lot are tested. If those bags fail, the lot is not used. Small amounts of sodium were observed on a couple of occasions (Table 13). Additional testing of lid bags resulted in more evidence of sodium in lid bags. The CAL is investigating new lid bags.

Bucket Bags

New bucket bags are acceptance tested as shipments of bags are received. If a bag fails the acceptance test, 1 to 2 bags from the same lot are tested. If those bags fail, the lot is not used. Magnesium was detected routinely in FR25B solutions for bucket bags (Table 13). However, the level of magnesium exceeded control limits by only 1 ppb, and no contamination was observed with the DI water blanks.

Table 13. Number of Results Outside of Targets for Lid and Bucket Bags

Parameter	Lid Bag DI 50 mL N = 24	Lid Bag FR25B 50 mL N=24	Bucket Bag DI 50 mL N=24	Bucket Bag FR25B 50 mL N=24
pH	0	0	0	0
Specific Conductance	0	0	0	0
Calcium	0	1	0	0
Potassium	0	0	0	0
Magnesium	0	0	0	13
Sodium	2	3	0	0
Chloride	0	0	0	1
Sulfate	0	0	0	0
Nitrate	0	0	0	0
Ammonium	0	0	0	0
Orthophosphate	0	NA	0	NA

Quality Assurance Discussion

Internal Blind Results

The analytical results from internal blind samples were used to assess accuracy and precision of the laboratory throughout the year. These results were evaluated to describe differences between the filtered and unfiltered samples. The relative standard deviation (RSD) and percent recovery were calculated to demonstrate precision and accuracy for the FR10, AES-05, and FR95 solutions.

DI Water

A few outliers were observed in the data for blind DI water samples during 2010 (Table 14). The single outlier for orthophosphate occurred during a time when the instrument was not operating properly, resulting in orthophosphate being just 1 ppb over the limit. Five ammonium measurements for filtered DI were above the MDL for ammonium; however, the levels detected were still below the allowable limit for DI blanks (Figure 9). The chloride measured in filtered DI blanks was higher than the MDL, but still less than the median chloride concentration at the 5th percentile of NTN samples (Figure 10). The outlier for potassium was above the MDL, but still met acceptance criteria established in the CAL QAP (Figure 11).

Table 14. Number of Results Outside of Target Limits in 2010 for Internal Blind DI Samples

Parameter	DI Unfiltered N = 25	DI Filtered N = 14
pH	0	NA
Conductivity	0	NA
Calcium	0	0
Potassium	0	1
Magnesium	0	0
Sodium	0	0
Chloride	0	2
Sulfate	0	0
Nitrate	0	0
Ammonium	0	5
Orthophosphate	1	0

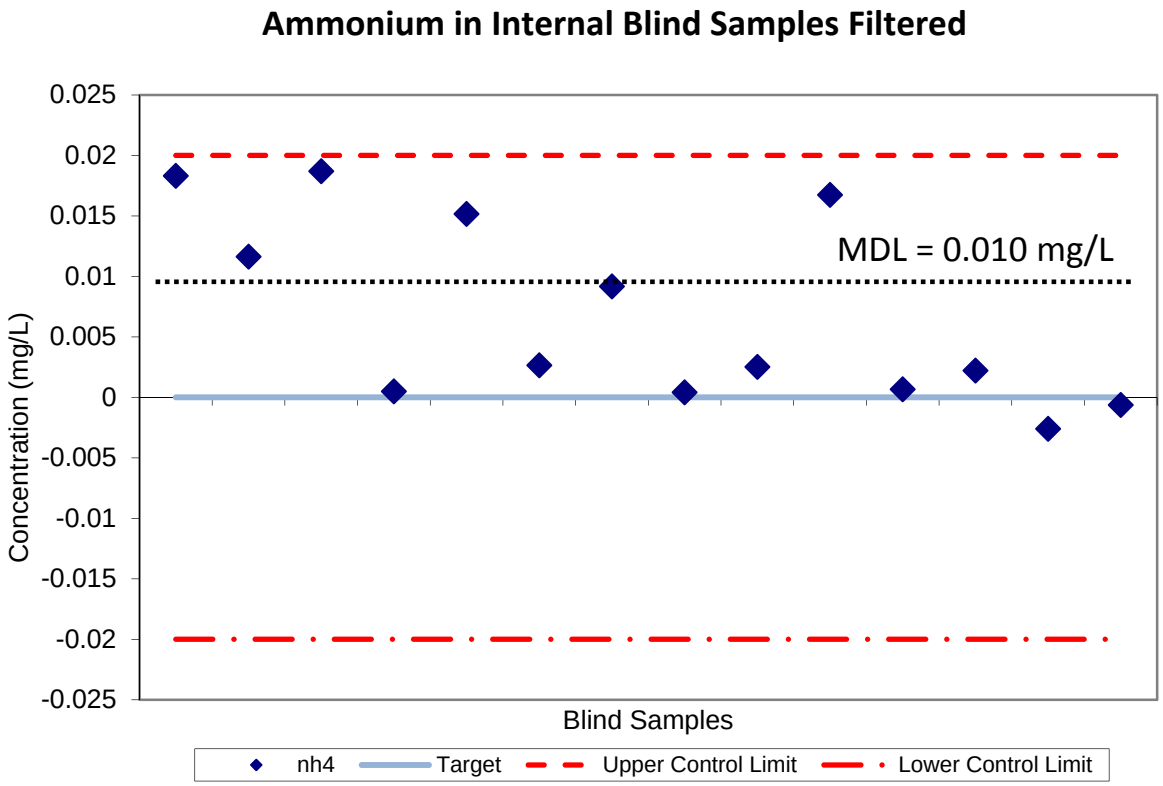

Figure 9. Control chart for ammonium in DI internal blind samples during 2010

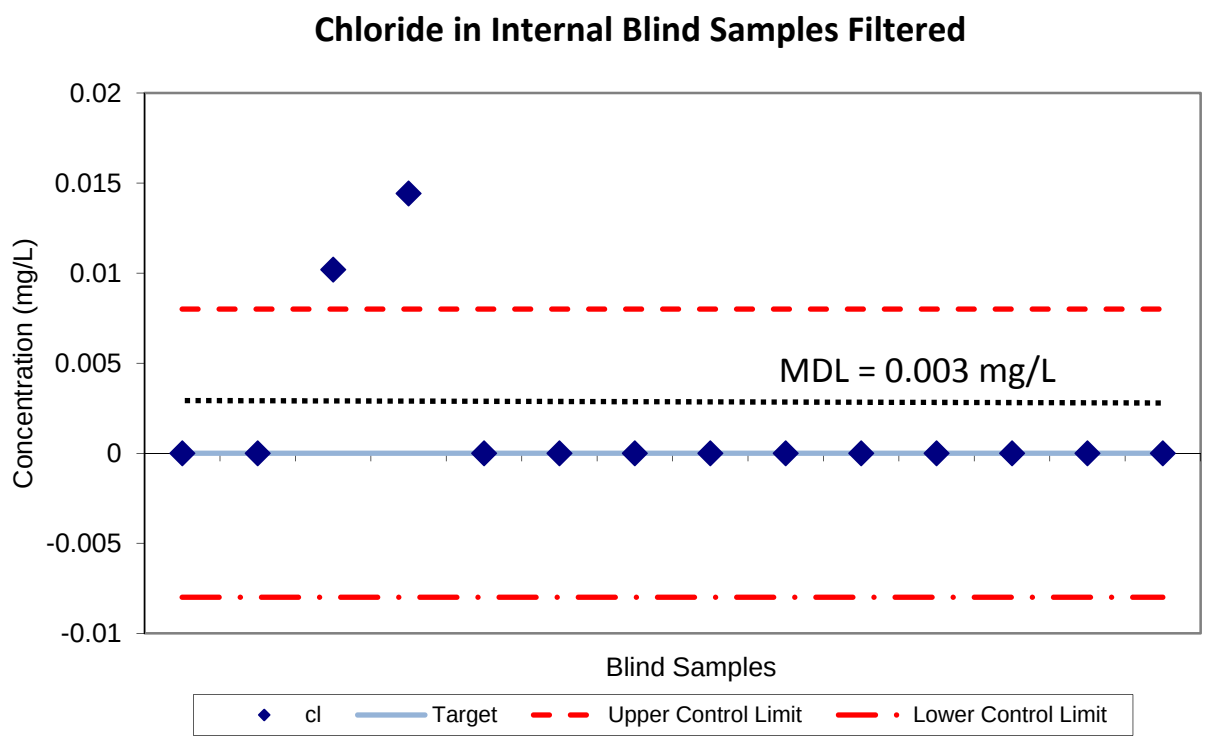

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Figure 10. Control chart for chloride measured in filtered DI internal blind samples during 2010

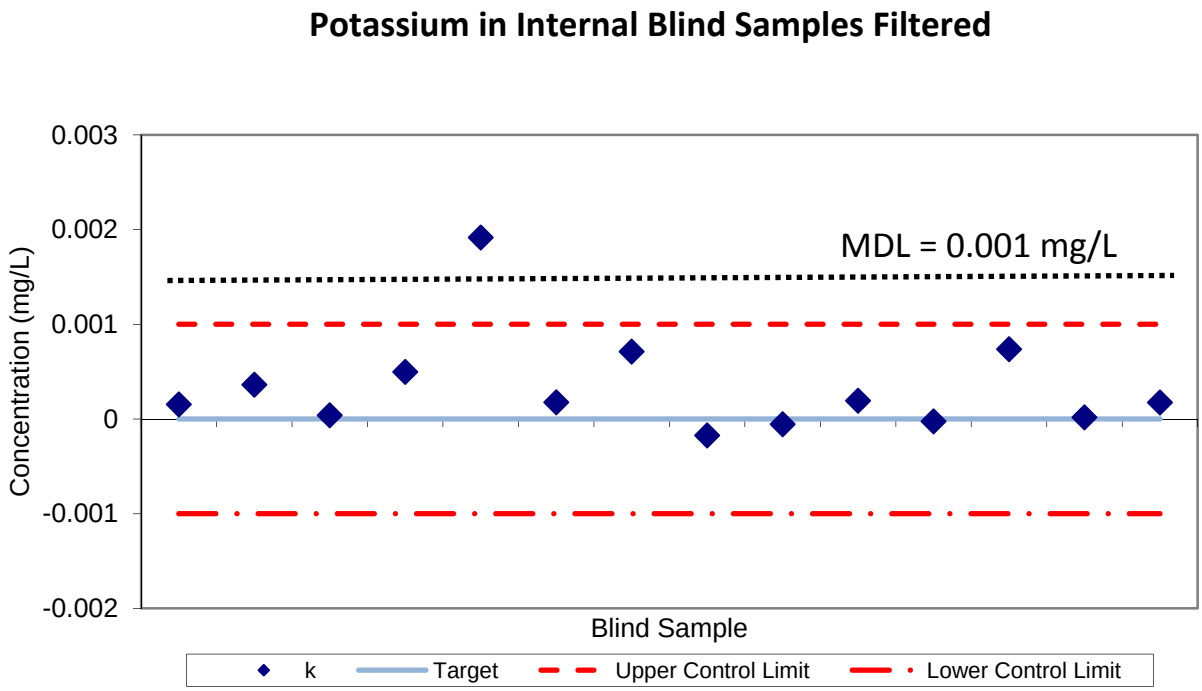

Figure 11. Control chart for potassium measured in filtered DI internal blind samples during 2010

FR10 Solution Results

The relative standard deviations (RSD) and percent recoveries (Table 15) meet acceptance criteria stated in the CAL QAP. Some of the RSDs appear higher compared to other analytes because some of the concentrations are very near the detection limits. All of the results are within expected limits. The differences between filtered and unfiltered samples are minimal with the largest difference occurring for calcium. The recovery of calcium in FR10 solutions is slightly higher, but the difference is negligible compared to instrument noise.

Table 15. Relative standard deviations (RSD) and percent recoveries for filtered and unfiltered FR10 Internal Blind solution

Parameter	RSD Unfiltered N = 27	RSD Filtered N = 13	Recovery Unfiltered N=27	Recovery Filtered N=13
pH	.9%	NA	100.3%	NA
Specific Conductance	3.3%	NA	99.2%	NA
Calcium	3.4%	5.0%	101.3%	110.5%
Potassium	10.9%	13.3%	104.8%	104.8%
Magnesium	5.8%	9.1%	106.6%	93.3%
Sodium	5.1%	7.4%	96.9%	100.7%
Chloride	3.3%	3.7%	101.8%	101.7%
Sulfate	1.8%	1.3%	100.7%	99.8%
Nitrate	1.5%	.9%	100.4%	99.8%
Ammonium	6.4%	8.8%	101.8%	105.5%
Orthophosphate	NA	NA	NA	NA

AES-05 Solution Results

The RSDs and accuracy met acceptance criteria for the AES-05 in 2010 (Table 16).

Table 16. Relative Standard Deviations (RSD) and Recoveries for Internal Blind AES-05 Solution

Parameter	RSD Unfiltered N = 22	RSD Filtered N = 11	Recovery Unfiltered N = 22	Recovery Filtered N = 11
pH	.9%	NA	100.8%	NA
Specific Conductance	2.0%	NA	103.4%	NA
Calcium	1.6%	1.6%	105.2%	109.5%
Potassium	1.4%	5.1%	99.5%	89.4%
Magnesium	1.2%	3.0%	99.7%	100.3%
Sodium	1.7%	3.3%	104.0%	98.8%
Chloride	3.2%	3.5%	102.7%	102.8%
Sulfate	1.0%	1.3%	99.2%	98.2%
Nitrate	.8%	1.7%	100.2%	98.7%
Ammonium	.8%	5.8%	101.7%	96.3%

The recovery and RSDs for the internal blind FR95 met all acceptance criteria in 2010 (Table 17).

Table 17. RSDs and recoveries for internal blind FR95 solution

Parameter	RSD Unfiltered N = 24	RSD Filtered N = 13	Recovery Unfiltered N = 24	Recovery Filtered N = 13
pH	0.8%	NA	100.0%	NA
Specific Conductance	1.2%	NA	99.6%	NA
Calcium	1.8%	2.9%	99.8%	99.6%
Potassium	1.9%	1.4%	98.1%	97.5%
Magnesium	1.3%	1.7%	98.6%	96.3%
Sodium	1.8%	2.1%	97.0%	97.7%
Chloride	0.6%	2.7%	99.9%	102.8%
Sulfate	0.5%	1.1%	99.8%	97.9%
Nitrate	0.5%	1.0%	99.8%	98.1%
Ammonium	0.7%	1.4%	100.6%	99.0%

Reanalysis and Split Samples

The CAL processed 245 pairs of split samples in 2010. The overall differences were minimal, with the median percent differences below 2 percent for all analytes. A few outliers were observed for calcium, magnesium, sodium, chloride, and ammonium. The differences are likely due to the sample filtration. The current procedure for sample splits allows for several days to elapse between the sample processing, including filtration. As for ammonium, it is very possible that the ammonium is changing in samples between the original and split analyses. In order to minimize this problem, a new procedure is being developed to analyze split samples side by side.

Chemistry results are reviewed on a weekly basis for data completeness before the data are released to the data manager. The data are then evaluated for Ion Percent Differences (IPD) and Conductivity Percent Differences (CPD). When samples exceed the designated limits for IPD and CPD, samples are flagged for reanalysis. An additional 2 percent of samples are selected at random for reanalysis. The reanalysis results generally are targeted for 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 39 edits were made for NTN samples and 2 edits were completed for AIRMoN samples. The total number of samples with complete analysis and total number of QC samples are listed in Table 18. The total number of control chart checks includes all samples that the analysts check against control charts during an analytical run.

Table 18. Number of real and quality control (QC) samples analyzed during 2010.

Network	Total Number Of Samples Analyzed	Total Number Of Reanalysis Samples	Total Number Of Split Samples	Total Number Of Blind Samples	Total Number of Control Chart Checks (percent of samples analyzed)
NTN	10383	938	245	155	pH/conductivity = 4673 (29%) ICP/OES = 4027 (26%) FIA = 6775 (37%) IC = 4771 (29%)
AIRMoN	938	140	18	48	

AMoN

Samples for the AMoN network are extracted with DI water upon receipt at the CAL. During the extraction process, 4 additional samples are created to evaluate the background levels. These samples are labeled as Lab DI Blank (water used for extractions, 1 per extraction period), Hood Blank (passive device with core located in the hood throughout the extraction period, 1 per extraction period) and New Core Blank (unused cartridge as received from supplier, 2 per extraction period). The results for these samples throughout 2010 are shown in Figure 12. All results were within acceptable limits, and were below the network detection limit of 0.100 ppm.

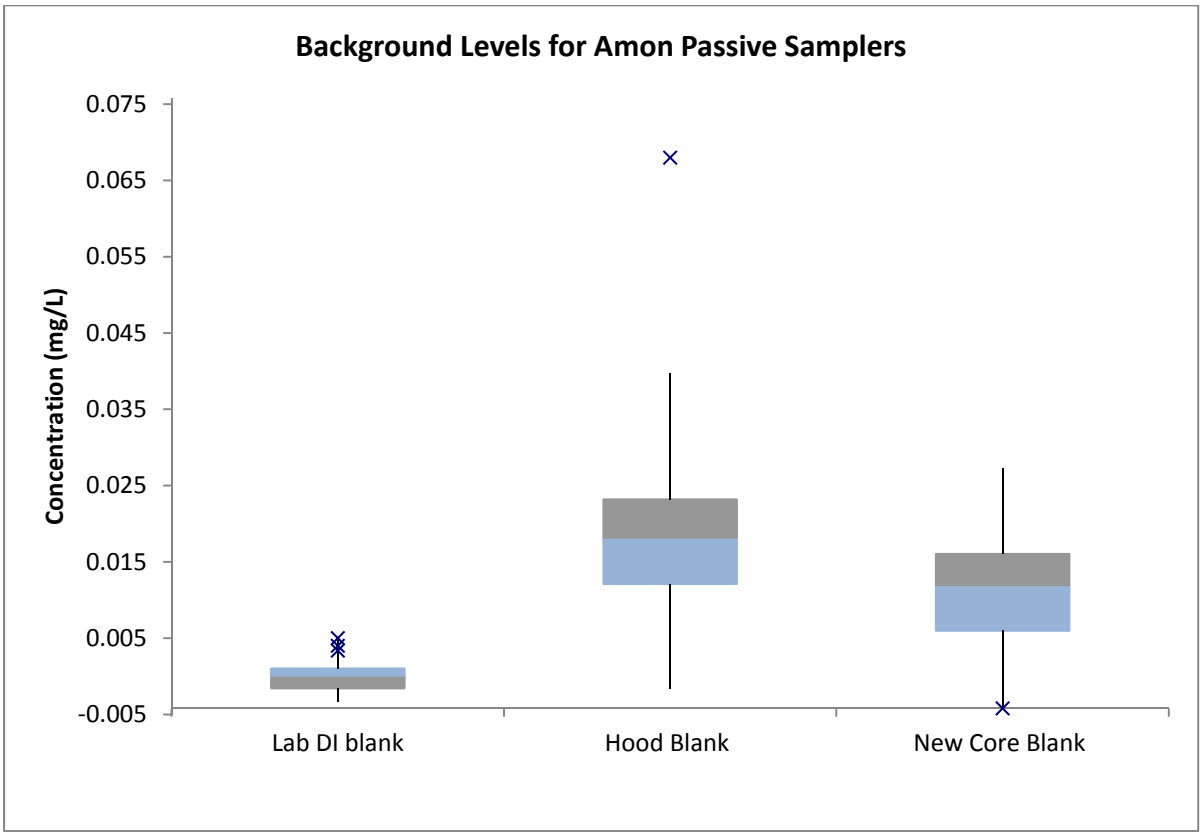

Figure 12. Box and whisker plot for ammonium ion concentrations in lab DI blanks, hood blanks, and new core blanks sampler extracts in 2010

External Quality Assurance

The CAL participated in four external proficiency testing studies throughout 2010. The study identifier and websites with study details and results are shown in Table 19. The CAL performance has been satisfactory for all of the studies reported to date. Note, the NILU study results are pending.

Table 19. 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 43 and 44	World Meteorological Organization/Global Atmospheric Watch (WMO/GAW)	http://www.qasac-americas.org/
Study 96 and 97	Environment Canada Proficiency Testing Program	Available upon request
Study 27	Norwegian Institute for Air Research (NILU)	Available upon request

Conclusions

The CAL performed consistently throughout 2010 and continued to process data in a manner that met the guidelines 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 4.0 April 2009. http://nadp.sws.uiuc.edu/lib/qaplans/qapCal2009.pdf

NADP Network Quality Assurance Plan 2009-09
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.