Quality Assurance Report
National Atmospheric Deposition Program
2009

Laboratory Operations
Central Analytical Laboratory

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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 four research monitoring networks, and the CAL analyzes samples for two of its networks, the Atmospheric Integrated Research Monitoring Network (AIRMoN) and the National Trends Network (NTN). The collection of precipitation samples for these two networks differ in that AIRMoN samples are collected daily and NTN samples are collected weekly. All samples 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. For consistency in this report, acidity is reported in pH units, conductivity is reported as µS/cm, and ions are reported as ppm (1 ppm = 1 mg/L).

The CAL is directed by guidelines specified in the NADP Network Quality Assurance Plan (QAP), which is available on the NADP website. 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	Meter
Conductivity	Meter
Chloride	Ion Chromatography (IC)
Nitrate	Ion Chromatography (IC)
Sulfate	Ion Chromatography (IC)
Ammonium	Flow Injection Analysis (FIA)
Orthophosphate	Flow Injection Analysis (FIA)
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 2009

- Stacey Henson qualified for supply washing (March 2009).
- Kim Attig qualified as back-up ion chromatography (IC) analyst (July 2009).
- Lee Green qualified as back-up flow injection analysis (FIA) analyst (September 2009).
- Nina Gartman qualified as back-up inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyst (November 2009).

- New laboratory space was acquired and renovated for IC analysis, allowing improved temperature control (August 2009).
- Beginning in March 2009, internal blind filtered samples were processed in cleaned and reused 1 L sample bottles instead of new 60 mL sample bottles.
- Bromide was evaluated as an additional IC analyte (June 2009–present).
- Measurement of total dissolved nitrogen (TDN) was evaluated in a special study at select NTN sites (2009).
- A preservation study for TDN analysis was completed at Bondville, IL (summer 2009).
- Ion exchange resin columns were explored for wet deposition measurements (2009).
- Passive ammonia study continued through 2009.

In June, 2007, a special study to establish a passive ammonia monitoring network was accepted at an NADP Executive Committee meeting in Annapolis, Maryland. The analytical work for this study was completed at the CAL, utilizing the same FIA used for NTN and AIRMoN ammonium quantification.

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 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 as new supplies are introduced for site use. Internal blind samples 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). The FR solutions are used for both NTN and AIRMoN samples. 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 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. Prior to March 2009, the unfiltered and filtered blind samples were not considered blind for pH/conductivity and filtering analysts. Beginning in March 2009, internal blind filtered samples were submitted in standard 1-L bottles used for NADP sites, and thus the samples from this point 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, Illinois State Water Survey, the NADP, or the CAL.

Table 2. Orthophosphate Control Solutions Concentrations

	Low standard	High standard
Orthophosphate (ppm)	0.023	0.125

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	5.09	4.90	4.60	4.48	4.89
Conductivity (µS/cm)	4.2	7.5	18.3	34.6	10.8
Calcium (ppm)	0.028	0.0509	0.2598	0.7073	0.186
Magnesium (ppm)	0.005	0.0096	0.0451	0.151	0.0374
Sodium (ppm)	0.011	0.0188	0.1379	0.714	0.181
Potassium (ppm)	0.005	0.0087	0.0369	0.113	0.026
Chloride (ppm)	0.032	0.051	0.244	1.275	0.226
Sulfate (ppm)	0.250	0.513	1.875	3.795	1.28
Nitrate (ppm)	0.312	0.568	1.857	3.852	1.15
Ammonium (ppm)	0.033	0.090	0.458	1.085	0.311

Routine supplies provided to sites are checked weekly for contamination. 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. Table 4 also includes the 5th percentile concentrations measured in NTN precipitation samples. 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.

Table 4. Target Concentrations for Weekly Supply Checks

Analyte	Target DI Blanks 3σ	Target DI Blanks 6σ	5th percentile Concentrations for all analytes	FR25 Blank Target concentration	3σ Limits for FR25	6σ Limits for FR25
pH	5.35-5.95	5.05-6.25	4.27	4.91	4.84-4.98	4.77-5.04
Conductivity (µS/cm)	<1.6	<2.2	3.1	6.8	6.4-7.2	6.1-7.5
Calcium (ppm)	<0.005	<0.009	0.021	0.052	0.049-0.055	0.046-0.058
Magnesium (ppm)	<0.001	<0.002	0.003	0.0097	0.008-0.010	0.008-0.010
Sodium (ppm)	<0.002	<0.003	0.006	0.019	0.018-0.021	0.016-0.022
Potassium (ppm)	<0.002	<0.003	0.004	0.0088	0.008-0.010	0.007-0.011
Chloride (ppm)	<0.009	<0.017	0.020	0.051	0.045-0.057	0.039-0.063
Sulfate (ppm)	<0.013	<0.025	0.1271	0.523	0.493-0.553	0.463-0.583
Nitrate (ppm)	<0.015	<0.029	0.156	0.577	0.541-0.613	0.505-0.649
Ammonium (ppm)	<0.005	<0.009	0.010	0.089	0.083-0.095	0.077-0.101
Orthophosphate (ppm)	<0.005	<0.010	NA	NA	NA	NA

Table 5. Summary of Supply Check Frequencies

Description of blank sample	Volume and solution	Frequency
Polisher DI	Sample preparations laboratory	Weekly
	Analytical laboratories	Weekly
	Supply preparations laboratory	Weekly
Washed Buckets	50 mL DI water	Weekly
	50 mL DI water	Weekly
	150 mL DI water	Weekly
	50 mL FR25B solution	Weekly
	150 mL FR25B solution	Weekly
Washed NTN 1 L Bottles	50 mL DI water	Weekly
	50 mL DI water	Weekly
	150 mL DI water	Weekly
	50 mL FR25B solution	Weekly
	50 mL FR25 solution	Weekly
	150 mL FR25B solution	Weekly
Filters	50 mL DI water	Weekly
	50 mL FR25B solution	Weekly
Lids	50 mL DI water	Weekly
	50 mL FR25B solution	Weekly
Lid Bags	50 mL DI water	Bi-weekly
	50 mL FR25B solution	Bi-weekly
Bucket Bags	50 mL DI water	Bi-weekly
	50 mL FR25B solution	Bi-weekly
New AIRMoN 250 mL Bottles	50 mL FR25B solution	Monthly
	150 mL FR25B solution	Monthly

Quality Control Discussion

Method Detection Limits

Method Detection Limits (MDLs) are defined by the 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” and provides guidelines for calculating them. 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 IC 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 results for all MDL study samples are compiled for an entire year and used to compute the method detection limit for the upcoming year. Standard deviations for the MDL samples are multiplied by Student's t value for the 99% confidence interval to compute the MDL's. The MDLs for 2009 are shown in Table 6 below.

Table 6. MDLs for 2009

Analyte	MDL (ppm)
Calcium	0.006
Potassium	0.001
Magnesium	0.001
Sodium	0.001
Chloride	0.004
Nitrate	0.006
Sulfate	0.004
Ammonium	0.003
Orthophosphate	0.002

Control Charts

Control charts met DQOs during 2009. It is important to note that there were two primary calibration standards used during 2009 for conductivity measurements. The mean concentrations for control standards changed when the analysts began using the second calibration standard. The differences were compared for each of the control solutions and found to be within acceptable limits as required by DQOs. Control charts for all analytes are available upon request from the CAL.

Weekly Blank Results

Tables 7–12 show results for all of the blanks for 2009. Target levels are based on historic MDLs and current MDLs for deionized water blanks and repeated measurements of the 25th percentile solution. When results exceeded 6σ, the data were plotted using box and whisker plots. The box shows the 1st, 2nd, and 3rd quartiles of the data. The whisker plot shows up to 1.5 times the box. "X" designates points outside the whisker plot. The plots are on the CAL's website (http://nadp.isws.illinois.edu/CAL).

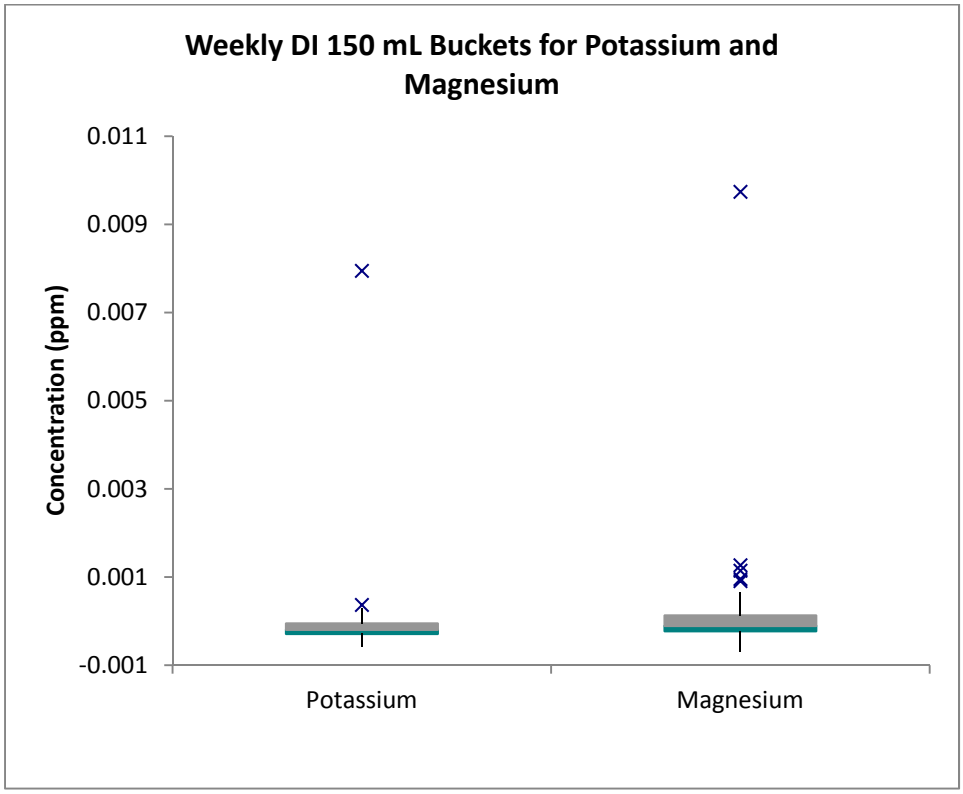

Figure 1. Example of box and whisker plot for potassium and magnesium concentration measured in bucket DI checks throughout 2009 available on the NADP website

Polisher DI Blanks

The polisher DI water blanks met all acceptance criteria for 2009 with the exception of one sample for conductivity. The conductivity measured for the single outlier was below the 5th percentile concentration for historic NTN network samples.

Filters

DI water blanks indicate low-level concentrations of sodium and chloride (Table 7), although the levels are lower than the 5th percentile of NTN sample concentrations. On three occasions, the DI filter blanks were found with higher concentrations of sodium and chloride (>0.006 ppm sodium and >0.020 ppm chloride). Additional filters were tested from the same batch and levels found were within the target limits.

Calcium was detected on some filters and exceeded target limits in the FR25B tests only (Table 7). About 30 percent of samples exceeded 6σ targets (6σ is within 15% difference between the target

concentration and measured concentration for calcium), and about 10% of samples had concentrations of calcium which exceeded 25% difference when compared to the target concentrations. The occurrence of elevated concentrations is infrequent. For the internal blind samples, differences were observed between filtered and unfiltered samples. The blind filtered and unfiltered samples for DI and FR10 showed slightly higher averages for calcium in filtered samples compared to unfiltered samples. The amount of calcium found on filters was within the noise of the instrument at the 10th percentile concentrations. The differences decreased as concentrations increased. The average percent difference at the 10th percentile concentration was found to be 14%. The percent difference for the AES-05 sample was 5%, and the average difference for the 95th percentile concentration was -2%. Given that elevated concentrations of calcium were not observed with the internal blinds, this suggests infrequent calcium contamination from filters. The CAL will continue to monitor the filters and troubleshoot as necessary.

The FR25 filter blanks indicated losses exceeding the set target limits for magnesium (Table 7), but the losses are small in magnitude, ≤ 1 ppb.

About 7% of the results exceeded 6σ limits for sodium (Table 7). The actual amount was at or below the average (0.004 ppm) amount of sodium found on filters when sampled with DI water.

Table 7. Number of Results outside of Target Limits in 2009 for Polisher and Filter Blanks

Parameter	Polisher DI 3σ N=129	Polisher DI 6σ N=129	Filter DI 3σ N=52	Filter DI 6σ N=52	Filter FR25B 3σ N=52	Filter FR25B 6σ N=52
pH	4	0	0	0	5	0
Conductivity	1	1	1	0	2	0
Calcium	0	0	0	0	38	16
Potassium	0	0	1	0	11	0
Magnesium	0	0	1	0	45	45
Sodium	1	0	16	10	9	4
Chloride	0	0	11	3	11	0
Sulfate	0	0	2	0	7	0
Nitrate	0	0	0	0	0	0
Ammonium	2	0	3	0	2	0
Orthophosphate	0	0	0	0	NA	NA

Buckets, Bottles, and Lids

When the analyte concentration for rewashed and reused supplies such as lids (Table 8), buckets (Table 9), and 1 L bottles (Table 10) exceed the target levels, they are rewashed and rechecked. If the supply does not pass a second check, it is discarded.

Table 8. Number of Results Outside of Target Limits in 2009 for Lids

Parameter	Lid DI 3σ N=52	Lid DI 6σ N=52	Lid FR25B 3σ N=52	Lid FR25B 6σ N=52
pH	2	1	5	1
Conductivity	1	0	3	0
Calcium	0	0	2	0
Potassium	11	10	22	14
Magnesium	0	0	22	22
Sodium	17	9	19	9
Chloride	11	5	7	1
Sulfate	1	1	0	0
Nitrate	0	0	0	0
Ammonium	30	11	33	13
Orthophosphate	0	0	NA	NA

Table 9. Number of Results Outside of Target Limits in 2009 for Buckets

Parameter	Buckets 50 mL DI 3σ N=104	Buckets 50 mL DI 6σ N=104	Buckets 150 mL DI 3σ N=104	Buckets 150 mL DI 6σ N=104	Buckets 50 mL FR25B 3σ N=52	Buckets 50 mL FR25B 6σ N=52	Buckets 150 mL FR25B 3σ N=52	Buckets 150 mL FR25B 3σ N=52
pH	26	2	8	2	6	0	3	1
Conductivity	86	15	32	1	32	11	12	3
Calcium	3	2	8	1	16	4	5	1
Potassium	2	1	1	1	27	11	26	7
Magnesium	6	2	6	1	41	41	37	37
Sodium	2	0	2	2	6	1	1	0
Chloride	13	0	3	1	20	1	8	1
Sulfate	1	0	2	1	5	0	0	0
Nitrate	1	0	1	1	11	1	1	0
Ammonium	59	36	35	23	31	26	31	21
Orthophosphate	2	0	1	1	NA	NA	NA	NA

Table 10. Number of Results Outside of Target Limits for Standard NTN 1 L Bottles

Parameter	1 L bottle 50 mL DI 3σ N=104	1 L bottle 50 mL DI 6σ N=104	1 L bottle 150 mL DI 3σ N=52	1 L bottle 150 mL DI 6σ N=52	1 L bottle 50 mL FR25B 3σ N=104	1 L bottle 50 mL FR25B 6σ N=104	1 L bottle 150 mL FR25B 3σ N=51	1 L bottle 150 mL FR25B 6σ N=51
pH	2	0	1	0	6	0	0	0
Conductivity	6	0	3	1	16	2	2	0
Calcium	1	0	0	0	3	0	2	1
Potassium	4	2	2	0	41	11	12	5
Magnesium	2	0	0	0	26	26	9	9
Sodium	1	1	2	0	3	0	1	0
Chloride	0	0	2	0	0	0	0	0
Sulfate	0	0	0	0	2	0	0	0
Nitrate	1	1	0	0	0	0	0	0
Ammonium	1	0	2	0	56	28	11	5
Orthophosphate	0	0	0	0	NA	NA	NA	NA

AIRMoN bottles are not rewashed or reused. The results for AIRMoN bottles (Table 11) were within acceptable limits. Only low contamination levels were observed for the analytes of interest.

Table 11. Number of Results Outside of Target Limits for AIRMoN 250 mL Bottles

Parameter	AIRMoN bottles 50 mL FR25B 3σ N=17	AIRMoN bottles 50 mL FR25B 6σ N=17	AIRMoN bottles 150 mL FR25B 3σ N=16	AIRMoN bottles 150 mL FR25B 6σ N=16
pH	0	0	0	0
Conductivity	1	0	0	0
Calcium	0	0	1	0
Potassium	1	1	1	1
Magnesium	2	2	2	2
Sodium	0	0	0	0
Chloride	1	0	0	0
Sulfate	1	0	0	0
Nitrate	0	0	0	0
Ammonium	0	0	0	0
Orthophosphate	0	NA	NA	NA

Lid Bags

New lid bags are acceptance tested as bags are needed. If a bag fails the acceptance test, additional bags from the same lot are tested. If those bags fail, the lot is not used. Small amounts of sodium and chloride were observed in lid bags (Table 12). The levels of contamination are below the 5th percentile concentration for both analytes. The ratio of chloride to sodium is close to 1.5 for more than half of the samples tested, indicating that sodium chloride (NaCl) is the source of contamination.

Bucket Bags

New bucket bags are acceptance tested as bags are needed. If a bag fails the acceptance test, additional bags from the same lot are tested. If those bags fail, the lot is not used. Magnesium was detected in FR25B solutions for bucket bags (Table 12). However, the level of contamination was only 1 ppb, and no contamination was observed with the DI water blanks.

Table 12. Number of Results Outside of Targets for Lid and Bucket Bags

Parameter	Lid Bag DI 3σ N = 31	Lid Bag DI 6σ N=31	Lid Bag FR25B 3σ N=32	Lid Bag FR25B 6σ N=32	Bucket bag 50 mL DI 3σ & 6σ N=17	Bucket bag 50 mL FR25B 3σ N=17	Bucket bag 50 mL FR25B 6σ N=17
pH	2	0	1	1	0	0	0
Conductivity	0	0	1	0	1	1	0
Calcium	0	0	1	0	0	1	0
Potassium	0	0	4	1	0	2	1
Magnesium	0	0	13	3	0	17	17
Sodium	17	6	18	9	0	2	0
Chloride	1	0	0	0	0	2	0
Sulfate	0	0	0	0	0	1	0
Nitrate	0	0	0	0	0	0	0
Ammonium	0	0	11	0	0	0	0
Orthophosphate	0	0	NA	NA	0	NA	NA

The number of rewash/recheck and discarded supplies during 2009 are shown in Table 13.

Table 13. Number of Supplies Flagged for Rewashing/Rechecking and Discarding

Supply	Rewash/Recheck	Discard	Total Evaluated
Lid	21	0	104
1 L Bottle	24	14	312
Bucket	77	16	260

Not all of the contamination found in cleaned supplies exceeded target limits; occasionally, analytes fell below the target limits particularly for bottles and buckets. It was noted that when evaluating the blanks with 150 mL of DI compared to 50 mL of DI that the number of supplies exceeding the target limits dropped by almost half for the larger volume of solution.

Quality Assurance Discussion

Internal Blind Results

Results from the internal blind samples were evaluated to describe differences between the filtered and unfiltered samples. These results were also evaluated to assess the accuracy and precision of the laboratory. The number of results that exceeded control limits is shown in Table 14. The data were plotted using box and whisker plots. The box shows the 1st, 2nd, and 3rd quartiles of the data. The whisker shows up to 1.5 times the box. "X" designates outliers. The plots are available on the CAL's website (http://nadp.isws.illinois.edu/CAL).

DI Water

In 2009, the only analyte of concern for DI water internal blinds was orthophosphate (Table 14). The variability of orthophosphate concentrations during 2009 was about 4 to 5 ppb. As a corrective action, the FIA method for orthophosphate was investigated. A new MDL study is scheduled for 2010 to evaluate the effect of the orthophosphate variability on the MDL. The single outlier for ammonium is 1 ppb outside of the limit and meets the accuracy required in the CAL QAP.

FR10 Solution Results

The deviation from the target concentration was within 1 ppb for all measurements of magnesium, potassium, and all but one for sodium. The single outlier for sodium is within the required accuracy requirement described in the CAL QAP. The outlier for calcium may be due to carryover during ICP analysis. This issue was investigated further. It has been documented that calcium carryover does occur randomly. As a corrective action, all samples that follow a sample with a calcium concentration over 500 ppb are repeated. The outliers for pH and conductivity exceeded the 3σ limits, but all were within 6σ limits.

FR95 and AES-05 Solution Results

All data were found to be within acceptable limits for these two samples. The AES-05 sample is an externally provided sample for which there were no outliers in 2009.

The blind data were used to calculate the percent difference between filtered and unfiltered samples for nitrate and sulfate. The highest percentage of loss occurred at the level of the 10th

percentile and was 14% for both analytes. As the concentration increased, the percent differences decreased and were found to be about 1% for the AES-05 and FR95 solution for both nitrate and sulfate.

Although both filtered and unfiltered samples were within acceptable limits, the standard deviation for some of the measurements was larger for the filtered samples as compared to the unfiltered samples. Data were compared between NTN filtered and unfiltered samples, AIRMoN and NTN unfiltered samples, and AIRMoN and NTN filtered samples. The probabilities for the 95% confidence interval were computed using Mann-Whitney Non-Parametric statistics. Statistical differences were observed between filtered and unfiltered data for some of the analytes. The average percent differences calculated for all of the results and are shown in Table 15. Results that were statistically different are denoted in red. There appears to be a slight negative bias due to filtration, however, it is small in magnitude. The larger differences were observed for the FR10 and DI solutions. These observations indicate a slight positive calcium bias for solutions with concentrations at the 10th percentile and some trace level contamination near the detection limit resulting from the filters.

Table 14. Number of Results Outside of Target Limits in 2009 for Internal Blind Samples

Parameter	DI N = 25	FR10 N=25	FR95 N=25	AES-05 N=25
pH	0	4	0	0
Conductivity	0	3	2	0
Calcium	0	1	0	0
Potassium	0	6	0	0
Magnesium	0	5	0	0
Sodium	0	12	0	0
Chloride	0	1	1	0
Sulfate	0	0	0	0
Nitrate	0	0	0	0
Ammonium	1	0	0	0
Orthophosphate	6	NA	NA	NA

Table 15. Average Percent Differences Calculated For Filtered and Unfiltered Internal Blind Samples and Between NTN Filtered and AIRMoN Internal Blind Samples

Parameter	NTN unfiltered Compared to AIRMoN Average % difference FR95	NTN filtered Compared to AIRMoN Average % difference FR95	NTN filtered Compared to NTN unfiltered Average % difference FR95	NTN filtered Compared to NTN unfiltered Average % difference AES-05	NTN filtered Compared to NTN unfiltered Average % difference FR10	NTN filtered Compared to NTN unfiltered Average % difference DI [3]
Calcium	-0.214	-1.38	-1.40	4.67	14.4	79.4
Potassium	-0.700	-1.19	-1.95	-7.57	-5.45	43.5
Magnesium	-.136	-2.33	-2.39	-1.68	-36.6	65.7
Sodium	-.574	-1.91	-1.20	-2.78	-4.63	92.9
Chloride	-.312	-.540	-.543	.263	-9.20	100
Sulfate	-.534	-.826	-.832	-1.39	-13.6	100
Nitrate	-.144	-1.11	-1.12	-.922	-14.3	96.9
Ammonium	-.107	-1.83	-1.86	-2.25	-14.0	13.3

Reanalysis and Split samples

The CAL processed 247 pairs of split samples in 2009. Just over 4% of the samples exceeded duplicate limits specified in the CAL QAP. Of these samples, three were for small differences for sodium and chloride, and three were for small differences for calcium. Review of the split samples resulted in edits to three data values in the database. Samples surrounding the suspicious sample were reanalyzed before edits were made to ensure that the issue was isolated.

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% of samples are selected at random pulled for reanalysis as well. The reanalysis results generally are targeted for reproducibility of 10%, but this can be extended if the concentration is near the MDL for a particular analyte. If samples fall outside the 10% difference windows, analysts try to determine the cause and analyze additional samples around the sample in question. The results are reviewed by the QA Chemist and required edits are made. 831 NTN samples were reanalyzed and 35 edits made. 121 AIRMoN samples were reanalyzed and 7 edits were made.

[3] The magnitude of analytes measured in DI water is very small, thus percent differences are larger.

External Quality Assurance

The CAL participated in four external proficiency testing studies throughout 2009. The study identifier and websites where the details and results of the studies can be found are shown in Table 16.

Table 16. 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 40 and 41	World Meteorological Organization/Global Atmospheric Watch (WMO/GAW)	http://www.qasac-americas.org/
Study 94 and 95	Environment Canada Proficiency Testing Program	http://nadpweb.sws.uiuc.edu/ops/cal/QA%20Data/Forms/Intercomparison.aspx
Study 27	Norwegian Institute for Air Research (NILU)	http://tarantula.nilu.no/projects/ccc/reports.html pending

Conclusions

The CAL performed consistently throughout 2009 and continued to process data in a manner that met the guidelines specified in the NADP Network Quality Assurance Plan (QAP).

Bibliography

Central Analytical Laboratory SOPs
http://nadpweb.sws.uiuc.edu/ops/cal/SOPs%20Final/Forms/SOPs.aspx

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.