2019* Quality Assurance Report

National Atmospheric Deposition Program

Central Analytical Laboratory

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***June 1, 2018 – December 31, 2019**

Revision Date: 8/31/2020

National Atmospheric Deposition Program

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Central Analytical Laboratory Quality Assurance Report June 2018 - 2019

1. Overview

The Wisconsin State Laboratory of Hygiene (WSLH) took on the role of the NADP Central Analytical Lab (CAL) on June 1, 2018 after a short transition period from the previous CAL operations at the Illinois State Water Survey (ISWS) within the Prairie Research Institute (PRI) located at the University of Illinois in Urbana-Champaign, Illinois. This report covers the period from June 1, 2018 through December 31, 2019, because the WSLH CAL did not prepare a separate QAR for that initial 7-month period in 2018. The ISWS CAL analyzed NADP/NTN samples from the network's inception in 1978 until May 31, 2018; NADP/AIRMoN samples from 1992 to May 31, 2018; and NADP/AMoN samples from 2007 to May 31, 2018. To ensure a seamless and analytically consistent transition the WSLH performed the CAL operations with as much duplication of the ISWS CAL processes as possible. However, after that initial transition period in 2018, processes and supplies have been evaluated by the WSLH CAL and improved as needed. The mercury analytical lab (HAL) was also successfully transitioned from another contract lab to the WSLH on June 1, 2019. Now the CAL and the HAL are both located at WSLH and benefitting from efficiencies with combined services, staff and cross-training.

The CAL provides the preparation and shipping of network supplies; sample processing; chemical analysis; and data validation services for precipitation samples collected by the NADP/National Trends Network (NADP/NTN), and air samples (passive samplers for ammonia) for the NADP/Ammonia Monitoring Network (NADP/AMoN). Until September 1, 2019 the CAL also operated the NADP/Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN). The AIRMoN network was disbanded in Fall 2019 due to network contraction and fiscal constraints. The networks (currently NTN and AMoN) and the support laboratory must follow strict quality assurance (QA) and quality control (QC) procedures. Results of key metrics are provided in this QAR.

2. CAL Staff

Staff responsible for CAL operations in 2019:

- Laboratory Manager – Chris Worley
- Sample and Data Processing Manager – Amy Mager
- QA Manager – Camille Danielson
- Systems QA and Special Projects Manager - Martin Shafer
- Assistant Data Managers – Zac Najacht, Dana Grabowski (2019)
- Chemists – Katie Blaydes, Jesse Wouters, April Grant, Marie Assem
- Associate Chemists – Nichole Davis, Kirsten Widmayer, James Sustacheck (2019), Erin Pierce (2019)

3. Sample Counts

The number of network samples received and processed by the CAL is tracked in real-time, however, the percentage of valid samples can only be determined after data are published to the Program Office (PO). The lapse in appropriations (federal government shutdown) in the last quarter of 2018 and first quarter of 2019 had an impact on sample numbers due to the temporary closure of some sites and some invalidation of

samples due to field issues such as long collection periods. Sample counts in **Table 1** include dry and trace samples. A dry sample is submission of only a field form for a sampling period without precipitation. As of 2019, a trace sample is one with less than 4 mL of sample (<2019 trace was defined as <1 mL). All samples over 3 mL are in the wet sample category (wet, wet dilute or wet incomplete depending on the volume). Valid samples include all samples that received a Quality Rating (QR) of A or B. QR of C is invalid. Very few criterion currently result in invalidation of AMoN samples and therefore less than 1.2% are invalidated.

Table 1. NTN Sample Count 2015-2019

Year	NTN Active Sites	Total Samples	Wet Samples		Trace Samples		Dry Samples		Valid Samples	
			Number	Percent	Number	Percent	Number	Percent	Number	Percent
2015	270	13716	11444	83	539	4	1733	13	11887	87
2016	272	13758	11280	82	411	3	2067	15	11874	86
2017	274	13569	10708	79	487	4	2073	15	11248	83
2018	262	13107	9912	76	413	3	1882	14	10337	79
2019	264	12937	10852	84	145	1	1826	14	10747	83

Table 2. AIRMoN Sample Count 2015-2019

Year	AIRMoN Active Sites	Total Samples	Wet Samples		Dry Samples		Valid Samples	
			Number	Percent	Number	Percent	Number	Percent
2015	6	1000	852	85	148	15	956	96
2016	6	927	776	84	151	16	897	97
2017	6	896	742	83	154	17	871	97
2018	6	648	592	91	56	9	633	98
2019	4	395	348	88	77	19	392	99

Table 3. AMoN Sample Count 2015-2019

Year	AMoN Sites	# of Sample Sets	Valid Samples	
			Number	Percent
2015	98	2400	2378	99.1
2016	103	2598	2580	99.3
2017	108	2529	2497	98.7
2018	103	2579	2551	98.9
2019	107	2665	2643	99.2

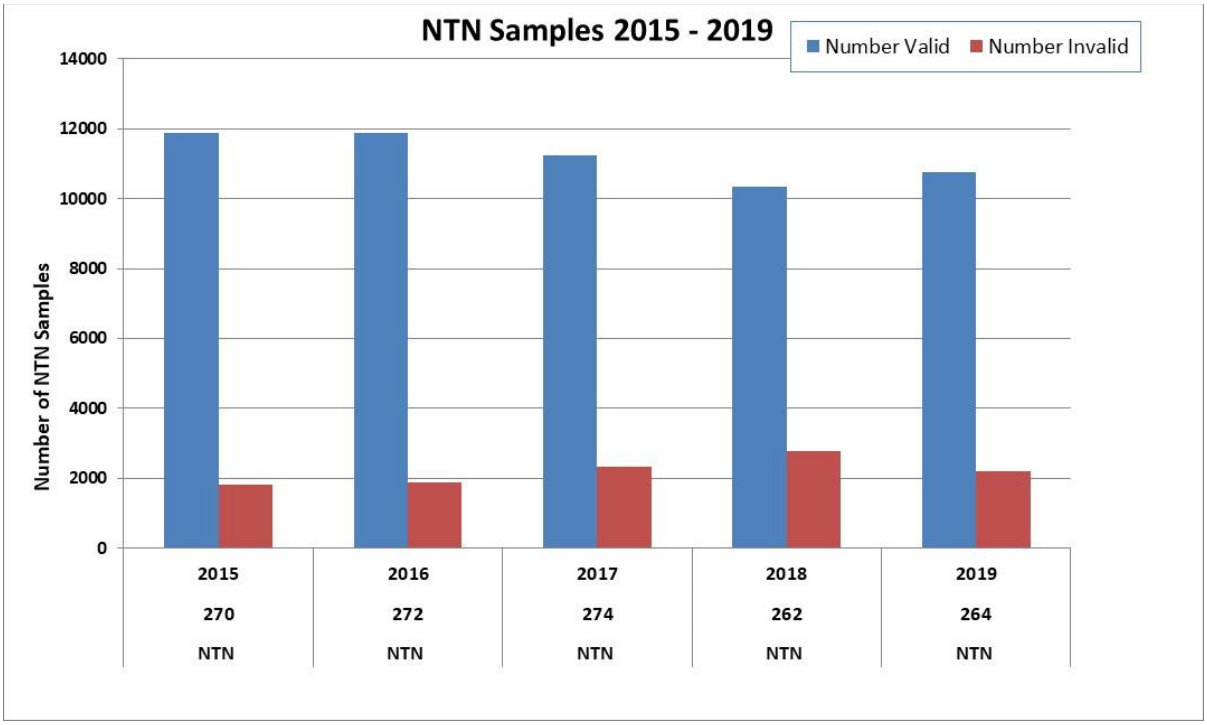

Figure 1. Total Valid and Invalid NTN Samples from January 2015 - December 2019.

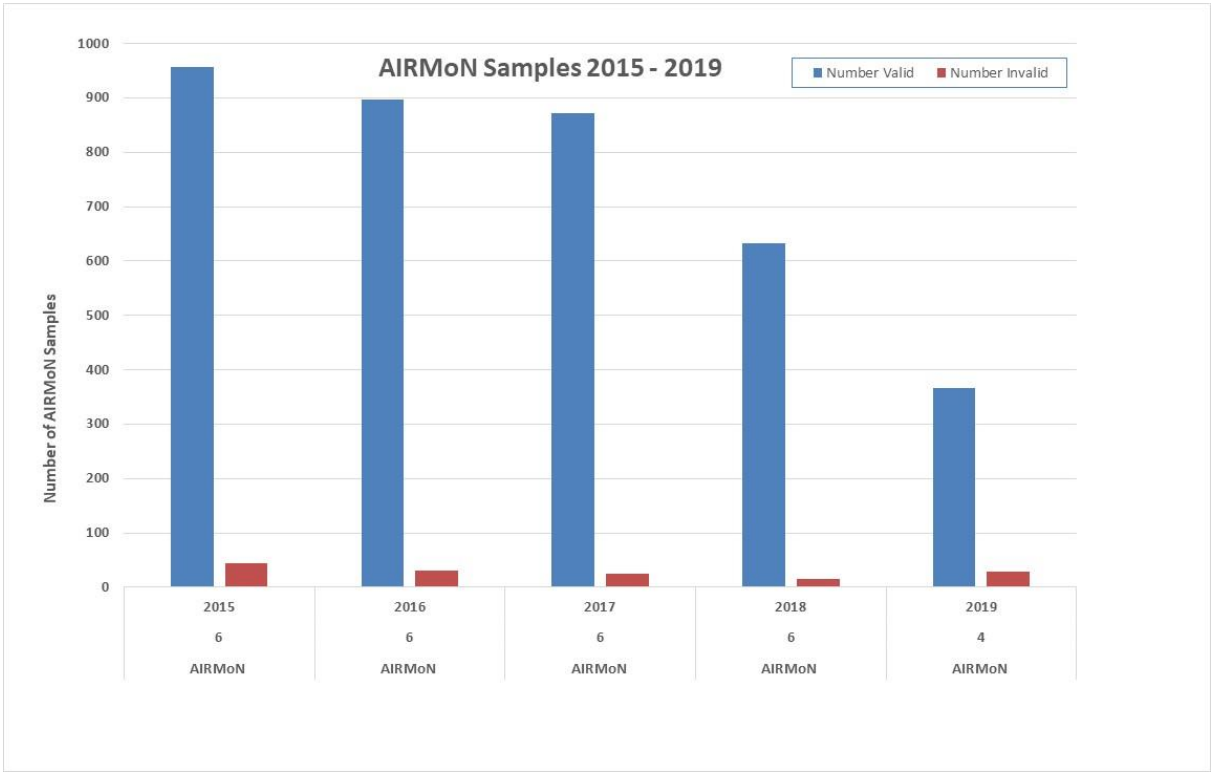

Figure 2. Total Valid and Invalid AIRMoN Samples from January 2015 - September 2019 (network ended 9/1/2019)

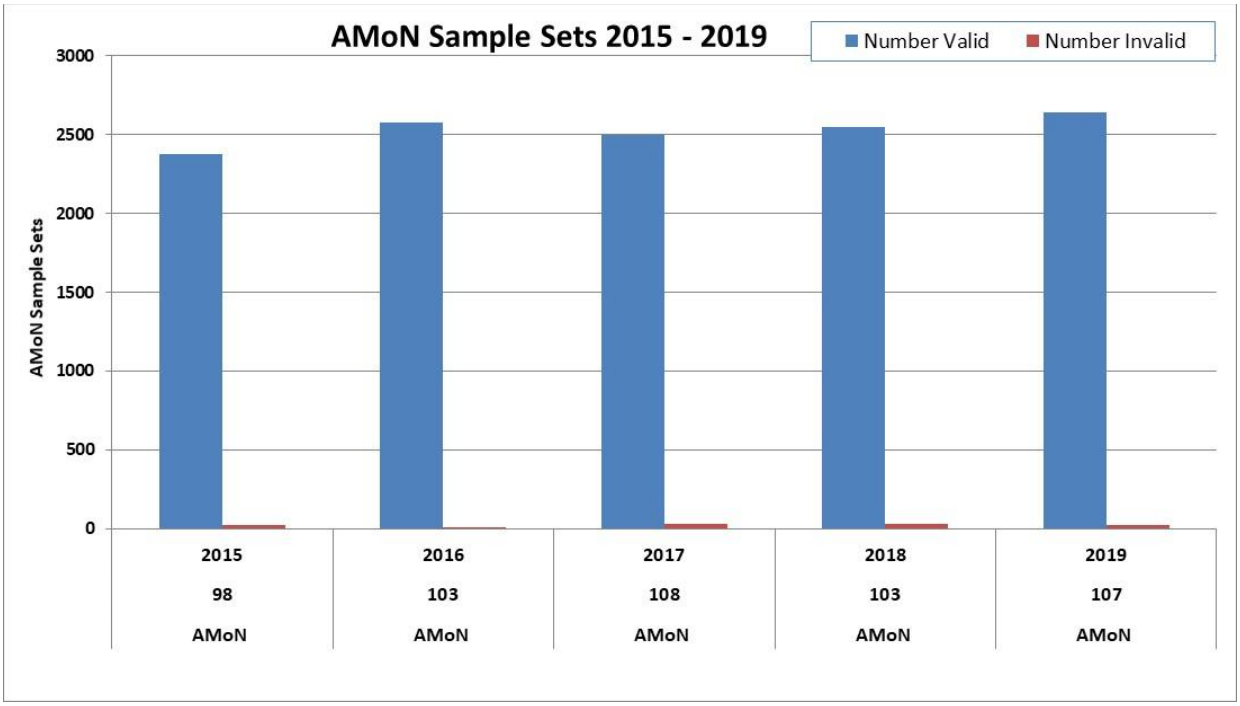

Figure 3. Total Valid and Invalid AMoN Samples from January 2015 - December 2019.

4. Network Operation

The three NADP networks have been operating for many years; with NTN over 40 years. The AIRMoN Network ended in September of 2019. **Table 4** shows the total samples (including dry and trace) received by the CAL through 2019.

Table 4. Total Number of Samples in the History of NADP by Network (All Samples Received Prior to 1/2020)

Network	Date Network Began	Date Network Ended	Number of Years in Operation	Total Samples
NTN	7/5/1978	Continuing	41	464,352
AMoN	10/29/2007	Continuing	12	20,485
AIRMoN	9/23/1992	9/1/2019	27	7,709
TOTAL				**492,546**

4.1. Active Sites

The number of sites in each network varies from year to year. AMoN has seen the steadiest growth but NTN remains consistent.

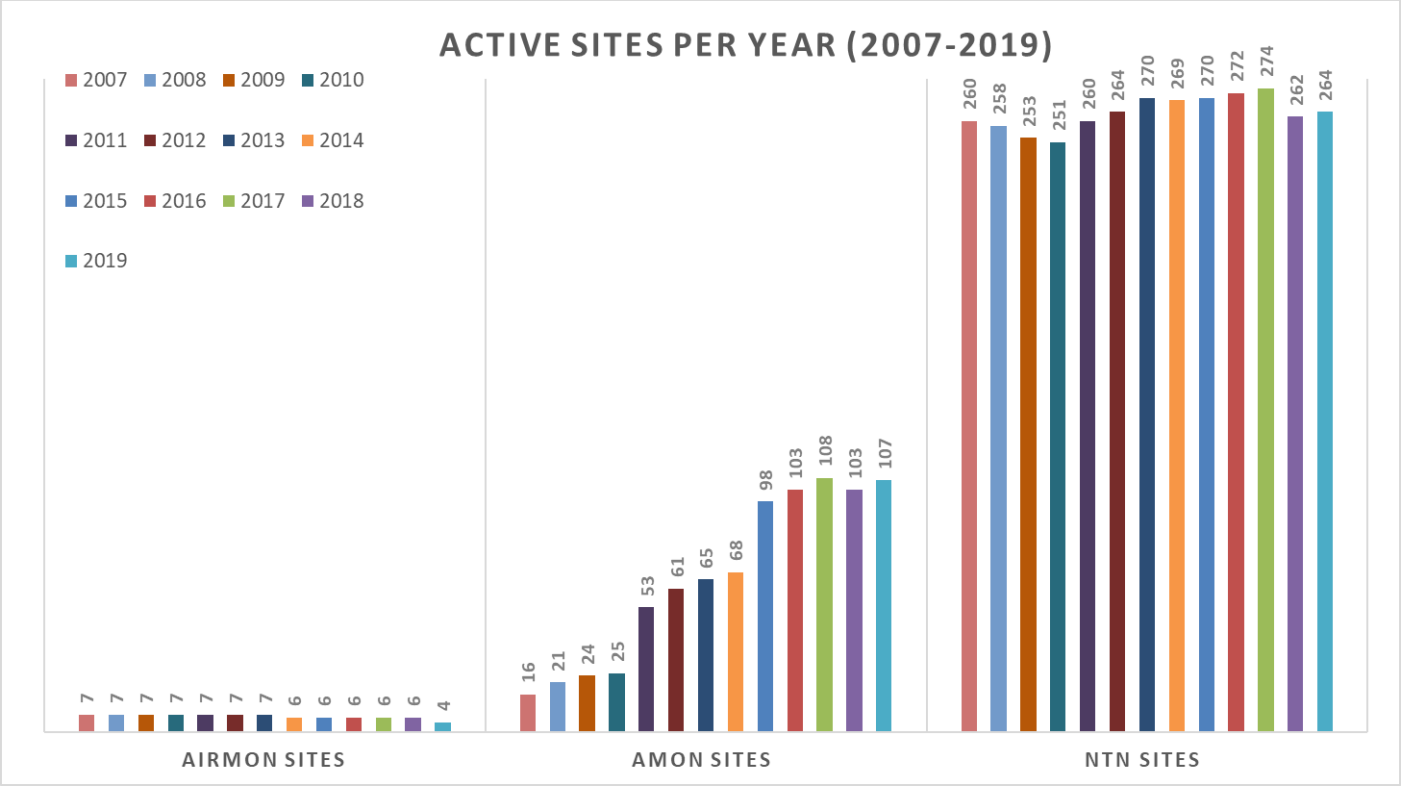

Figure 4. Active Sites per Network per Year.

5. Major Changes

The CAL has attempted to track all dates of major changes in network operations, sample processing and supply preparation that might affect sample results as shown. Major changes are noted in **Table 5**.

Table 5. Major CAL Changes June 1, 2018 - December 31, 2019

Date	Change	Notes
6/1/2018	Started processing all NTN, AMoN, and AIRMoN samples at WSLH	
8/17/2018	Stopped washing new NTN bottles	All lots QC checked before use
8/17/2018	Switched to vinyl gloves for all sample handling at login/pH/filtering and most platforms	
9/18/2018	Started new IC method for elimination oxalate interference	All samples with bromide detections from June - Sept 2018 were reanalyzed
11/21/2018	Began acid matrix-matching standards and QC samples for AMoN FIA analysis	
10/5/2018	Began using quadratic curve fit for IC analysis	
1/1/2019	Replaced 1 in 100 sites with Fixed sites and added WI06 to forever archive site.	Not sure on exact date
2/7/2019	Replaced both ICs due abnormal wear issue	Black powder issue - manufacturer replaced Ics
6/1/2019	Started new NTN site in WI -WI06	AMoN duplicate and TB each deployment
5/27/2019	Moved all Sample Receiving and Shipping to Henry Mall Location	
6/7/2019	Bromide analysis stopped	
8/29/2019	Moved AMoN Prep to 200B from 200C	
9/1/2019	AIRMoN Network Ended	

6. Annual Management Review

The annual management review for calendar year 2019 was completed on January 27, 2020. The review covered all major changes in the WSLH Environmental Health Division (EHD) over the previous year, including the CAL. The CAL section of the report is compiled along with reports from the other sections of the EHD, into one document that the division director reviews and approves. Significant operational changes in the CAL that were included in that report are summarized below.

CAL-Agriculture Drive 2019 report: the CAL continues to focus on improving processes and efficiencies.

- Staff
  All chemists have rotated to their 2nd analytical platform successfully. With the integration of the HAL and Litterfall at the WSLH/NADP a small percent of CAL staffing resources has now been allocated to support the HAL. Katie and Kirsten are each devoting 20 % of their time to the HAL (Litterfall and MDN samples). Jesse is now performing Atmospheric Mercury Network (AMNet) site audits, with 12% of his time dedicated to this area. This shift in staff resources will be monitored to make certain CAL functions are not negatively impacted.
- Audits
  No external audits were performed during this period. An internal audit was conducted in December 2019 by Camille Danielson (QA Manager).
- Equipment/Facilities
  An additional Ion Chromatograph (IC) was purchased for sample overflow, backup and research applications (The IC was installed 10/14/2019). The AMoN prep area transitioned from room 200C to 200B (8/29/2019) which is a larger area and accommodates the AMoN prep much better. The AIRMoN network ended on September 1st, 2019.
- Samples
  The CAL continues to process AMoN and NTN samples well before the respective analytical holding times. There have been preliminary discussions of a large expansion of the AMoN network (100+ additional sites). Depending on the exact scale of this expansion, additional CAL staffing may be required.
- Analysis Issue
  Bromide was removed as an official NADP analyte after the CAL discovered a positive bias/interference due to an oxalate ion in the IC chromatograms. Analysis of bromide ended June 7, 2019. There is one year of bromide data from June 2018 – June of 2019 that was analyzed with a new method at the WSLH CAL without interference. A summary report of these bromide data will be prepared in calendar year 2020.
- CAL-Data Management
  Going into 2019 the CAL data review group was turning around data to the Program Office within 90 days from the month of sample receipt. This rate slowed down in 2019 due to a major increase in "problematic" samples resulting from the Federal Government shutdown (late 2018 through early 2019) as well as time allocated to the HAL/MDN integration which had Zac taking time to train Dana (HAL Data review person). Zac and Dana have been cross-training (blending between the CAL/HAL) and expect to reduce turnaround times from >90 to 60 days in 2020. CAL continues to look for avenues to improve data quality; the data review process; and how final data results are presented to the customer.

CAL-Henry Mall (sample receiving and initial chemistry)

- Transition of CAL Receiving Unit
  The CAL sample receiving unit (which includes the NTN filtration and pH/conductivity protocols) moved its operations to Henry Mall on May 27, 2019 to merge with the CAL supply preparation and

shipping operations. This was initiated to improve efficiency and cross-training. Multiple areas within Henry Mall are being remodeled to accommodate this move as well as the arrival of the HAL (supply prep, shipping and receiving). Jimmy Sustachek was hired in late September to fill Maisie Dantuma's position. The entire NTN/AIRMoN/AMoN sample archive (>80,000 samples) has now been labeled and entered in our FreezerPro software. All archive samples generated by the WSLH CAL are frozen.

7. Staff Training

In addition to reviewing applicable SOPs, CAL staff must complete annual reviews of the QAP, policies on data integrity, safety, chemical hygiene, and more. A detailed sign off sheet is completed each year by all staff.

Analytical staff also complete an annual analytical demonstration of capability (DOC) for each platform they operate. New staff undergo even more rigorous DOC, initial document review and training protocols. Analysts rotate between different platforms usually on an annual basis. This allows for extensive backup capability as well as a fresh perspective and ideas for each platform.

8. CAL Instrumentation

TABLE 6. NADP Dedicated Major Analytical Equipment

Analysis	Type	Species	Instrument
Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES)	Base Cations	Na^+, K^+, Ca^{2+}, Mg^{2+}	Agilent 5100
Ion Chromatography (IC)	Acid Anions (and Br until 06/2019)	Cl^-, NO_3^-, SO_4^{2-} (Br until 6/2019)	3 Dionex Integrions
Flow Injection Analysis: Precipitation Samples (FIA- NTN)	NH_4 and PO_4	NH_4^+ and PO_4^{3-}	Lachat Quik Chem 8500 S2
Flow Injection Analysis: AMoN Extracts (FIA – AMoN)	NH_4	NH_4^+	Lachat Quik Chem 8500 S2
pH (pH Meter - Manual Method)	pH Manual	H^+	Mettler S700 Meter
Specific Conductance – (Conductance Probe – Manual Method)	Specific Conductance Manual	Charged Species	Mettler S700 Meter

9. QA Documents

The NADP CAL Quality Assurance Plan (QAP) was completed on June 20, 2019 (revision 0) and was revised to incorporate the mercury analytical lab (HAL) in 2020. An Annual Management Review, QAR and Internal Systems Audit will be completed. The CAL/HAL QAP contains detailed QA information on all aspects of the CAL.

9.1. Standard Operating Procedures

The CAL has prepared the standard operating procedures (SOPs) outlined in **Table 7** as of the QAR date. SOPs are available upon request. The analytical SOPs are revised as necessary in a time-sensitive manner when method updates are introduced and tracked using version control. Staff that work on a particular task are required to review the SOPs annually for those tests or processes and to affirm completion of their reviews.

Table 7. NADP CAL Standard Operating Procedures Table of Contents (as of 8/2020)

NADP CAL and HAL Standard Operating Procedures Table of Contents					
Revision Current 8/20/2020					
SOP Number	**Rev #**	**Current Effective Date**	**Title**	**SOP Original Effective Date**	**Category**
100	**2**	**7/6/2020**	**Sample Login and Data Entry**	3/20/2019	shipping
101	**1**	**1/2/2020**	**Sample Coding**	3/18/2019	Shipping
102	**1**	**7/7/2020**	**AMoN Supply Shipping**	6/18/2019	Shipping
103	**1**	**7/12/2020**	**NTN Shipping and Receiving of Supplies**	5/10/2019	Shipping
200	**2**	**7/30/2020**	**NTN and MDN Supply QC**	10/1/2018	QA
201	*NA*	*Draft*	*Analyst Training and Demonstration of Capability*	*Draft Target Dec 2020*	*QA*
202	**0**	**4/3/2019**	**Analytical QC Audit**	4/3/2019	QA
300	**0**	**10/30/2019**	**NTN Data review**	10/30/2019	Data
301	**0**	**11/18/2019**	**AMoN Data Review**	11/18/2019	Data
400	**0**	**9/4/2019**	**Preparation of Passive Ammonia Diffusive Samplers**	9/4/2019	Preparation
401	**0**	**10/17/2019**	**AMoN Sampler Extraction**	10/17/2019	Preparation
402	**2**	**7/30/2020**	**NTN Sample filtration**	3/25/2019	Preparation
403	**0**	**7/30/2020**	**NTN Supply Preparation**	5/10/2019	Preparation
404	**0**	**4/3/2020**	**Sample Archive Procedure**	4/3/2020	Preparation
407	**0**	**7/24/2020**	**CALNAT Sample Preparation**	**7/24/2020**	**Preparation**
500	**1**	**7/27/2020**	**ICP - OES**	1/8/2019	Analytical
501	**2**	**3/4/2020**	**Ion Chromatography**	2/4/2019	Analytical
502	**0**	**4/2/2019**	**Determination of Ammonium from Passive Ammonia Samplers by FIA**	4/2/2019	Analytical
503	**1**	**8/14/2020**	**Determination of Ammonium and Orthophosphate by FIA**	4/23/2019	Analytical
504	**1**	**7/30/2020**	**pH Manual**	3/15/2019	Analytical
505	**1**	**7/30/2020**	**Conductivity Manual**	4/3/2019	Analytical

10. Method Detection Limits

10.1. NTN Method Detection Limits (MDL)

When sufficient data points from daily NTN MDL spike samples, analytical blanks, processed NTN MDL spikes, and processed blanks have been generated (minimum of 7 but ideally 15 or more) the QA staff will calculate the Lab and Network detection limits respectively for NTN for use in assessing data for the following year. MDLs are calculated and verified using a process based on the current EPA MDL procedures.

Due to the CAL transition process (ISWS to WSLH) the 2018 WSLH network MDLs for NTN were those listed in the Readiness Verification Plan Final Revision (RVP), which was approved by the QAAG in spring of 2018. Therefore, the 2018 NTN Network MDLs were not statistically derived. The RVP Network MDLs were "goal" MDLs based on ISWS past MDL performance.

For 2019 data, the NTN Network MDL was calculated using results from 20 MDL spike samples which had gone through the entire process to mimic the handling of actual NTN samples. In both 2018 and 2019, the Lab MDL was calculated using the daily MDL solution (analyzed without processing) results (**Table 8**).

In the future, MDLs will be assessed using blanks and spikes at least annually to verify the established NTN MDLs (both Lab and Network) and will not be changed if the new MDL is within 0.5 to 2 times the established MDL and if fewer than 3% of the method blanks are above the established MDL.

The Lab MDL is used primarily to validate instruments and as a tool for the QA staff to assess validity of Network MDL. It is not used for qualifying NTN data.

The Network MDL is used for blank assessment and is applied to the NTN data published by the PO.

The field sample ID ranges for each network MDL are documented in the Historical MDL table (**Table 11**). The NTN sample results less than the Network MDL for each time period are published on the NADP website with the Network MDL value in place of the measured value and a less than (<) symbol in the qualifier column adjacent to the result.

Table 8. NTN Laboratory and Network Method Detection Limits 2018 -2019 (*Bromide analysis ended in June of 2019).

Analyte	2018 Lab MDL	2019 Lab MDL	2018 Network MDL	2019 Network MDL
Ca (mg/L)	0.004	0.001	0.011	0.023
Mg (mg/L)	0.002	0.001	0.003	0.006
Na (mg/L)	0.003	0.002	0.004	0.010
K (mg/L)	0.002	0.003	0.005	0.005
Cl (mg/L)	0.006	0.004	0.006	0.018
SO_4 (mg/L)	0.008	0.007	0.007	0.018
NO_3 (mg/L)	0.003	0.003	0.008	0.018
Br* (mg/L)	0.003	0.002	0.006	0.006
NH_4 (mg/L)	0.004	0.002	0.008	0.017
PO_4 (mg/L)	0.003	0.003	0.008	0.010
pH (S.U.)	0.01	0.01	0.01	0.01
Conductivity (µS/cm)	0.9	0.9	0.9	0.9

10.2. AMoN MDLs

The AMoN Lab MDL is based on mean core blanks. The Lab MDL is used for bench level QC (e.g. assessing blank acceptability, establishing low level standard values, and identifying samples <10*MDL). The AMoN Lab MDL is also used to flag travel blanks that are less than the Lab MDL with a "d" flag. This flag results in a sample data quality rating of B. In 2018, the CAL utilized the ammonium NTN Lab MDL as the AMoN Lab MDL due to the similar analytical platforms and a lack of core data to generate a true AMoN Lab MDL. In 2019, the AMoN Lab MDL was set equal to the mean core blank value from June – December 2018 = 0.016 mg/L. This Lab MDL reflects the variability in the background ammonia present in the core prior to deployment.

The AMoN Network MDL is based on mean travel blanks and is used to flag data from deployed samplers that is below the Network MDL with a "d" which will change the sample QR code from "A" to "B" (other factors could further reduce the QR to a "C"). The Network MDL is calculated based on all valid travel blanks for the most recent 11-12 months of data that has been published to the PO.

AMoN data prior to 2018 was assessed and flagged by the former CAL and PO based on a historical Network MDL of 0.04961 mg/L. The WSLH obtained the ISWS 2017 valid travel blank data in order to calculate the 2018 Network MDL for AMoN which was 0.119 mg/L NH_4.The 2019 AMoN MDL_N was calculated using all valid 2018 travel blanks. Travel blank data from January through June 2018 were generated from ISWS analyses,

while June through December 2018 data were generated from WSLH data. The 2019 Network MDL was calculated from 636 valid travel blanks to be 0.104 mg/L NH_4 (**Table 9**).

Refer to AMoN notes code information in the CAL/HAL QAP for additional details on flagging a QR codes. AMoN data is reported as measured, along with a QR code and is not "censored" by the Network MDL (AMoN results < Network MDL are reported as measured with a "d" flag).

Table 9. AMoN Laboratory and Network Method Detection Limits 2018 -2019 (*2018 Lab MDL was based on NTN FIA MDL due to lack of data for AMoN at beginning of network).

AMoN	2018 Lab MDL*	2019 Lab MDL	2018 Network MDL	2019 Network MDL
mg/L NH_4	0.008	0.016	0.119	0.104
Use	Analytical/Supply QC and to flag TB	Analytical/Supply QC and to flag TB	To flag deployed samplers	To flag deployed samplers

Table 10. AMoN Historical MDLs based on AMoN Sample Set ID. Note: The 2018 Lab MDL was based on NTN Lab MDL due to lack of WSLH data for AMoN.

AMoN Historical Method Detection Limits			
Sample ID Range	**Year of Sample Receipt**	**AMoN Network MDL mg/L NH_4**	**AMoN Lab MDL mg/L NH_4**
All Prior to N18005002	<2018	0.0469	0.0469
N18005002 - N18006407	2018	0.119	0.008
N19000001 - N19002669	2019	0.104	0.016

Table 11. NTN Historical Network MDLs based on Sample ID

NTN Historical Method Detection Limits (mg/L) Revision 7/2020												
Sample Start ID	Sample End ID	Aproximate Year RCV	Ca	Mg	Na	K	NO3	SO4	Cl	Br	NH4	PO4
NA0001	NA0067	1978	0.010	0.002	0.004	0.002	0.030	0.010	0.050	NA	0.030	0.005
NA0068	NA0104	1978	0.010	0.002	0.004	0.002	0.030	0.010	0.050	NA	0.030	0.004
NA0105	NA0221	1978	0.010	0.002	0.004	0.002	0.030	0.010	0.050	NA	0.020	0.004
NA0222	NA0335	1978	0.020	0.002	0.004	0.002	0.030	0.010	0.050	NA	0.020	0.004
NA0336	NA0446	1978	0.010	0.002	0.004	0.004	0.030	0.010	0.050	NA	0.020	0.004
NA0447	NA0452	1978	0.010	0.002	0.004	0.002	0.030	0.010	0.050	NA	0.020	0.004
NA0453	NA0668	1978	0.010	0.002	0.004	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA0669	NA1331	1979	0.020	0.002	0.004	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA1332	NA1675	1979	0.020	0.002	0.004	0.004	0.030	0.010	0.050	NA	0.020	0.003
NA1676	NA1800	1979	0.020	0.002	0.004	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA1801	NA3361	1980	0.020	0.002	0.004	0.004	0.030	0.010	0.050	NA	0.020	0.003
NA3362	NA3475	1980	0.008	0.002	0.004	0.004	0.030	0.010	0.050	NA	0.020	0.003
NA3476	NA3695	1980	0.008	0.002	0.002	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA3696	NA4254	1980	0.006	0.002	0.002	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA4255	NA6000	1981	0.008	0.002	0.002	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA6001	NA6328	1981	0.008	0.002	0.002	0.003	0.030	0.010	0.020	NA	0.010	0.003
NA6329	NA6543	1981	0.024	0.009	0.002	0.003	0.030	0.010	0.020	NA	0.010	0.003
NA6544	NA6650	1981	0.009	0.002	0.002	0.003	0.030	0.010	0.020	NA	0.010	0.003
NA6651	NA7299	1981	0.009	0.002	0.002	0.003	0.030	0.010	0.020	NA	0.020	0.003
NA7300	NA7741	1981	0.009	0.003	0.002	0.003	0.030	0.010	0.020	NA	0.020	0.003
NA7742	ND1937	1981-1985	0.009	0.003	0.003	0.003	0.030	0.010	0.020	NA	0.020	0.003
ND1938	ND1938	1985	0.009	0.003	0.003	0.003	0.030	0.010	0.030	NA	0.020	0.003
ND1939	ND2633	1985	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.003
ND2634	NF4630	1985-1987	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.010
NF4631	NH6700	1987-1989	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.020
NH6701	NM6824	1989-1993	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.020
NM6825	NS3700	1993-1998	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.003
NS3701	NU7200	1998-2000	0.009	0.003	0.003	0.003	0.010	0.010	0.005	NA	0.020	0.003
NU7201	NW0218	2000-2001	0.009	0.003	0.003	0.003	0.010	0.010	0.005	NA	0.020	0.009
NW0219	NZ9957	2001-2004	0.009	0.003	0.003	0.003	0.010	0.010	0.005	NA	0.020	0.006
NZ9958	TA0214	2004	0.009	0.003	0.003	0.003	0.009	0.013	0.008	NA	0.020	0.006
TA0215	TA0334	2004	0.002	0.001	0.003	0.001	0.009	0.013	0.008	NA	0.020	0.006
TA0335	TB4169	2005	0.002	0.001	0.003	0.001	0.009	0.013	0.008	NA	0.005	0.006
TB4170	TE3724	2006-2007	0.002	0.001	0.001	0.001	0.017	0.010	0.003	NA	0.004	0.004
TE3725	TG9571	2007-2009	0.006	0.001	0.001	0.001	0.009	0.010	0.004	NA	0.006	0.004
TG9572	TI2460	2009-2010	0.004	0.001	0.003	0.001	0.005	0.004	0.003	NA	0.010	0.008
TJ5599	TM2704	2011-2013	0.005	0.002	0.002	0.003	0.010	0.010	0.009	0.005	0.009	0.005
TM2705	TN2615	2014	0.019	0.005	0.005	0.001	0.007	0.005	0.008	0.005	0.017	0.009
TN2616	TP0369	2015	0.009	0.002	0.006	0.002	0.005	0.005	0.005	0.005	0.016	0.005
TP0370	TQ4360	2016	0.009	0.002	0.003	0.004	0.005	0.004	0.005	0.004	0.019	0.005
TQ4361	TS9999	2017	0.006	0.002	0.002	0.002	0.005	0.005	0.003	0.004	0.018	0.006
TT0001	TT7317	2018	0.011	0.003	0.004	0.005	0.008	0.007	0.006	0.006	0.008	0.008
TT7318	TV0257	2019	0.023	0.006	0.010	0.005	0.018	0.018	0.018	0.006	0.017	0.010

11. External Field QA Programs

Information for Sections 13.1 – 13.3 is extracted from the USGS External Quality Assurance Project Report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network, 2017–18 (Section 11.0).

11.1. The U.S. Geological Survey (USGS) Programs

The USGS used two programs to provide external quality assurance monitoring for the National Atmospheric Deposition Program's (NADP) National Trends Network (NTN) in 2019. The field audit program assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of NTN samples. Two interlaboratory comparison programs assessed the bias and variability of the chemical analysis data from the CAL and other participating laboratories that analyze precipitation samples for major ions, and nutrients.

11.2. Field Audit Samples

The field audit program uses equipment-rinse samples (bucket samples) paired with corresponding deionized water or synthetic precipitation solutions (bottle samples) to identify changes to chemical concentrations in NTN wet-deposition samples resulting from field exposure of the sample-collection apparatus (Wetherbee and Martin, 2020 in press). After a week without wet deposition, site operators pour 75 percent of the volume of their field audit solution into the sample bucket and seal the bucket with a lid for 24 hours prior to decanting the solution to a clean sample bottle (bucket sample = DF). The 25 percent of the field audit sample volume that remains in the sample bottle (bottle sample = DK) never contacts any field sampling materials. Both these samples are sent to the CAL for analysis. Contamination can be introduced to NADP samples by dissolution of materials residing on the bucket walls. In contrast, loss of dissolved constituents from the solution is possible through adsorption into the bucket walls. Dissolved constituents from the solution can also be lost through other chemical or biological processes. Contamination and sample stability are evaluated by the USGS for network data by statistical analysis of paired "bucket-minus-bottle" concentration differences for field audit samples.

11.3. Field Audit Results

The 2019 USGS Field data has not yet been assessed. However in the USGS report covering the 2017-2018 data (11.0) the following was reported. Variable levels of sample contamination over the past 10 years are small in terms of their absolute concentrations. However, the 2016–18 calcium, magnesium, sodium, and potassium NMCLs were equivalent to the 22nd, 26th, 20th, and 13th percentile concentrations, respectively, in NADP samples during the same period. The NMCLs for chloride (0.022 mg/L), nitrate (0.071 mg/L), and sulfate (0.054 mg/L), were at the 9th, 2nd, and 2nd NTN concentration percentiles, respectively. This program also estimated the maximum loss of ammonium, nitrate, and hydrogen ion in weekly NTN samples. Ammonium loss increased from 0.010 mg/L (2014–2016) to 0.020 mg/L (2015–2017), which is approximately 2.2 times the 2018 MDL for (0.009 mg/L). Hydrogen ion maximum loss was 2.50 microequivalents per liter, which has not changed since 2014.

11.4. PT Study results

The CAL participates in the USGS Inter-laboratory Comparison (monthly) as well as two other PT programs (semi-annual) under WMO and ECCC. The 2019 USGS results per USGS assessment had the exceedances listed in **Table 12**. However, it should be noted that the CAL assessment of these results against the USGS most probable value (MPV) showed that all of our results "recovered" within 10% of the MPV (or +/- our MDL) except one sample which appeared to be problematic for all analytes. USGS was contacted regarding that sample and it was confirmed that some other labs in the study also had issues. Consequently, there was a possible sample preparation or shipping issue with that particular PT sample. Therefore, the majority of the PT results generated by the CAL in 2019 were considered acceptable by the WSLH with the primary exception being pH on synthetic samples.

To address pH bias, a pH intercomparison study with the ECCC lab, including comparisons of probe and buffer type, was initiated. The pH recovery on USGS PTs showed a low pH bias (especially on low pH PTs) with recoveries ranging from 97-100 percent of MPV (using S.U.). Internal investigations identified that the current probe used in conjunction with Orion buffers and stirring would result in the most consistent results that are comparable to ECCC. In addition, we discovered an error in our calibration protocols during preparation for the study. The error found was the pH meter calibration protocols were set to default pH standards of 7.00 and 4.00. Correcting the standard values to the certified standard value (i.e. 6.97 versus 7.00) should resolve the bias seen in past low pH PTs.

TABLE 12. Proficiency Testing June 2018 – December 2019

PT Provider	CAL ID #	PT Studies Completed	Number of Samples as of 12/2019	Number of Analytical results submitted	Number of results outside of Control Limits	Website Results
ECCC	F303	ECCC 112, 113, 114 and 115	40	**400**	**2 - NO3, pH**	Not on website - Available upon Request
WMO Global Atmosphere Watch (GAW)	700175	WMO 58, 59, 60, 61	12	**120**	**7 - 1-Mg, 3-pH, 1-SO4, 1-NO3, 1- Conductivity**	http://www.qasac-americas.org/study-results
USGS	NA	2018-2019	48	**528**	**47 – Ca, Mg, Na, K, NH4, all 1 or 2 exceedances, pH 19, NO3 10, SO4 5, and Cl 4**	https://bqs.usgs.gov/PCQA/Interlaboratory_Comparison/graphOutput.php?page=start

WMO = World Meteorological Organization

USGS = United States Geological Survey

12. Analytical QA and Acceptance Criteria

Each QC solution has a set target value and acceptable range of values based on the applicable criteria (some are +/-10%, MDL etc.).

Table 13. Analytical Limits for Internal QC Solutions

NADP Combined Control Limits - Target Values (Acceptable Range)					
Revision: 22	8/25/2020				
ID	**Criteria**	**Ca**	**K**	**Mg**	**Na**
FB190001	**±MDL**	**0.000 (-0.023-0.023)**	**0.000 (-0.005-0.005)**	**0.000 (-0.006-0.006)**	**0.000 (-0.01-0.01)**
FR50200#	**±MDL**	**0.13 (0.107- 0.153)**	**0.022 (0.017-0.027)**	**0.023 (0.017-0.029)**	**0.057 (0.047-0.067)**
FLP18001	**90-110%**	**2.5 (2.25-2.75)**	**2.5 (2.25-2.75)**	**2.5 (2.25-2.75)**	**2.5 (2.25-2.75)**
FH180002	**90-110%**	**5.0 (4.5-5.5)**	**5.0 (4.5-5.5)**	**5.0 (4.5-5.5)**	**5.0 (4.5-5.5)**
FL190001	**80-120%**	**0.05 (0.04 - 0.06)**	**0.05 (0.04 - 0.06)**	**0.05 (0.04 - 0.06)**	**0.05 (0.04 - 0.06)**
FM180002	**90-110%**	**0.5 (0.45-0.55)**	**0.5 (0.45-0.55)**	**0.5 (0.45-0.55)**	**0.5 (0.45-0.55)**
ID	**Criteria**	**NH_4 (NTN/AIRMON)**	**OPO_4**		
FB190001	**±MDL**	**0.000 (-0.017-0.017)**	**0.000 (-0.01-0.01)**		
FR50200#	**90-110%**	**0.250 (0.225-0.275)**	**NA**		
FL190001	**80-120%**	**0.05 (0.04 - 0.06)**	**0.015 (0.012-0.018)**		
FM190002	**90-110%**	**0.600 (0.660-0.540)**	**0.200 (0.220-0.180)**		
ID	**Criteria**	**Cl**	**SO_4**	**NO_3**	
FB190001	**±MDL**	**0.000 (-0.018 - 0.018)**	**0.000 (-0.018 - 0.018)**	**0.000 (-0.018 - 0.018)**	
FR50200#	**90-110%**	**0.104 (0.094 - 0.114)**	**0.958 (0.862-1.054)**	**0.898 (0.808-0.988)**	
FL190001	**80-120%**	**0.025 (0.02-0.03)**	**0.025 (0.02-0.03)**	**0.025 (0.02-0.03)**	
FM180003	**90-110%**	**0.5 (0.45-0.55)**	**0.5 (0.45-0.55)**	**0.5 (0.45-0.55)**	
ID	**Criteria**	**NH_4 (AMoN)**			
FB190001	**±MDL**	**0.000 (-0.013- 0.013)**			
FR50200#	**90-110%**	**0.250 (0.225-0.275)**			
FL190001	**80-120%**	**0.05 (0.04 - 0.06)**			
FMAM2001	**90-110%**	**0.750 (0.675-0.825)**			
QC ID	**Description**				
FB190001	Calibration Blank - Type 1 Water.			AMoN LDR= 10 mg/L; No Carryover up to 10 mg/L	
FR50200#	Faux Rain Solution - ~50% NTN Concentration.			Lachat NH4 & OPO4 LDR= 10 mg/L; No Carryover up to 10 mg/L	
FL190001	Quality control sample at low level - second source.			ICP LDR= Mg=13 mg/L, K,Ca, Na =20mg/L ; No carryover up to 10 mg/L	
FLP18001	Quality control sample at low level - second source. For high curve on ICP				
FH18002	Quality control sample at high level for ICP high curve - same source as curve.				
FM180002, FM180003 or FM190002	Quality control sample at mid level - same source as curve.			IC LDR= 15 mg/L; No carryover up to 15 mg/L	
FMAM2001	Quality control sample at mid level - for AMoN (NH_4 only no PO_4) - same source as curve.				
O:\Teams\NADP\NADP Lab\LAB Final Forms\QC acceptance limits					

12.1. Analytical Sample Duplicates

Duplicate sample analysis is performed to assess the overall laboratory analytical precision. A second aliquot of a sample is analyzed and the precision between the two results is evaluated. Duplicates are chosen at random (volume permitting) and must be performed at a frequency of 10% (i.e. one per group of 10 samples). If a sample set/group has fewer than 10 samples, a duplicate is still analyzed. Refer to **Table**

14 for the duplicate acceptance criteria for the ICP, IC and FIA platforms. Criteria for the pH and conductivity duplicates must is within 0.2 pH units and 1 uS/cm, respectively.

Table 14. Sample and Duplicate Scenarios and Criteria

Sample Result	Duplicate Result	Calculation	Criteria
MDL – 10x MDL	MDL – 10x MDL	Absolute Difference (AD)	AD must be ±MDL
<MDL	>MDL	Absolute Difference (AD)	AD must be ±MDL
<MDL	<MDL	AD=ND (Absolute Difference = No Difference)	Passes
<10x MDL	>10x MDL	Relative Percent Difference (RPD)	RPD must be within 10%
>10x MDL	>10x MDL	RPD	RPD must be within 10%

Table 15. Analytical Duplicates and Percent Exceedances in 2019

Platform	# Replicates in 2019	# Failures in 2019	% Exceedance (prior to reanalysis)	# Reanalyzed successfully
FIA (AMoN and NTN)	1514	31	2.0%	28
ICP-OES	1443	5	0.3%	5
IC	1543	2	0.1%	0
pH/Conductivity	1187	33	2.8 %	31

13. Network Supply QC

Each network within the NADP long-term monitoring program requires very specific sampling supplies, all cleaned and prepared using established specialized protocols to maintain data consistency throughout the networks. The CAL must supply materials of identical quality to those being replaced at the sites. The laboratory cleans and provides supplies for NTN and AMoN (and previously for AIRMoN). In order to verify that supplies are adequately clean, supply blanks are measured as outlined in **Table 16** and **Table 19**.

13.1. New Supply Assessment

New lots of NTN bottles, ICP/FIA test tubes, filters, and sampling bags that are not routinely pre-washed must meet established "Lot QC" based criteria before use within the networks. Details are provided in NADP SOP 200 "NTN and MDN Supply QC" – a brief summary is provided below.

13.1.1. New Filter Lot Testing

All viable NTN samples are filtered upon receipt. Polyethersulfone 0.45 µm filters are used to isolate the insoluble particulate matter from the operationally defined soluble/dissolved fraction in all NTN precipitation samples. Extractable contaminants in these filters are assessed with each new filter lot prior to use and additionally with one filter at the start/end of each filter day.

13.1.2. New Bottle, Bag and Test Tube Testing

New bottles, sampling bags and test tubes are lot tested prior to use per the protocols in **Table 16**.

Table 16. New Lot Supply QC for NTN and MDN

NADP Supply Lot Approval QC Frequency and Log In (Revision 6/23/2020)					
Item	**Solution**	**Amount & Frequency**	**Project LOG IN**	**Client Number**	**LIMS Description**
BAG LOTS					
NTN Sample Bags	~150 mL MQ	20/new lot (unless <500 then 10)	**New Sampling Bag Lot Check**	Date Prepared and Preparer Initials	Bag Type, Lot #, Bag# (i.e. NTN Sample Bag Lot 32344 1 of 20)
NTN Bucket Bags	~150 mL MQ	5/new lot	**Bag Blank Study**	Date Prepared and Preparer Initials	Bag Type, Lot #, Bag# (i.e. NTN Bucket Bag Lot 32344 1 of 5)
NTN LID Bags	~150 mL MQ	5/new lot	**Bag Blank Study**	Date Prepared and Preparer Initials	Bag Type, Lot #, Bag# (i.e. NTN lid bag Lot 32344 1 of 5)
BOTTLE LOTS					
NTN 60mL HDPE Bottles	~60mL MQ	10/new lot (unless <100 in lot then 5)	**NADP New Bottle Blanks**	Date Prepared and Preparer Initials	Bottle Type, Lot #, Bottle# (i.e. 60mL NTN Lot23238 1 of 10)
NTN 1 Liter HDPE (New)	~150 mL MQ	10/new lot (unless <100 in lot then 5)	**NADP New Bottle Blanks**	Date Prepared and Preparer Initials	Bottle Type, Lot #, Bottle# (i.e. 1L NTN Lot44348 1 of 10)
MDN 250 mL, 1L or 2L PETG	20 mL 1% HCl + 100mL MQ	10/new lot (unless <200 in lot then 5)	**MDN Bottle Blanks**	Date Prepared and Preparer Initials	Bottle Type, Lot #, BottleID, Bottle# (i.e. 250mL MDN Lot 126 Bottle 1 of 10)
FILTER LOTS					
NTN 47mm Disc Filters	60 mL MQ	20/New Lot min 2 boxes from lot	**Filter Blank Lot Testing**	Date Prepared and Preparer Initials	Lot, Box#, Filter #, Brand and filter type
NTN Syringe Filters	20 mL MQ	5 per lot of 150 or less	**Filter Blank Lot Testing**	Date Prepared and Preparer Initials	Lot, Box#, Filter #, Brand and filter type
TUBE LOTS					
NTN Test Tubes	2-10 mL MQ	10/New Lot ICP/FIA	**Test Tube QC Blank**	Date Prepared and Preparer Initials	Brand, Test tube type, lot # and tube # (i.e. Fisher, ICP, Lot 3434, 2 of 10)
OTHER LOTS					
MDN Acid Preservative	30 mL	1/Batch of Acid Preservative	**Acid Checks**	Date Prepared and Preparer Initials	"Acid Preservative Blank", Acid Lot # and Batch ID
Must Meet LOT Approval Before Use of these Supplies					

13.1.3. Lot Testing Criteria

The CAL lot testing criteria states that the mean of at least 10 samples per lot must be < NTN MDL_N and none of the supply blanks in the batch tested may exceed 3 times the NTN MDL_N. If the criteria are met the new lot can be used. If the QC criteria are not met then another set of 10 must be tested or the entire lot is rejected and returned to manufacturer. If the second test fails, the lot must be rejected. For lots of filter or bag supplies greater than 1000 a minimum sample set of 20 QC checks are analyzed. Lot approval criteria are listed in **Table 17**, and results for the numbers of samples that exceeded criteria in 2019 are shown in **Table 18**.

Table 17. NTN Lot Approval QC Samples and Failures

Item tested	# of 2019 QC Samples	Number Failed	Lots Tested	Lots Rejected	Lots Approved
Bottles - 60 mL, 250 mL, 1L	192	0	19	0	19
Large NTN PES Disk Filters	92	58	3	2	1
Test Tubes - ICP and FIA	160	0	16	0	16

Table 18. NTN Ongoing Supply QA Percent that Exceeded Criteria in 2019.

Item Tested	Ca	Na	K	Mg	Cl	SO_4	NO_3	NH_4	PO_4
Used 1L Bottles (n=202)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Used Buckets (n=239)	0.8	0.0	0.0	0.0	0.0	0.0	2.1	1.7	0.0
Used Lids (n=429)	0.2	7.0	4.2	0.0	6.1	0.5	0.2	0.0	0.0
NTN Filters (n=403)	0.0	1.2	0.2	0.0	1.0	0.0	0.2	0.0	0.0
MQ H20 (n=166)	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0
Lid/Bucket Bags (n=93)	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0
New Buckets/Lids (n=4)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

13.2. Ongoing Supply Assessment

Data from the ongoing supply QC program (**Table 19**) is assessed, at a minimum, on a quarterly basis. Trends are investigated and corrective action taken as needed. Analysts are asked to notify the QA Manager if they notice high supply blanks in analytical runs so that they can be followed up on as quickly as possible. Reused (or new washed) NTN supplies are assessed for blank values above the supply criteria which are set to the NTN MDL_N. Results for 2019 ongoing supply QC testing are shown in Figure 5.

Table 19. Ongoing Supply QC, Performance Test Solutions, and Standards (NTN and MDN)

NADP Ongoing Supply QC Frequency/Log In (Revision 6/24/2020)

Item	Project Log In	Client Number	LIMS Description	Solution	Amount/Frequency
TYPE I WATER					
MDN Type 1 Water	MQ Water System Blanks	Date Prepared & Initials	"Hg Type 1 Water Blank", BLDG, Lab # (i.e. Type 1 Blank, AG 200, HM135)	100 mL MQ	1/purifier/week
NTN Type 1 H_2O Blanks	MQ Water System Blanks	Date Prepared & Initials	"Type 1 Water Blank", BLDG, Lab # (i.e. Type 1 Blank, AG 200B, HM135)	60 mL MQ	1/purifier/week
ONGOING Supply Tests NTN					
NTN 47mm Disc Filters	Filter Blanks DI	Date Prepared & Initials	"Start/End Filter" and Sample Range	60 mL MQ	2/ Filter Day
NTN Syringe Filters	Weekly Syringe Filter Blank	Date Prepared & Initials	"Syringe Filter Blank", Syringe and Filter Lot#	20 mL MQ	1 per week
NTN Sample Bags	Bag Blank Study	Date Prepared & Initials	Bag Type, Lot#	~150 mL MQ	1/week
NTN 1 Liter HDPE	Bottle Blanks	Date Prepared & Initials	"1L NTN Washed"	~150 mL MQ	1/wash day
NTN Buckets	Bucket Blanks	Date Prepared & Initials	"New" or "Used" "Bucket"	~150 mL MQ	1/wash day
NTN LIDS	Lid Blanks	Date Prepared & Initials	Lid Type	~100 mL MQ	1/wash day /per type
ONGOING Supply Tests MDN					
MDN Sample Train	Sample Train Blanks	Date Prepared & Initials	"Sample Train Preparation Week"	~ 100 mL MQ	1/week in bag for ≥2 days
MDN Acid Bath	Acid Checks	Date Prepared & Initials	"Acid Bath Blank", BathID	10 mL	1/Acid Bath/month
USGS System Blanks	USGS System Blanks	Date Logged & Initials	USGS ID for blanks, Blank 1 of 2	Hi purity H_2O	2/Quarter
PTs					
NTN WMO PTs	WMO/GAW	WMO Sample ID	"WMO PT X of X"	As Sent	2/year
NTN ECCC PTs	ECCC PT Samples	ECCC Sample ID	"ECCC NTN PT X of X"	As Sent	2/year
NTN USGS PTs	USGS Intercomparison	USGS Sample ID	"USGS NTN PT X of X"	As Sent	Monthly
MDN USGS PTs	MDN PT Samples	USGS Sample ID	"USGS MDN PT X of X"	As Sent	Monthly
MDN ECCC PTs	ECCC PT Samples	ECCC Sample ID	"ECCC MDN PT X of X"	As Sent	Annual
QC STANDARDS					
NTN MDL Sample	NTN MDL Sample	Date Prepared & Initials	NADP MDL Solution ID, Bag Lot if new	200 mL MDL solution	As needed
Special Checks	Special QA Checks	Date Prepared & Initials	Information on what is being tested	Varies	As needed
Test QC Standards	QA New Standard Check	FMDL# (i.e. FMDL2003), Initials	NADP Solution# (for testing of new FMDL or new FR50 or other QCS)	Varies	As needed
Official QC Standard	Lab QC	FXXXXXXX (8 digits req), initials	NADP Solution# (for any standard with limits set in LIMS)	Varies	As needed

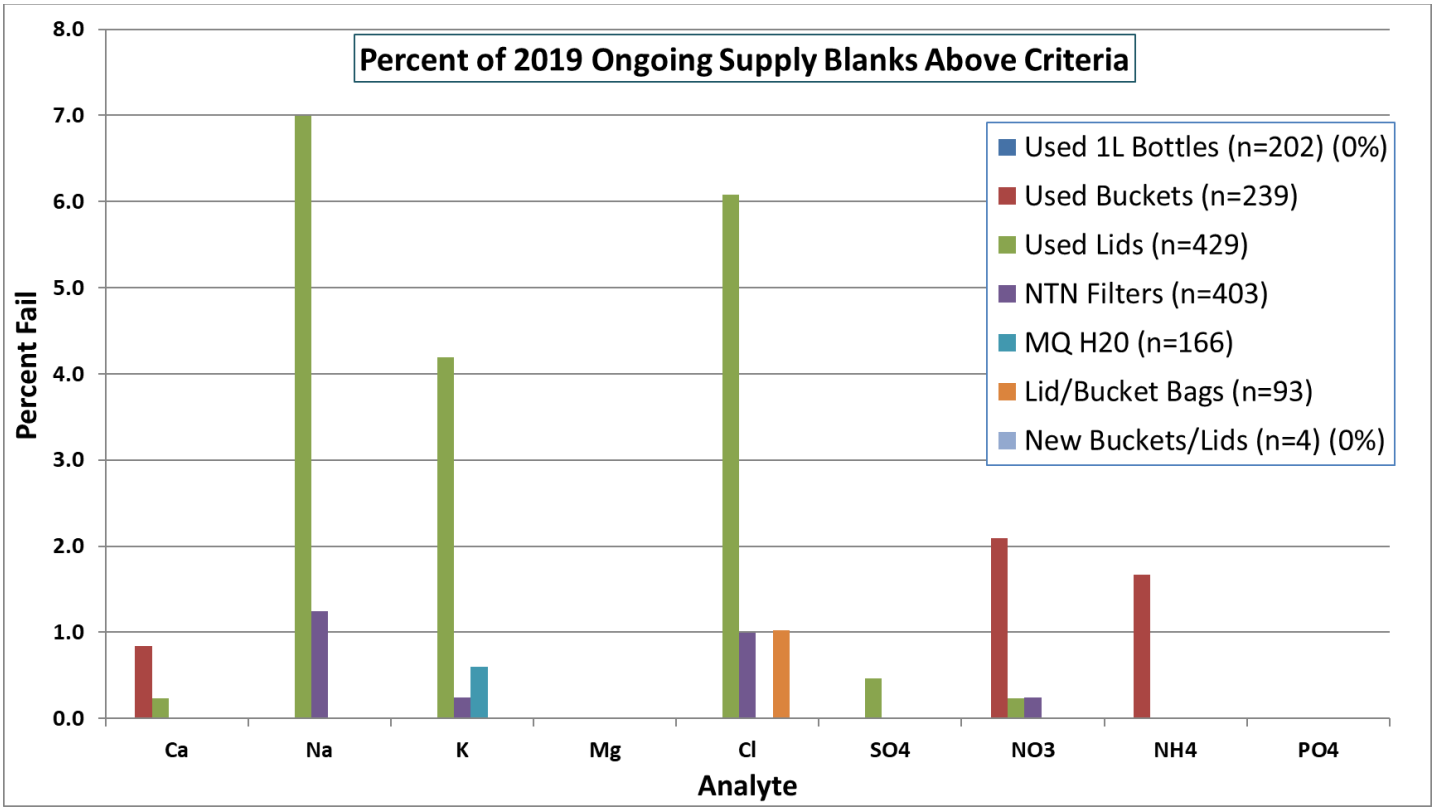

Figure 5. Percent of 2019 Ongoing Supply QC Tests that Exceeded NTN Network MDLs (no exceedances for used 1 L bottles, new buckets or new lids).

14. Laboratory Supplies Used for AMoN samples

Atmospheric sampling is done using Passive Diffusion Samplers (PDS) approved by NADP (currently restricted to Radiello® products). These samplers and associated shipping supplies undergo extensive cleaning practices. A variety of QC samples are tested to ensure background ammonium remains low in all prepared supplies as well as the preparation and extraction environment.

As outlined in **Table 20**, "AMoN Supply QC", the diffusive bodies and cores are "blank" tested as well as the glass storage/shipping jars, extraction water and various hood/room blanks from the AMoN processing suite.

Table 20. AMoN Supply Quality Control 2019

NADP CAL AMoN Preparation QC (Revision 2/28/2020)					
QC Type	**Description**	**Frequency**	**Criteria**	**Origin of Criteria**	**Corrective Action**
Preparation Blank	Fully Assembled core, body, coupler placed in jar/bag, frozen overnight before extraction	1 per sampler preparation batch (each sonicator batch is 1 batch)	<0.044 mg/L NH_4	Less than median travel blank level 2018	Determine if the whole batch or a core lot issue. If possible re-clean samplers in batch and/or replace cores and retest. Or add qualifier to samplers (h flag = QR B).
Core Blank	Brand new core extracted along with other QC	1/sampler assembly day/previous lot 2/sampler assembly day/new lot	<0.044 mg/L NH_4	Less than median travel blank level 2018	Assess scope of issue/number of cores high. Action can include: test 2-3 more cores from lot, reassemble cleaned samplers with new cores/retest, return core lot, prepare entire batch of samplers, qualify data from batch of samplers (h flag = QR B).
Jar Blank	Cleaned new or used jar + 10 mL Type I, turned upside down, left overnight, and analyzed	1 per wash batch	<0.016 mg/L NH_4	Less than median travel blank level 2018	Pull additional jar(s) from wash batch if possible. Look at related core/prep blanks for root cause. Check cleaning including: bins, bin liner, dishwasher, jar caps.
Method Blank	Type I water from the auto dispenser used to do extractions	1 per extraction day	<0.022 mg/L NH_4	1/2 Prep blank criteria	Compare to samplers/QC from same extraction. If possible take another sample from dispensing jar. Samples associated with blank must be qualified due to possible contamination (h flag = QR of B).
Sonicator Blank	Water from the sonicator after last step in the cleaning process	1 per preparation day per sonicator	<0.016 mg/L NH_4	Analytical NH_4 MDL_L	Use with other QC samples to determine root cause. Indicates potential issue with cleaning. Action includes: cleaning of the sonicator baths, racks and covers, test Type I water, check source of cleaning solutions.
Water Blank	Sample of Type I water from MilliQ system used to fill sonicator/auto dispenser	1 per preparation day	<0.016 mg/L NH_4	Analytical NH_4 MDL_L	Repeat test of MilliQ system. If fails again have the system serviced and utilize another water source if possible. Review other QC samples from the same system (weekly MQ blanks) to assess longevity of the issue.
Hood Extraction Blank	Sampler hung in the hood during the extraction (deployment of 1-5 hours normally)	1 per extraction day	<0.2 mg/L NH_4	Travel Blank Criteria	Check filters and review QC from same extraction for correlation with higher blank values. Check for power failures or other issues with hoods.
Room Blank	Sampler deployed in the extraction room (not in a hood) for 2 week period	1 per two week period	<0.8 mg/L NH_4	2 X Hood Criteria	Room should be checked for possible sources of ammonia or ventilation issue.
Hood - 2 Week Blank	Sampler deployed in hoods for two week period	1 per two week period per hood	<0.4 mg/L NH_4	2 X the travel blank criteria	Review QC samples from same time period for a correlation with higher blank values if hood criteria is exceeded. Check for power failures or other issues (filters) with hoods.

14.1. AMoN Supply QA Results June 2018 – 2019

Over 900 AMoN supplies/environmental QC samples were tested in 2018 and 2019. There were 10 samples (2.2%) that exceeded criteria in 2018 and 2 samples (0.3%) in 2019. The supply preparation continues to maintain extremely low levels of ammonium which is reflected in the low travel blanks as well.

Table 21. Summary of AMoN Supply QC Results June 2018 – December of 2019

QC TYPE	2018 MEAN	2019 MEAN	2018 # TESTED June - Dec	2019 # TESTED	Number of Exceedances 2018	Number of Exceedances 2019	Criterion mg/L NH_4
Preparation Blanks	0.019	0.013	60	99	0	0	0.044
Core Blanks	0.013	0.01	46	73	1	1	0.044
2 Week Hood Blanks	0.263	0.051	28	52	5	0	0.44
Room Blanks	0.524	0.51	14	25	1	0	0.88
Hood Extraction Blanks	0.047	0.017	25	51	0	0	0.2
Water Blanks	0.002	0.002	120	171	2	0	0.016
Jar Blanks	0.002	0.003	62	112	1	1	0.016
Totals			**355**	**583**	**10**	**2**	
Percent Exceedance					**2.2%**	**0.3%**	

15. Travel Blanks and Field Triplicates for AMoN

At least 25% of sites receive a travel blank each 2-week deployment and sites are rotated to ensure that all sites receive a travel blank several times per year. In 2018 and 2019 triplicate samplers were sent to approximately 15% of the sites also in a rotating fashion. This field QA program was fully implemented in August 2018 once the AMoN program was well established at the WSLH.

15.1. Travel Blanks

Over 1000 travel blanks were returned from the field and analyzed between June of 2018 and November of 2019. Results for the travel blanks are shown in **Table 22** and **Figure 6**. There were no valid travel blanks above 0.2 mg/L NH_4 during June 2018–November 2019. The mean/median travel blanks have remained very consistent at less than 20% of the criterion of 0.2 mg/L. It should be noted, mean core blanks in 2019 were 0.01 mg/L NH_4 which equates to ~1/3 of the mean travel blank concentration. This demonstrates that actual ammonium contamination during field handling is very small as over 1/3 is from the core background.

Table 22. AMoN Travel Blank Results 2018-2019

	June - Dec 2018	Jan 2019 Thru Nov 2019	June 2018- Nov 2019
	mg/L NH_4	mg/L NH_4	mg/L NH_4
Mean	0.038	0.036	**0.036**
Median	0.034	0.033	**0.033**
Max	0.184	0.125	**0.184**
Number of Valid Travel Blanks	363	666	**1029**
Number of Invalid (QR=C) Travel Blanks (not used)	6	2	**8**

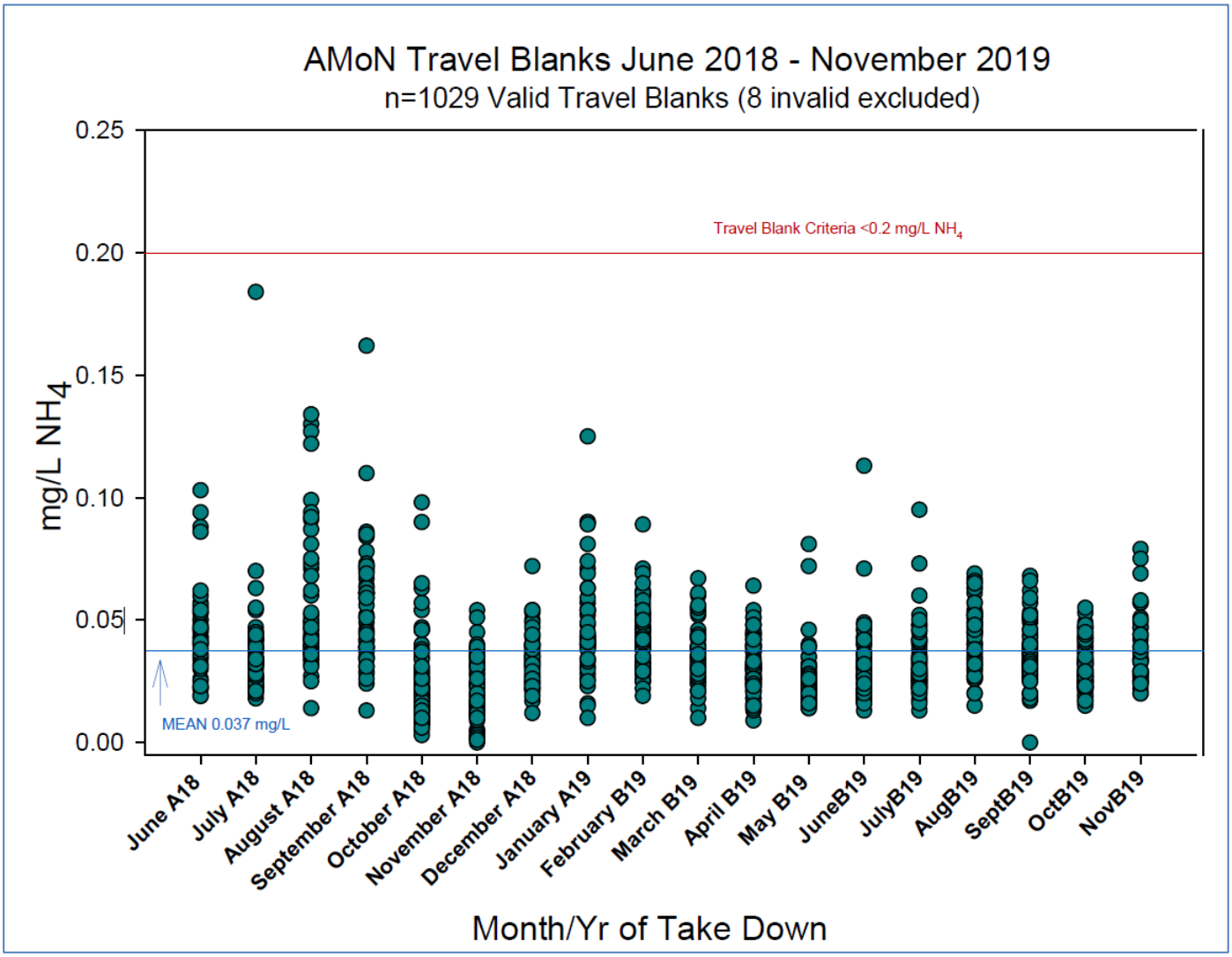

Figure 6. AMoN Travel Blank Ammonium Levels June 2018 – November 2019

15.2. AMoN Triplicates

From August 2018 through November of 2019 there were 472 sets of valid (not excluded due to major lab or field error) triplicates deployed and assessed. Triplicates that exceed 15% RSD are retested, and noted in the qualifiers spreadsheet.

The average relative standard deviation for the data set is 6.1% RSD while the median RSD is 2.6 %. Over this time period, approximately 97% of the sample sets had less than 20% RSD (**Table 23**). As can be seen in Figure 7 those above 20% are generally substantially above 20% usually due to that fact that one of the 3 samplers is significantly different in ammonium level than the others. This indicates supply, field or shipping issues because any results above 15% RSD are reanalyzed and confirmed by the CAL (not analytical).

Table 23. AMoN Triplicate Relative Standard Deviations

Triplicate Outcomes	#	% Overall
Sets over 10% RSD	48	10.2
Sets over 15% RSD	31	6.6
Sets over 20% RSD	16	3.4
Sets over 30% RSD	7	1.5

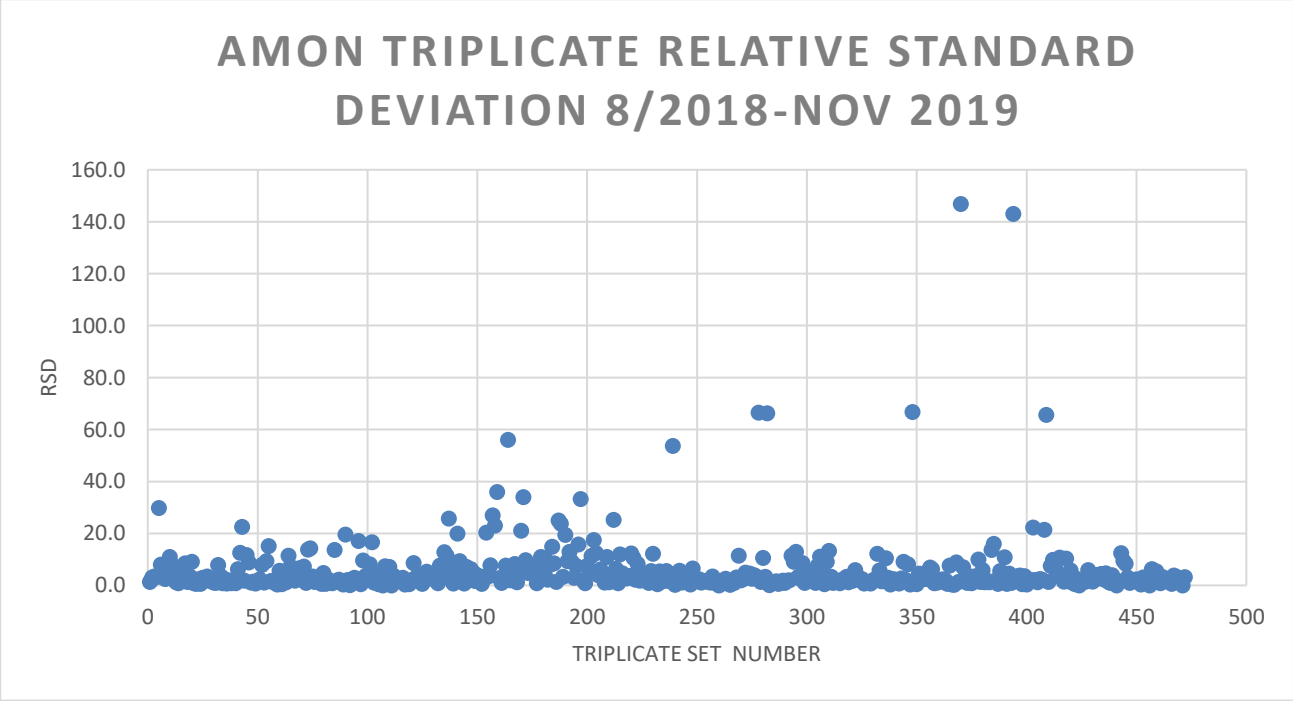

Figure 7. Variability (% RSD) of field triplicates from August 2018–November 2019; n=472 sets, 1410 individual samplers – some were duplicates rather than triplicates).

16. Audits - *June 2018-December 2019*

External NADP "Mini" Audit July 2018 – Conducted by Greg Wetherbee (USGS), Mark Nilles (USGS), Cheryl Sue (ECCC), and Mike Kvitrud (Wisconsin Department of Natural Resources).No lab-related findings – report available upon request.

Internal Audit – December 2019 – First full-scale audit of the lab.

Table 24. CAL Findings from 2019 Internal Audit (Finding #s skipped are HAL or PO findings)

CAL/HAL Finding #	Finding Summary (refer to Report for Details)
1	Most analytical SOPs are lacking a reference to an equivalent federally approved method
2	SOPs have not been completed: M Analyst Training, NTN MDL Methods, Sample Archive Process
4	Temperature records used for monitoring of the temperatures in coolers and freezers at Henry Mall do not have document control and do not include acceptable criteria or the thermometer ID
5	Multiple kinds of records at Henry Mall included write-overs, scribbles or additions without proper method of corrections
6	The bucket and Lid weight log has lines without initials and dates when done on the same day
7	On several platforms the peer review cover sheet reagent codes, standard codes and pipettes are not filled out in the lab at the time of analysis.
8	Standards log for FMDL and FR50 standards needs to have the A and B bottles recorded in the lab notebook when making large batches of standards.
9	For NTN and AMoN login there is no tracking of the analyst completing the sample login.
12	A WI sample TU4277SW) had pH accidentally reported for it and the data was in LIMS without filling out possible qualifiers spreadsheet or notifying data staff.
13	Raw data for failed QC samples for pH and conductivity is not recorded.
14	Fresh calibration standard is not used for pH/Cond recalibration in the afternoon.
15	Conductivity QC standards are sometimes recorded under the incorrect 1900 number.
16	FB failure at end of conductivity run (1:16 PM) on 8/1/19 without another rerun recorded in LIMS or data qualified.
17	One AIR Science AMoN hood is overdue for filter replacement.
18	Date of AMoN sample extraction needs to be recorded for traceability purposes.
19	FIA NTN Standards and reagents warmed in hot tap water must be discontinued.
20	FIA NTN analytical test tubes being used did not have QA approval prior to use
21	FIA NTN data packet 4/24/19 analysis date had errors on the cover sheet dates and was lacking explanation of late upload to LIMS.
22	For ICP - potassium variability of blank as well as low bias on the FL (low level) standard noted over last 6 months especially.
23	ICP peer review packet needs to contain the LIMS upload sheet.
32	Need to record the completion of "Compare Review" data comparison (1st and 2nd data entry) for all networks with the initials and date of completion.
33	NTN analytical QC failures are not conveyed to data users on reports due to a lack of intermediate flag for indicating slight concern with a sample.
34	There is no AMoN gap report to help identify sites that are not sending samples to the lab.
37	Data in the data review program for AMoN time on did not match the field form for sample N19001013.
40	NTN sample TU1319SW invalid phosphorus data reported in preliminary report without analytical flagging due to inability to flag individual analytes.
42	Dilution factors for analytes diluted at each platform are not saved in LIMs despite being uploaded.
43	Analytical MDLs for NTN are not adjusted for dilution at each platform.
48	Occurrences not entered for some system failures at Henry Mall – including cooler #1 failure in October 2018 and RO system issues in December of 2019.
49	Overall labwide use of spreadsheets that are unlocked need at least annual verification of built in formulas.
50	Some instruments have a preventative maintenance schedule while others do not.
51	When samples are transferred to a secondary vessel (i.e. test tube) a clear link to the sample ID must be maintained
52	PT issues for pH need to be investigated further.

17. Occurrence Management

The CAL uses a lab-wide reporting system to record all major deviations from standard protocol, reoccurring issues and corrective actions. Occurrences are reviewed bimonthly at staff meetings and corrective actions are detailed, implemented and verified before occurrences can be closed out. Occurrence management is a tool to help track issues, identify trends, implement changes and educate staff on common problems.

Table 25. Summary of Occurrences Recorded 6/18-12/19

Number of Recorded Occurrences	Category of Issue
13	Instrument*
8	Sample Receiving
7	Known Standard
9	QC
7	Reporting
44	**Total**

*Most of the instrument occurrences were barcode scanner issues or IC problems.

18. Method Improvement Projects

The CAL has continued to test and assess new techniques and supplies that might improve outcomes for the networks. Some of the initiatives pursued in 2018-2019 include:

- Sample Archive Organization project
- WI Wet - Dilute Syringe Filtration Study
- Titrec Method development
- AMoN Sampler Bag shipping studies
- AMoN sampler permeability study
- NTN sample bag QC testing
- pH probe and buffer evaluation
- Five-year Archive preservation study (112 samples preserved frozen and refrigerated)
- Ammonium acid matrix study
- Interference free bromide method
- Nitrogen species stability – AIRMoN versus NTN

19. Special Studies

Special studies are required to go through a rigorous multi-step approval process at the CAL and PO. This begins with the completion of an official request form and review by PO and CAL. If approved, the requested NADP samples can be used for the research project. It is the goal of the CAL/PO review to provide constructive feedback to the researcher to improve the study outcomes. Special Studies that were in-place or

implemented in 2018-2019 are shown in **Table 26**. Some of the projects were grandfathered in because they were approved by the former CAL. Any new projects must undergo the assessment. There are fees for these samples and NADP data needs are always the first priority.

Table 26. NADP Samples Provided to Outside Research Groups (all for NTN) June 2018 – December 2019

Cooperator and Affiliation	# of Samples Provided	Description
Greg Wetherbee (USGS) Richard Dabundo (Univ. Pittsburgh) Sheila Murphy (USGS)	208 filtered water samples 42 filters	Water samples analyzed for stable isotopes; filters analyzed for urban pollution tracers.
Sydney Clark (Brown University)	23 filtered water samples	Characterize precipitation isotopic end-members for nitrate/ammonium in 2 CO Front Range watersheds (Loch Vale/Niwot)
Janice Brahney (Utah State Univ)	531 filters	Atmospheric dry deposition study
Jessica Zais-Bowman and Dr. Lowell Stott (Univ. of S. California)	63 filtered water samples	CA/OR/WA stable isotope study
David Clow (USGS)	50 filtered water samples	Estimate water residence times in the Loch Vale research watershed.
Ty Coplen (USGS)	149 filtered water samples	Measure stable hydrogen and oxygen isotopic abundances to generate a historic time-line of these data in the subject area.
Jessica Conroy (Univ. of Illinois)	323 filtered water samples	Investigate controls on the stable isotopic composition of North American mid-continent rainfall on weekly timescales.
Breanna Waterman (Kansas State Univ.)	47 filtered water samples (archive & incoming)	Stable isotope ratios for $^{2}H/^{18}O$ precipitation samples to understand drivers of isotopic signatures across Kansas aridity gradient
Michael O'Driscoll (E. Carolina Univ.)	6 unfiltered water samples	Compare Hurricane Florence runoff isotopic composition versus hurricane rainwater isotopic composition.
Benjamin Serpa (Univ. of Nevada)	27 filtered water samples (archive & incoming)	Lassen National Forest Stable Isotope Analysis
Martin Shafer (UnivWisconsin/WSLH)	56 unfiltered water samples	PFAS Analysis in precipitation
Tom Ladell (Univ. of Wisconsin)	20 unfiltered water samples	Provide rainwater samples for pH analysis in undergraduate lab class.
Monica Ramirez-Andreotta (Univ. of Arizona)	30 unfiltered water samples	Samples will be analyzed to compare results from sample collected from rooftop systems for home agriculture purposes.

20. Data Review

20.1. Analytical Data Review

There are several steps to ensure that data are accurate and properly qualified before moving to the data review stage. These include:

- Peer review – a second analyst reviews all data packets prior to results being uploaded/released.
- A pH and conductivity QC review – secondary QC review of pH and conductivity packets and QC due to the automatic upload of instrument data to the Laboratory Information Management System (LIMS) at the time of analysis.
- Possible Qualifiers spreadsheet – record of all anomalies with samples during preparation/analysis.
- Duplicate failures spreadsheet – record of all duplicate failures even those corrected by rerun to assess trends.
- LIMS Compare – monthly data packet review per platform compared to LIMS analytical data. Extra checks on duplicates and dilutions.

20.2. Network Data review

Prior to releasing reports to sites or publishing data to the PO, the CAL reviews all NADP sample data for completeness and consistency. This includes comparison to historical site values, precipitation review, second data entry and review of possible analytical qualifiers.

21. Data Management

Table 27. WSLH CAL Data Deliverables: Preliminary Reports to Sites and Data Delivered to the NADP Program Office by Network as of April 2020 (Samples Received June 2018–December 2019). Complete through months Listed.

Network	Preliminary Reports Sent [a]	Published to NADP Website [b]	CAL Average Turnaround Time (days)
NTN	November 2019	October 2019	119
AMoN	November 2019	November 2019	115
AIRMoN	September 2019	April 2019	110
MDN [c]	August 2019	January 2019	210

[a] Reviewed by CAL, delivered to the NADP Program Office, and preliminary reports sent to sites

[b] Data available on NADP website for public release (http://nadp.slh.wisc.edu/)

[c] Network acquired by WSLH on 06-01-2019

NTN, AIRMoN and AMoN samples are analyzed within the hold times (2 weeks from receipt for AIRMoN, 3 weeks from receipt for NTN and 3 weeks from date off for AMoN), and data are peer reviewed within 1-3

weeks of analysis and then uploaded to the NADP LIMS. Therefore, most data are input to the LIMS within 4 weeks of sample receipt. Data delivery from the CAL to the PO and the PO to the website is current as of April 2020 in **Table 27**. For example, this means November 2019 NTN data has been published to the PO and data through October 2019 is available on the website. CAL data turnaround time is calculated from the end of the month in which a sample was received to the exact date that either the data were reported to the site or published to the PO. Publishing on the website is the responsibility of the PO. The end of 2018/beginning of 2019 was complicated by the U.S. Federal Government shutdown which had a significant impact on data review (due to increased sample lags, unconventional practices at sites, precipitation issues and more). In addition, the Mercury Deposition Network was transitioned to the WSLH in June of 2019, requiring the development of a completely new LIMS for sample/data management, and data assessment and reporting by the HAL. This caused significant delays in all networks data review process.

22. References

- National Atmospheric Deposition Program Laboratory Quality Assurance Plan, Mercury and Central Analytical Laboratories. Revision 1, June 25, 2020 (**http://nadp.slh.wisc.edu/lib/qaPlans.aspx**
- Wetherbee, G.A., and Martin, RoseAnn, 2020, External quality assurance project report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network, 2017–18: U.S. Geological Survey Scientific Investigations Report XXXX–XXXX, In Press

23. Approvals

- 2019 CAL QAR (including 7 months of 2018 data) Prepared by Camille Danielson, NADP CAL/HAL QA Manager in consultation with Lab Manger Chris Worley and Data Processing Manager Amy Mager
- Approved by the NADP Program Office – Mark Olson on 5/4/2020
- Shared with the QAAG on 5/5/2020
- Reviewed and revised by Systems QA and Special Projects Manager – Martin Shafer in July 2020
- Approved by QAAG by vote: 8/24/2020