2021 Quality Assurance Report

January 01 – December 31, 2021

National Atmospheric Deposition Program

Central Analytical Laboratory and

Mercury Analytical Laboratory

Supply and Sample Shipping Address:
465 Henry Mall
Madison, WI 53706

Analytical Laboratories Address:
2601 Agriculture Drive
Madison, WI 53718

University of Wisconsin-Madison
Wisconsin State Laboratory of Hygiene
Website: http://nadp.slh.wisc.edu/

Approved Version Date: 6/1/2023

National Atmospheric Deposition Program

Table of Contents

1. OVERVIEW 3
2. SAMPLE COUNTS 4
3. NETWORK OPERATIONS 8
4. MAJOR CHANGES 10
5. ANNUAL MANAGEMENT REVIEW SUMMARY 11
6. STAFF TRAINING 16
7. INSTRUMENTATION 16
8. QA DOCUMENTS 17
9. NTN METHOD DETECTION LIMITS (MDL) 19
10. AMON MDLS 22
11. MDN AND LITTERFALL (MLN) MDLS 23
12. EXTERNAL FIELD QA PROGRAMS 25
13. INTERNAL FIELD QA PROGRAMS 27
14. ANALYTICAL QUALITY ASSURANCE 42
15. SUPPLY QC 59
16. AMON SUPPLY QC 64
17. OCCURRENCE MANAGEMENT 65
18. METHOD IMPROVEMENT PROJECTS 66
19. SPECIAL STUDIES 66
20. DATA REVIEW 68
21. DATA MANAGEMENT REVIEW 68
22. REFERENCES 69
23. APPROVALS 69

Central Analytical Laboratory (CAL) and Mercury Analytical Laboratory (HAL) Quality Assurance Report (QAR)

January 1 – December 31, 2021

1. Overview

The CAL provides sample processing, chemical analysis, and data validation services for precipitation samples collected by the NADP/National Trends Network (NADP/NTN), and for passive ambient air ammonia samplers for the NADP/Ammonia Monitoring Network (NADP/AMoN). The CAL initiated and expanded on many special projects in 2021, including continuing to provide support for per- and polyfluoroalkyl substances (PFAS) research at several NTN sites and is continuing the development of a secondary sampler that can be attached to NTN buckets for alternate sample collection and analysis (e.g. Total Nitrogen and Phosphorus). The CAL developed a new standard set of laboratory qualifying statements for lab issues that was incorporated into the NTN QR sample coding (as well as provide additional information to the client). The CAL sample load continues to hold steady for NTN and continues to increase for AMoN.

The Mercury Analytical Laboratory (HAL) prepares and provides field-sampling supplies, and performs sample processing, chemical analysis, and data validation services for precipitation and leaf litter samples collected by the NADP/Mercury Deposition Network (MDN) and Litterfall Initiative. The HAL chemical analysis for total mercury (THg) and methyl-mercury (MeHg) takes place inside a dedicated room of a Class 1000 (209E) (ISO 6) trace element clean laboratory at the Wisconsin State Laboratory of Hygiene (WSLH) in Madison, Wisconsin. This space, mercury analysis instrumentation, and staff are shared with the WSLH Trace Element Clean Laboratory (TECL) group.

An MDN specific Laboratory Information Management System (LIMS) was developed by WSLH for use by HAL sample receiving, analytical and data review staff. This was a significant project as an MDN LIMS did not previously exist within NADP and required substantial NADP and WSLH-IT staff effort to complete.

All Litterfall Initiative samples are currently managed in a spreadsheet format. This report covers the 2020 Litterfall season (Fall 2020 to Spring 2021). Litterfall samples are always collected in the fall (through early Spring for some southern sites) of the calendar year and dried, processed, analyzed, and reported in the following calendar year after all samples have been received. During the 2021 NADP Spring Meeting, the Litterfall Initiative was accepted as an official network starting in the 2021-2022 season, now known as the Mercury Litterfall Network (MLN). Further information about the first MLN season will be available in the 2022 QAR.

2021 NADP Staff

- Systems QA and Special Projects Manager - Martin Shafer
- CAL Laboratory Manager, Chemist Supervisor – Chris Worley, Katie Blaydes (as of December 2021)
- HAL Laboratory Manager – Mark Olson (until December 2021)
- HAL Analytics/Trace Element Clean Lab Supervisor – Christa Dahman
- Sample and Data Processing Manager – Amy Mager
- QA Manager – Camille Danielson
- Assistant Data Manager – Zac Najacht, Dana Grabowski

- CAL Chemists – Katie Blaydes (until December 2021), Jesse Wouters (until September 2021), Nichole Davis, Marie Assem
- HAL Chemists – Kirsten Widmayer, Chris Leply (as of October 2021)
- Associate Chemists – James Sustacheck (until November 2021), Erin Pierce (until July 2021), Chris Lepley (moved to HAL October 2021), Margaret Johnson (until May 2021), Abby Carr (as of September 2021)
- Environmental Health Technologists – Colin Kelly, Kat McKinnon (as of December 2021), Anita Peterson (as of December 2021)

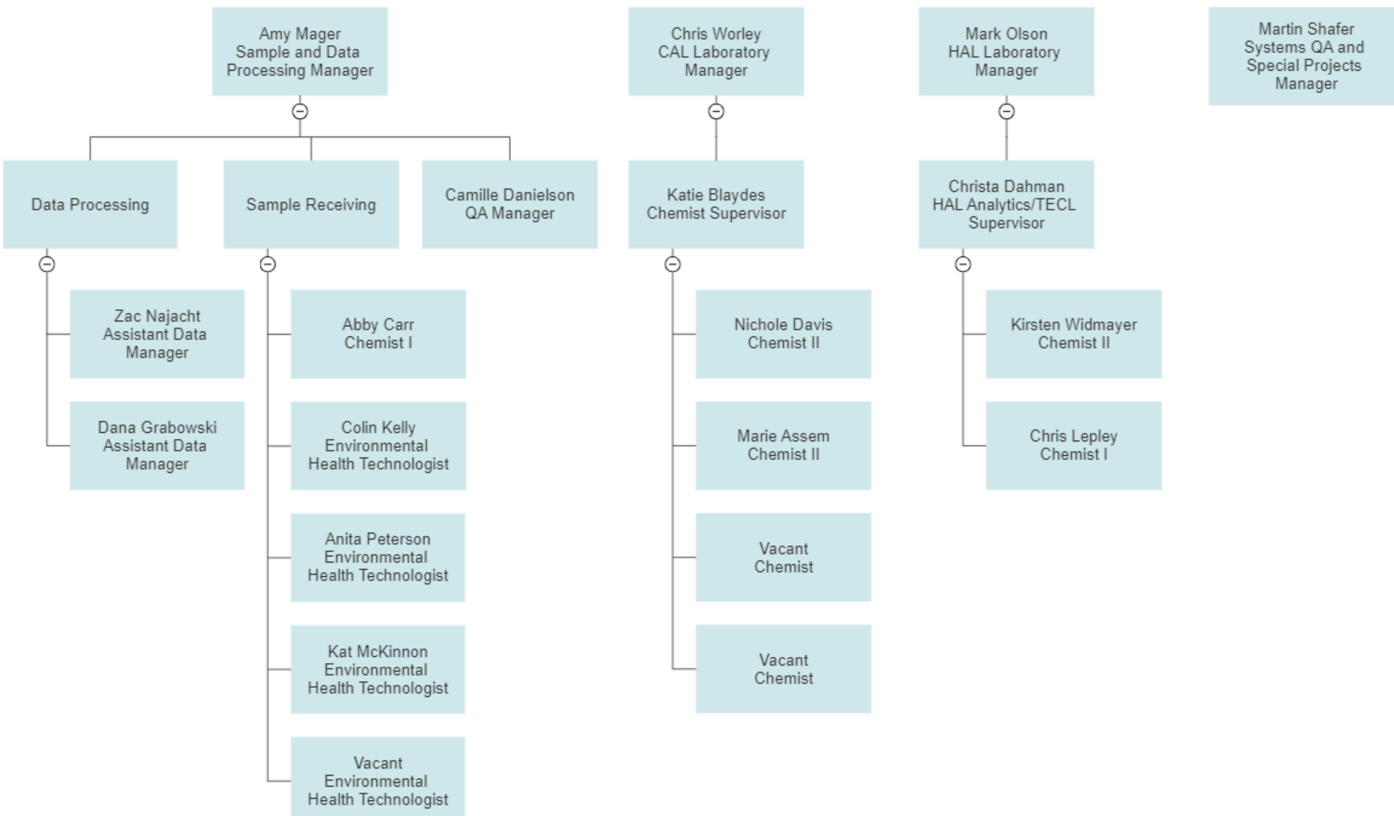

Figure 1. Organizational chart of laboratory staff as of December 2021.

2. Sample Counts

The total number of network samples received and processed is tracked in real-time; however, the percentage of valid samples can only be determined after data are published to the Program Office (PO). Valid samples include all samples that received a Quality Rating (QR) of “A” or “B”. While a quality rating of “C” is invalid. Sample numbers listed in **Table 1** include dry and trace NTN samples. A dry sample is from a sampling period without precipitation, and only a field form is submitted to the CAL. Trace and dry samples are not analyzed in the lab. Sample volumes are determined gravimetrically as the difference between the 1L collection bottle tare weight and the sample + bottle weight.

NTN Volume Assessment - Lab Codes (for sample volume):

- W (“Wet”) = ≥ 28 mL

- WD ("Wet Dilute") = 14-27 mL
- WI ("Wet Incomplete") = 4-13 mL
- T ("Trace") = < 4 mL
- D ("Dry") = 0 mL

Table 1. National Trends Network (NTN) Total Sample Counts, 2017-2021.

Year	Active Sites	Total Samples	Wet Samples		Trace Samples		Dry Samples		Valid Samples	
			Number	Percent	Number	Percent	Number	Percent	Number	Percent
2017	274	13569	10708	78.9	487	3.6	2073	15.3	11248	82.9
2018	262	13107	9912	75.6	413	3.2	1882	14.4	10337	78.9
2019	256	12945	10363	80.1	142	1.1	1878	14.5	10426	80.5
2020	257	12791	9796	76.6	231	1.8	2173	17.0	10430	81.5
2021	260	12937	10518	81.3	229	1.8	2190	16.9	10691	82.6

MDN sample counts in **Table 2** include both dry and wet MDN samples. A dry sample is defined as a field collection with less than 1.5 mL of precipitation and are not analyzed in the lab. All samples 1.5 mL or greater are considered wet samples. Valid samples include all samples that received a Quality Rating (QR) of "A" or "B". While a quality rating of "C" is invalid.

Table 2. Mercury Deposition Network (MDN) Total Sample Counts, 2017-2021.

Year	Active Sites	Total Samples	Wet Samples		Dry Samples		Valid Samples	
			Number	Percent	Number	Percent	Number	Percent
2017	99	5042	4383	86.9	659	13.1	4582	90.9
2018	98	4766	4193	88.0	540	11.3	4318	90.6
2019 (EFGS) 1/19-5/19	92	1880	1741	92.6	127	6.8	1702	90.5
2019 (WSLH) 6/19-12/19	92	2536	2261	89.2	263	10.4	2374	93.6
2020	80	4039	3474	86.0	514	12.7	3671	90.9
2021	80	3930	3450	87.8	480	12.2	3577	91.0

There are very few field or lab criteria that currently result in invalidation of AMoN samples (QR of C); therefore, less than 1% were invalidated as can be seen in **Table 3.** Following the tables, **Figure 2** shows total sample numbers, valid and invalid counts, for the past 5 years for NTN. **Figure 3** depicts these same metrics for MDN and **Figure 4** for AMoN.

Table 3. Ammonia Monitoring Network (AMoN) Total Sample Sets Count, 2017-2021.

Year	AMoN Sites	Number of Sample Sets	Valid Samples	
			Number	Percent
2017	108	2529	2497	98.7
2018	103	2579	2551	98.9
2019	107	2665	2643	99.2
2020	111	2760	2735	99.1
2021	115	2981	2962	99.4

Note: A sample set is data from a single site for a single deployment and can include just one single sampler or may include duplicates and/or travel blanks. This table is based on the Sample Set or "N" number.

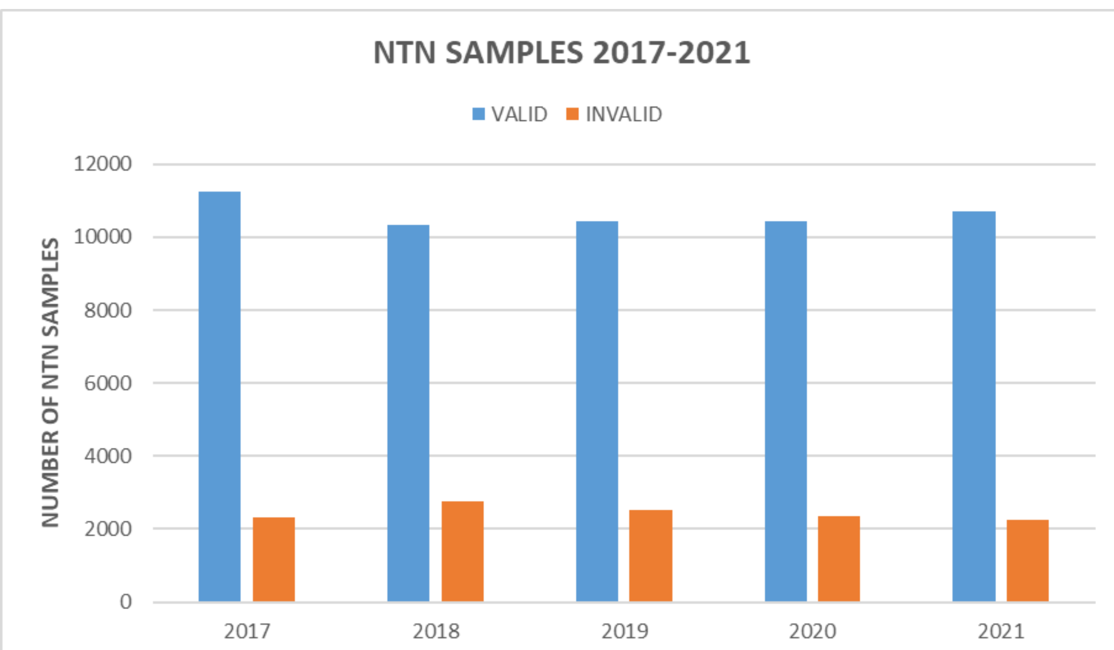

Figure 2. Total Valid and Invalid National Trends Network (NTN) Samples from January 2017 - December 2021.

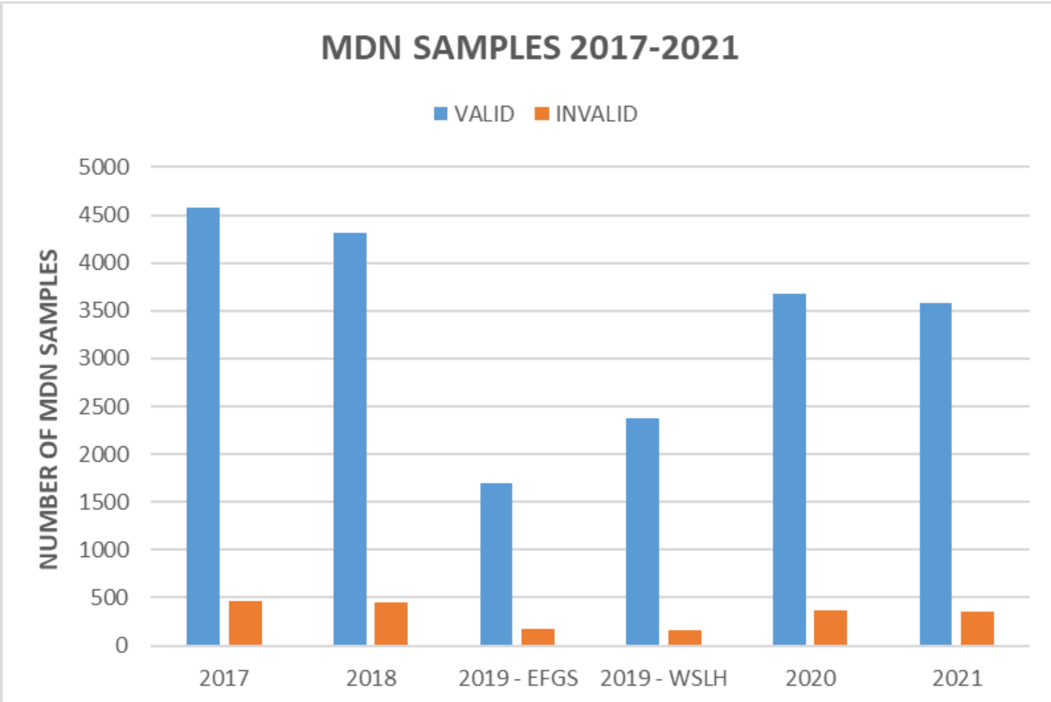

Figure 3. Total Valid and Invalid Mercury Deposition Network (MDN) Samples from January 2017 - December 2021.

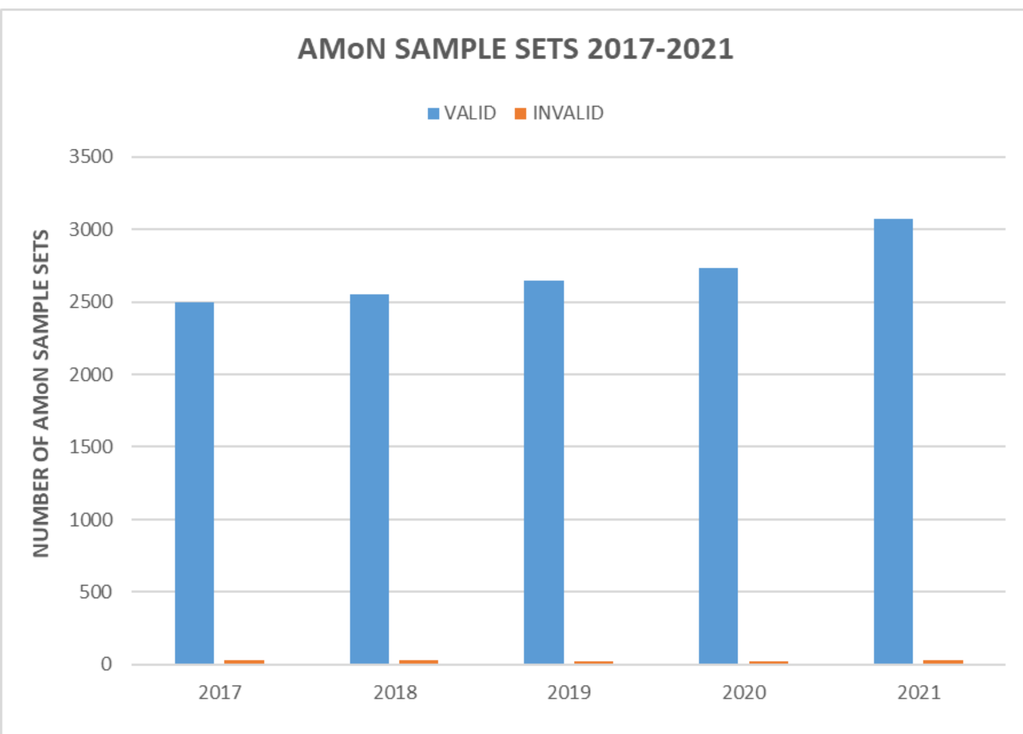

Figure 4. Total Valid and Invalid Ammonia Monitoring Network (AMoN) Samples from January 2017 - December 2021.

In 2021, seven sites requested methylmercury (MeHg) analysis on their MDN samples. MeHg sites require an aliquot of sample to be removed prior to in-bottle sample oxidation. MeHg samples are composited on a monthly basis for each site, per historic precedent. After monthly composites are complete, the samples are distilled to increase the pH and remove chloride and organic interferences, and are subsequently analyzed by Gas Chromatography – Cold-Vapor Atomic Fluorescence Spectrophotometry (GC-CVAFS).

Following discussion during the 2021 NADP Spring Meeting, it was decided that MeHg would temporarily be measured from individual samples rather than from composites to evaluate and isolate possible links between contamination of a specific sample comprising the composite, and MeHg detectability.

There were 37 MeHg composites collected in 2021 before compositing was discontinued. Due to insufficient volume and a few distillation issues, just 24 of these composite samples were analyzed. An additional 73 individual samples from 2021 were analyzed for MeHg and subsequently mathematically processed (volume-weighted) into 32 monthly composites.

Of the 24 physically composited samples, no samples were measured above the Limit of Quantitation (LOQ, 0.1 ng/L) and 7 (29%) were measured above the Method Detection Limit (MDL, 0.03 ng/L).

Of the 73 individual aliquot samples, only 10 samples were above the LOQ (all with debris, contamination, or quality notes), and 23 (32%) were above the MDL. When recalculated as theoretical weighted composites, just four samples (13%) were above the LOQ.

There were 21 Litterfall Initiative sites contributing samples for the 2020-2021 season. Each site consists of four collectors and at least two retrievals are submitted from each collector every season (under normal circumstances). There were 217 individual samples submitted for the 2020-2021 sample season. After grinding and compositing (all retrievals from a given collector are composited), there were a total of 84 samples (21 sites x 4 collectors) measured for THg (four per site) and 21 composite samples measured for MeHg (one per site – the four collectors are composited). Measured MeHg concentrations contributed between 0.2% - 0.6% of the total mercury measured.

3. Network Operations

The NTN has been in operation for 43 years, MDN for 25 years, and AMoN has been operating for 14 years. The AIRMoN ended operation in September of 2019. **Table 4** shows the total number of samples (including dry and trace) received through December 2021 since inception of the networks. **Figure 4** depicts the numbers of active sites per network per calendar year. The Litterfall Initiative began in 2007 and became an active network (MLN) in 2021 for the 2021-2022 season.

Table 4. Total Number of Samples in the History of NADP by Network (All Samples Received < 1/2022).

[NTN, National Trends Network; AMoN, Ammonia Monitoring Network; AIRMoN, Atmospheric Integrated Research Monitoring Network; MDN, Mercury Deposition Network; THg, Total Mercury]

Network	Date Network Began	Date Network Ended (if applicable)	Number of Years in Operation	Total Sample
NTN	7/5/1978	Continuing	43	490,435
AMoN	10/29/2007	Continuing	14	43,019
AIRMoN	9/23/1992	9/1/2019	27	7,709
MDN - THg	2/27/1996	Continuing	25	113,294
TOTAL				**654,457**

3.1. Active Sites

The number of field sites in each network has varied from year to year. Over the last decade, AMoN has experienced steady growth while NTN site numbers remain relatively constant. MDN sites have steadily declined since 2016, attributed primarily to site sponsor budget cuts. The Litterfall Initiative (now MLN) active sites have had minor fluctuations since its beginnings in 2007.

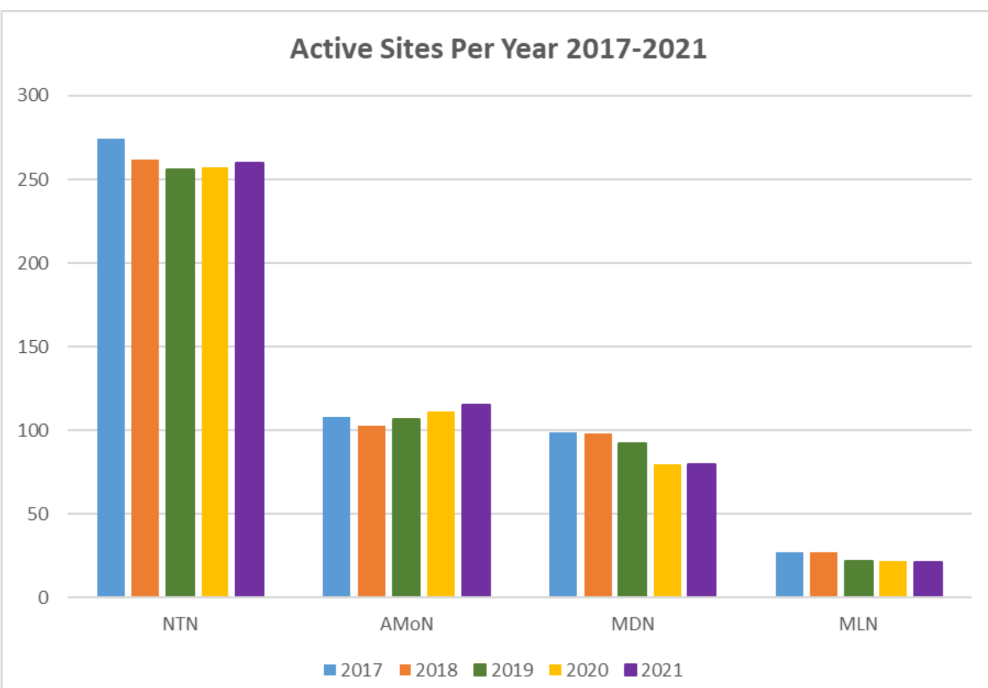

Figure 5. Annual numbers of active NADP sites by network for National Trends Network (NTN), Ammonia Monitoring Network (AMoN), Mercury Deposition Network (MDN), and Mercury in Litterfall Network (MLN).

4. Major Changes

Significant changes to NADP laboratory operations that were implemented in 2021 are summarized in **Table 5**. Major changes are normally substantive changes in protocol or network operations that require significant Management involvement.

Table 5. Major Changes in the NADP laboratories, 1/1/2021 to 12/31/2021.

NADP Major Laboratory Related Changes *(1/3/2022)*					
Date	**Network**	**Change**	**Reason**	**Highest Approval**	**Notes**
1/1/2021	**MDN**	Started assessing MDN samples for contamination at receiving	HAL staff noticed samples with no contamination noted were contaminated - no built in coding step like NTN	WSLH Management	Contamination not noted on field form added to possible qualifiers sheet
2/1/2021	**NTN**	Started cleaning new bucket lids with 2 runs through dishwasher and NO citrajet	Lid QC sample issues led us to investigate and decide to change process	WSLH Management	
2/1/2021	**NTN**	Added FR50 QC standard to pH run immediately after FL (pH 4 standard)	Identified standard carryover issue due to replicate failures	CAL Management	Low ionic strength standard causing low bias on natural matrix sample immediately after it.
2/12/2021	**AMoN**	Use of 15 mL Falcon vials approved for AMON QCS on 02/12/21. Started using 15 mL falcon vials for all AMON QCS for extraction 02/23/21	Radiello tubes expensive and these met our QC	CAL Management	15 mL Conical Tubes (from Fisher Scientific NUNC)
4/1/2021	**NTN**	Renamed most analytical QC standards for CAL and started QC rounding rules for 5 - even down, odd up	Improving clarity on QC IDs and standardizing rounding	CAL Management	to remove excess 0s
4/1/2021	**ALL**	Began using new 2021 MDLs at the bench (starts in January for Data Review)	MDL recalculated	CAL Management	AMoN QC updated for MDLs starting 4/19/21
4/20/2021	**ALL**	Custodial staff at HM will sweep rooms 134, 135 and 136 nightly and once a week will mop with water only	In response to Lid QC issues	WSLH Management	
4/26/2021	**NTN**	Started new rinse in protocol after pH standard FLPH	Identified standard carryover issue due to replicate failures	CAL Management	Carryover issue with this standard needs to be avoided.
5/3/2021	**NTN**	Stirring of pH measurement and calibration sample tubes begins	Improved precision and accuracy with stirring protocol	CAL Management	All samples run prior to 5/3/2021 were not stirred
5/3/2021	**MDN**	MDN glassware/bottle Prep moved to new lab HM 511	Improved safety and efficiency in new room with new hood and bath	HAL Management	
5/20/2021	**MDN**	Reuse of CVAFS vials begins - Triple rinse vial, store with 2% HCl, rinse before use, and replace entire cap assembly.	QC test showed this was acceptable and will save resources	HAL Management	All samples run prior to 5/20/21 were not analyzed in re-used vials.
5/27/2021	**NTN**	Beginning May 28, 2021 a second order calibration curve will be used for orthophosphate on the Lachat.	Improving accuracy	CAL Management	The orthophosphate values for the FM have been biased low, by going from a first order (linear) to second order calibration curve the FM values improved (closer to its true value, but still biased low).

6/1/2021	**MDN**	Starting in June 2021, the NADP Mercury Analytical Lab (HAL) will begin testing methylmercury on individual weekly collections with sufficient volumes rather than composites. A bright yellow sticker will be placed on MDN bottles that also need methyl analysis.	Issues with the compositing and increased change for contamination from multiple samples have led to this change	HAL Management	Approximately 60% of all historical methylmercury data are either qualified with a debris note (“d”) or invalidated with QR code “C”. Of the remaining high quality results, the vast majority are non-detects. The issue of contamination is exacerbated by the compositing protocol—if one out of four sample components of the composite is contaminated, the whole composite is contaminated
6/3/2021	**NTN**	Starting on 6/3/2021 a second archive sample bottle for NTN will NOT be collected. One 60 mL bottle will be filled as full as possible and sent over for analysis and any remaining sample will be saved and returned for archiving. The exceptions to this are the fixed and forever sites which will still have archive samples collected in a second bottle per usual process.	Due to major supply shortages worldwide this will also be more efficient and save resources	WSLH Management	This change was made due to national shortage of many plastics and potential issue with obtaining 60 mL bottles. This may be a temporary change.
7/6/2021	**ALL**	Not a permanent change but due to worldwide shortages of plastics our supply QC for some things such as bottles will be less than the SOPs/QAPs require until supplies are no longer so limited.	Due to major supply shortages worldwide this will also be more efficient and save resources	WSLH Management	We will do QC per lot but much more limited to conserve supplies.
7/21/2021	**NTN**	ICP analysis changed to a single curve, dropped High FL since single curve	To simplify ICP data assessment after much validation	CAL Management	LDR determined to be 10 mg/L for Mg and 20 for K, Na, and calcium, no carryover at 20 mg/L
8/20/2021	**AMoN**	Expiration date for AMoN reagents extended to 3 weeks.	After validating this was acceptable it will save resources	CAL Management	
2/1/2021-2/5/2021	**All**	Plaster and paint work at Henry Mall on NADP hallways	Recorded due to potential contamination	NA	Doors kept closed as much as possible. This was linked to lid contamination with Ca and Cl - labs extensively cleaned in late March and all shelf liner replaced.
8/1/2021	**MLN**	First official Litterfall season	Spring 2021 NADP voted to make official network	NADP Executive Committee	
10/15/2021	**NTN**	Began Using new Filter apparatus for filtering NTN Samples	Old Filter Apparatus used for over 4 years and some QC issues	NADP Management	QC checked and labelled with the year so they can be rotated out in the future and replaced in 3 years or so.
11/1/2021	**AMoN**	Reduced AMoN QA to minimum of 3 TBs and Dups per site per year	Fall 2021 Joint Subcommittees approved	NADP Executive Committee	Need to assess quarterly against new criteria
12/17/2021	**All**	Migrated SOPs to OnBase Document Management Software. Revisions are now “versions”. All SOPs moved to version 1 upon upload to OnBase.	Lab-wide initiative to streamline and improve document control.	WSLH Management	

5. Annual Management Review Summary

All sections of the WSLH EHD complete an annual management review to track changes in their sections, and document audits and issues to address. For NADP, this review is carried-out by NADP management and approved by the EHD director. An excerpt of this report is shared here.

Dates covered by review: January 1, 2021 to December 31, 2021
Department: NADP

Person responsible for department's review: Chris Worley, Amy Mager, Christa Dahman, and Katie Blaydes

Note: this summary was condensed from the original report

5.1. Status of policies/procedures including updates and new procedures that need to be written:

5.1.1. Annually, NADP staff are required to sign off that they have reviewed the following WSLH and NADP policy documents: Safety Checklist, Chemical Hygiene Plan, Data Integrity Policy, NADP QA Plan, Emergency Action Plan, HIPAA Refresher, Disability/Accommodation training, Occurrence Reporting Procedure, Occurrence System Management Policy, and Lab Wide Accident Reporting. **This all has been completed for 2021**.

5.1.2. Laboratory staff are required to read those SOPs that apply to their routine and backup work duties. Each applicable SOP must be reviewed and documented within a month of taking on a new task/responsibility. These SOPs must be reviewed annually in order to continue with that same responsibility. When a new SOP revision is available, relevant staff must review the latest revision within a month of the new revision date.

5.1.3. All analytical, sample preparation, data review, and sample receiving SOPs have been completed. We are working on the following SOPs: MDLs and NADP Data Management/Backup.

5.2. Reports from managerial and supervisory personnel:

5.2.1. **Staffing.** Jesse Wouters accepted a supervisory position in the Radiochemistry unit at WSLH. In anticipation of Chris Worley's retirement, this vacant position (Jesse's) was used to fill the next Chemist Supervisor of the CAL. Interviews were completed and Katie Blaydes accepted the offer late in 2021. Chris will be retiring 3/10/2022. HAL staffing consists of one full-time analytical chemist (Chris Lepley), one partially-dedicated analytical chemist (Kirsten Widmayer), a partially-dedicated HAL supervisor (Christa Dahman), and sample receiving staff (shared with the CAL). Chris began working full-time for the HAL in November 2021 after being promoted. Kirsten reduced dedicated HAL time to 20% in January 2022. Sample receiving brought-on three new staff members in 2021: Abby Carr, Anita Peterson, and Kathryn McKinnon.

5.2.2. **Audits.** No internal audits were conducted in 2021. The NADP Executive Committee approved a schedule where internal audits are only required on years when there is no external audit. The NADP CAL, HAL, and Program Office (PO) were reviewed on September 20 – 22, 2021 by a team of six scientists from various agencies and organizations. Overall, the review was positive. Many recommendations were made. The findings are summarized below in section 5.3.

5.2.3. **Pandemic Impacts.** The pandemic only had intermittent impacts on site operations for all networks (usually due to operators being ill, or not having access to a site due to workplace closures). All NADP functions continued to operate normally. We continue to meet analytical holding times for samples. There are still occasional delays in supply availability.

5.2.4. **Major Network Changes.** Stirring of pH measurements has been tested and implemented on 5/3/2021. This process involves individual, pre rinsed with Type I water, stir bars being placed in the empty sample tubes. During analysis, the rack is placed on a stir plate. Stirring the sample improves precision and accuracy of results.

The amount of annual AMoN QA per site has been reduced. Each AMoN site will receive a minimum of 3 travel blanks and 3 duplicates per year. This was approved by the Fall 2021 Joint Subcommittees and will begin in 2022.

The Litterfall Initiative was voted to be made an official network, Mercury Litterfall Network (MLN), at Fall Conference in 2021 Joint Subcommittees. The first official season is the 2021-2022 season.

The CAL and PO have committed some time/resources to a Total Phosphorus and Total Nitrogen secondary sampler to be used in conjunction with the NTN sampler bucket. Katie Blaydes has been working on an analytical TN/TP method development on our Lachat FIA system. This has the potential to increase capabilities of the CAL.

5.2.5. **Data Review**. In 2021, the data review group was turning around data to the Program Office within 90 days (+/- 10 days) from the month of sample receipt. This was a great improvement from the 2020 turnaround times (120-170 days). The reduction in time to submission to the PO was due to completion of systems development, extra resources (staff devoted to helping with initial data review) and a decrease in the amount of pandemic impacted samples.
Two specific data items came out of the Fall 2021 Joint Subcommittees. One – to change all data on the website to Valid/Invalid as opposed to QR rating; and two – to update the hold time notes codes, flagging and validity to be consistent across networks and more appropriate for each network. Work on both items began in late 2021 and will continue into 2022.

5.2.6. **Sample Archive Program**. The fixed and forever archive samples were pulled out of the archived ICAL samples, and the ICAL long-term archive was moved from the UW Biotron to Henry Mall. The IL11 archive samples were also transferred to the CAL in early 2021.

5.3. External Audits

5.3.1. The NADP CAL, HAL, and Program Office (PO) were reviewed on September 20 – 22, 2021 by a team of six scientists from various agencies and organizations.

5.3.2. External Audit Findings:

a. Finding 1 Description: Review flagging and qualifiers for AMoN in QAAG to reduce ambiguity in flagging AMoN data.
b. Finding 2 Description: Find and correct null values in AMoN data record for ammonium concentration and extract volume.
c. Finding 3 Description: Evaluate disconnect between PO precipitation data acquisition and analytical data whereby analytical data are “B” coded instead of “C” coded when an undefined sample cannot be confirmed due to missing rain gage data.
d. Finding 4 description: A draft data review SOP and draft data editing SOP are requested to be delivered to the QAAG for review by the 2022 Spring Meeting.
e. Finding 5 Description: Perform a QA check of web data and review/document the SAS data checking code.

f. Finding 6 description: Prepare a detailed and up to date data change log as part of the metadata that accompanies the NADP data by the end of summer 2022.
g. Finding 7 Description: Document the LIMS and all databases no later than summer 2022.
h. Finding 8 Description: Plan now for replacement and conversion of LIMS system in a contemporary, well-supported language.
i. Finding 9 Description: Replace all existing PDAs in the field with Androids.

Table 6. Major corrective and preventive actions that were implemented during 2021 in the NADP Central Analytical Laboratory.

Occurrence Number	Priority	Status	Subject	Date Submitted	Date Closed
4090	Medium	Closed	Expired PO4 Standard	01/04/2021	07/15/2021
4091	Medium	Closed	Reporting results with rejected QC	01/04/2021	07/15/2021
4095	Medium	Closed	ERA 1000 mg/L phosphorus stock solution	01/05/2021	02/04/2021
4099	Medium	Closed	Expired Phenolate Reagent	01/11/2021	07/15/2021
4107	Medium	Closed	NADP NTN sample filters Used before fully QC checked	01/22/2021	04/19/2021
4108	Medium	Closed	NADP: MDN reports blank for some samples	01/24/2021	04/20/2021
4146	Medium	Closed	Connecting hardware to external internet access	03/19/2021	04/19/2021
4156	Medium	Closed	NADP FLID contamination	03/31/2021	07/15/2021
4169	Medium	Closed	NADP USGS SRS for Hg reported incorrectly	04/07/2021	07/15/2021
4173	Medium	Closed	Tekran 2600 Software Glitch	04/08/2021	08/11/2021
4183	Medium	Closed	NADP Low bias on Rerun AMoN Samples	04/20/2021	07/15/2021
4185	Medium	Closed	ICP torch and internal standard issues	04/22/2021	07/15/2021
4207	Medium	Closed	pH probe issues	05/19/2021	07/15/2021
4217	Medium	Closed	NADP WMO PT 63-3 21002800 analyst error	06/02/2021	07/15/2021
4236	Medium	Assigned	NADP Carryover items from 2020 Internal Systems Audit to address	06/22/2021	(no data)

4263	Medium	Closed	ICP K drifting	07/15/2021	02/08/2022
4264	Medium	Closed	NADP Pipette 03 High bias when verified	07/15/2021	07/27/2021
4267	Medium	Closed	NADP 2L MDN bottles exceed QA limit	07/21/2021	12/28/2022
4274	Medium	Closed	Ongoing Demonstration of Capability Not completed on time	08/03/2021	07/28/2022
4322	Medium	Closed	NADP ongoing supply QC failures related to filtering	09/27/2021	07/28/2022
4325	Medium	Closed	NADP: missed filtering sample TX2736SW	09/30/2021	11/03/2022
4332	Medium	Closed	NADP Conductivity Calibration failure	10/06/2021	07/28/2022
4345	Medium	Assigned	Low recovery on USGS SRS for sulfate	10/25/2021	(no data)
4347	Medium	Closed	ICP trend for Mg and Ca biased high on FM Standard	10/26/2021	11/02/2022
4392	Medium	Assigned	Data Review and Coding External Review Finding 2	12/13/2021	(no data)
4394	Medium	Assigned	Data Review PO External Audit finding 1	12/14/2021	(no data)
4395	Medium	Assigned	OIS External Audit Finding 1	12/14/2021	(no data)
4397	Medium	Assigned	NADP OIS External Audit Finding 3	12/14/2021	(no data)
4398	Medium	Assigned	NADP OIS External Audit Finding 4	12/14/2021	(no data)
4401	Medium	Closed	NADP OIS External Audit Finding 5	12/14/2021	01/06/2023
4402	Medium	Closed	NADP PO/OIS External Audit Finding	12/14/2021	07/28/2022
4404	Medium	Closed	NADP Magnesium ECCC PT result reported incorrectly RN118-2 lab F303	12/15/2021	07/28/2022
4410	Medium	Closed	NADP AMoN Glass Jar Blank failures	12/27/2021	07/28/2022

5.4. Internal Audits

5.4.1. No internal audits were performed during 2021 (refer to section 5.2.2).

5.5. Changes in the scope/scale and type of work during 2020:

5.5.1. The PFAS in precipitation study sponsored by EPA continued throughout 2021 with eight NTN sites participating. This involves NADP staff tracking the samples received, filling out a submission form for the Organics Department and transferring whatever is remaining of the sample to Organics for testing. Several more sites will likely be added to this study in 2022.

5.5.2. EPA continues to hold preliminary discussions of a significant expansion of the AMoN network (100+ additional sites). At this point it is still in discussion and no action was needed in 2021.

5.5.3. Total Nitrogen and Total Phosphorus samples were collected at Eagle Heights and at NC30 to evaluate recoveries and methodology. Although this did not represent a significant sample load increase, if this becomes an official NADP analyte we will see a significant increase in sample load and effort.

5.6. .Recommendations for improvement:

5.6.1 Continue working on data quality objectives (DQO) and how data is presented to end users.

5.6.2 Continue research on the TN/TP secondary sampler and analytical method to help address client needs.

5.7. List of issues regarding resources, staff training, and other QA-related activities:

5.7.1 The current staffing is adequate to address the needs of our customers at this time. If there is a large increase in AMoN sites (discussed above) and/or TN/TP becomes an official NADP analyte, then we will need to re-evaluate circumstances. We continue to strive to improve data quality and data presentation to our customers. We plan to convene a DQO Summit as an important step in working with our data users to determine their needs.

5.7.2 Camille Danielson was drafted by WSLH upper management to assist with bringing online the state lab's new OnBase software package. This impacted her ability to continue some of her other routine QA/QC responsibilities. Nichole Davis volunteered to help cover roughly 10% of that load.

6. Staff Training

Analytical staff 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 fresh perspective/ideas for improving the performance and efficiency of each platform.

7. Instrumentation

Table 7. NADP-Dedicated Major Analytical Equipment.

Analysis	Type	Species	Instrument
Inductively Coupled Plasma – Optical Emission Spectrometery (ICP-OES)	Base Cations	Na^+, K^+, Ca^{2+}, Mg^{2+}	Agilent 5100
Ion Chromatography (IC)	Acid Anions	Cl^-, NO_3^-, SO_4^{2-}	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	H^+	Mettler S700 Meter
Specific Conductance – (Conductance Probe – Manual Method)	Specific Conductance	Charged Anions & Cations	Mettler S700 Meter
Automated Cold Vapor Atomic Fluorescence (CVAFS)	CVAFS	Total Hg	Tekran 2600 with IVS
Automated Cold Vapor Atomic Fluorescence (CVAFS) with Chromatographic separation	CVAFS	Methyl Hg	Tekran 2700 with IVS
Thermal Decomposition, Gold Amalgamation, and Atomic Absorption Spectroscopy (AAS)	AAS	Total Hg (solids)	Nippon MA-3000

8. 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 (Revision 1, June 2020). The QAP is now stored in OnBase (OB Version 2 December 2021) and is revised every three years. An Annual Management Review (summarized above) was completed in 2021. The NADP QAP contains detailed QA information on all aspects of the NADP laboratories.

8.1. Standard Operating Procedures

The NADP has prepared the standard operating procedures (SOPs) outlined in **Table 8** as of the QAR effective date. SOPs are available upon request. The analytical SOPs are revised annually or 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. A table of analytical SOPs is maintained showing status of revisions. Note that in December 2021, all SOPs at WSLH migrated to OnBase document management system. This transition forced a change in title structure and version tracking. Previous revision numbering was reset to version 1 in OnBase.

Table 8. NADP Central Analytical Laboratory and Mercury Analytical Laboratory Standard Operating Procedures Table of Contents.

OnBase SOP ID	Division	Section	SOP Type	Title
NADP PO GENOP 001	EHD	NADP	GENOP	NADP QUALITY MANAGEMENT PLAN
NADP PO GENOP 002	EHD	NADP	GENOP	NADP SITE SELECTION AND INSTALLATION MANUAL
NADP PO GENOP 003	EHD	NADP	GENOP	NTN OPERATIONS MANUAL
NADP PO GENOP 004	EHD	NADP	GENOP	AMON OPERATIONS MANUAL
NADP PO GENOP 005	EHD	NADP	GENOP	MDN OPERATIONS MANUAL
NADP PO GENOP 006	EHD	NADP	GENOP	AMNET OPERATIONS MANUAL
EHD NADP LAB GENOP 100	EHD	NADP	GENOP	SAMPLE LOGIN AND DATA ENTRY
EHD NADP LAB GENOP 101	EHD	NADP	GENOP	SAMPLE CODING
EHD NADP LAB GENOP 102	EHD	NADP	GENOP	AMON SUPPLY SHIPPING
EHD NADP LAB GENOP 103	EHD	NADP	GENOP	NTN SHIPPING AND RECEIVING OF SUPPLIES
EHD NADP LAB GENOP 104	EHD	NADP	GENOP	MDN SUPPLY SHIPPING AND RECEIVING
EHD NADP LAB GENOP 300	EHD	NADP	GENOP	NTN DATA REVIEW AND REPORTING
EHD NADP LAB GENOP 301	EHD	NADP	GENOP	AMON DATA REVIEW
EHD NADP LAB GENOP 302	EHD	NADP	GENOP	MDN DATA REVIEW
EHD NADP LAB GENOP 400	EHD	NADP	GENOP	AMON PREP OF PASSIVE NH3 SAMPLERS
EHD NADP LAB GENOP 401	EHD	NADP	GENOP	AMON SAMPLER EXTRACTION
EHD NADP LAB GENOP 402	EHD	NADP	GENOP	NTN SAMPLE FILTRATION
EHD NADP LAB GENOP 403	EHD	NADP	GENOP	NTN SUPPLY PREPARATION
EHD NADP LAB GENOP 404	EHD	NADP	GENOP	SAMPLE ARCHIVE
EHD NADP LAB GENOP 405	EHD	NADP	GENOP	MDN SUPPLY PREP
EHD NADP LAB GENOP 406	EHD	NADP	GENOP	LITTERFALL SAMPLE PROCESSING
EHD NADP LAB GENOP 407	EHD	NADP	GENOP	CALNAT SAMPLE PREPARATION
EHD NADP LAB METHOD 500	EHD	NADP	METHODS	ICP-OES
EHD NADP LAB METHOD 501	EHD	NADP	METHODS	ION CHROMATOGRAPHY
EHD NADP LAB METHOD 502	EHD	NADP	METHODS	AMON AMMONIUM BY FIA
EHD NADP LAB METHOD 503	EHD	NADP	METHODS	NTN AMMONIUM AND PO4 BY FIA
EHD NADP LAB METHOD 504	EHD	NADP	METHODS	PH MEASUREMENT
EHD NADP LAB METHOD 505	EHD	NADP	METHODS	CONDUCTIVITY MEASUREMENT
EHD NADP LAB METHOD 508	EHD	NADP	METHODS	LITTERFALL TOTAL MERCURY IN SOLIDS
EHD NADP LAB QA/QC 200	EHD	NADP	QA/QC	NTN AND MDN SUPPLY QUALITY CONTROL
EHD NADP LAB QA/QC 201	EHD	NADP	QA/QC	ANALYST TRAINING AND DEMONSTRATION OF CAPABILITY
EHD NADP LAB QA/QC 202	EHD	NADP	QA/QC	PEER REVIEW OF ANALYTICAL DATA
EHD NADP LAB QAP	EHD	NADP	QA/QC	NADP LABORATORY QUALITY ASSURANCE PLAN
EHD TECL METHOD 541.2	EHD	TECL	METHODS	TOTAL HG BY AUTO CVAFS
EHD TECL METHOD 545.1	EHD	TECL	METHODS	METHYL HG IN SOLIDS BY CVAFS

EHD TECL METHOD 545.2	EHD	TECL	METHODS	METHYL HG IN WATER BY AUTO-CVAFS
EHD GENOP 041	EHD	DIVISION WIDE	GENOP	ANTISTATIC DEVICES CONTAINING A RADIOACTIVE MATERIAL

9. NTN Method Detection Limits (MDL)

9.1. NTN Laboratory Method Detection Limits (MDL_L) – (Spiked Sample Matrix)

The analytical laboratory method detection limit (MDL_L) for a given analyte is the minimum measured concentration of a substance that can be reported with 99 percent confidence that the measured concentration is distinguishable from respective method blanks. The lab MDL is calculated using the standard deviation from a minimum of seven measurements (analyzed on different days) of spiked samples in the matrix of concern (at a concentration of approximately 2-5 times the MDL). The lab MDLs are provided in **Table 9.**

9.2. NTN MDL_L Blank calculations

A minimum of seven calibration blanks are also assessed to determine a lab MDL_L for each analyte based on blank measurements (per 40 CFR 136). The blank MDL_L is determined using the equation: (mean of the blanks + blank standard deviation * t-value at 99% confidence) per federal MDL protocols. The MDL_L based on the blanks should be used as the analytical lab MDL_L if the result is greater than the spiked lab MDL_L result.

9.3. NTN MDL_L Usage

Analytical laboratory MDLs are a data quality indicator and are reviewed annually by the CAL and revised by the QA Manager as warranted (i.e. a new instrument or a critical new part is installed on an existing instrument). The analytical laboratory MDL is primarily used to validate instruments and is used as a tool for the QA Manager to assess the network MDLs validity. It is not used for qualifying NTN data.

9.4. NTN Network MDL Process

The network specific MDL (MDL_N) for NTN is based on results from a minimum of 7 MDL solutions (spikes) or Type I water (blanks) which go through all processing steps and are analyzed with routine network samples. The network MDL accounts for the potential additional uncertainty introduced due to exposure to sample collection equipment and processing. The difference from the lab MDL solution is that the network spikes or blanks go through the entire process (i.e. bucket/bag exposure, filtering and transferring to bottles) and are blind to the bench chemists. MDLs are assessed annually and if MDL results are within +/- ½ MDL of the previous year, the MDL values may remain the same for another year.

9.5. Network MDL_N Usage

The MDL_N is used at the bench to provide reference for routine QC samples. It is also used to censor NTN data published by the PO for samples received in the calendar year. The calendar year is a bit nebulous with respect to NTN sample intake, as it depends on the date that the lab receives the sample. Therefore, the sample IDs for that calendar year are also documented in the Historical MDL table so that it is clear which samples fall into a particular year. The NTN sample results that are less than the MDL_N for that calendar year are published on the NADP website with the MDL_N value in place of the measured value and a less than (<) symbol in the column adjacent to the result. For NTN, the **data reported to the sites** in their monthly reports includes the less than MDL_N values (such data are italicized if less than the NTN MDL_N for that calendar year).

The most recent (past four years) NTN network MDLs are provided in **Table 9,** and **Table 10** provides the Network MDLs for NTN analytes from 1987-2021. It should be noted that the 2018 MDLs were established per the readiness verification plan and were unrealistically low.

Table 9. National Trends Network Method Detection Limits, 2018 – 2021.

Analyte	2018 Lab MDL_L	2019 Lab MDL_L	2020 Lab MDL_L	2021 Lab MDL_L	2018 Network MDL_N	2019 Network MDL_N	2020 Network MDL_N	2021 Network MDL_N
Ca	0.004	0.001	0.008	0.002	0.011	0.023	0.023	0.010
Mg	0.002	0.001	0.001	0.002	0.003	0.006	0.006	0.006
Na	0.003	0.002	0.001	0.003	0.004	0.010	0.010	0.008
K	0.002	0.003	0.002	0.003	0.005	0.005	0.005	0.006
Cl	0.006	0.004	0.003	0.008	0.006	0.018	0.018	0.020
SO_4	0.008	0.007	0.005	0.009	0.007	0.018	0.018	0.020
NO_3	0.003	0.003	0.0006	0.004	0.008	0.018	0.018	0.020
Br	0.003	0.002	N/A	N/A	0.006	0.006	N/A	N/A
NH_4	0.004	0.002	0.007	0.010	0.008	0.017	0.017	0.014
PO_4	0.003	0.003	0.004	0.006	0.008	0.010	0.010	0.010
pH	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Conductivity	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

Note: Ca, Mg, Na, K, Cl, SO_4, NO_3, Br, NH_4, and PO_4 have units of mg/L and conductivity has units of µS/cm.

Table 10. National Trends Network (NTN) Historical Network Method Detection Limits, 1987-2021.

NTN Historical Network Method Detection Limits (mg/L) Revision 2/2023											
Sample Start ID	Sample End ID	Aproximate Year RCV	Ca	K	Mg	Na	Cl	NO_3	SO_4	NH_4	PO_4
NA0001	NA0067	1978	0.010	0.002	0.002	0.004	0.050	0.030	0.010	0.030	0.005
NA0068	NA0104	1978	0.010	0.002	0.002	0.004	0.050	0.030	0.010	0.030	0.004
NA0105	NA0221	1978	0.010	0.002	0.002	0.004	0.050	0.030	0.010	0.020	0.004
NA0222	NA0335	1978	0.020	0.002	0.002	0.004	0.050	0.030	0.010	0.020	0.004
NA0336	NA0446	1978	0.010	0.004	0.002	0.004	0.050	0.030	0.010	0.020	0.004
NA0447	NA0452	1978	0.010	0.002	0.002	0.004	0.050	0.030	0.010	0.020	0.004
NA0453	NA0668	1978	0.010	0.002	0.002	0.004	0.050	0.030	0.010	0.020	0.003
NA0669	NA1331	1979	0.020	0.002	0.002	0.004	0.050	0.030	0.010	0.020	0.003
NA1332	NA1675	1979	0.020	0.004	0.002	0.004	0.050	0.030	0.010	0.020	0.003
NA1676	NA1800	1979	0.020	0.002	0.002	0.004	0.050	0.030	0.010	0.020	0.003
NA1801	NA3361	1980	0.020	0.004	0.002	0.004	0.050	0.030	0.010	0.020	0.003
NA3362	NA3475	1980	0.008	0.004	0.002	0.004	0.050	0.030	0.010	0.020	0.003
NA3476	NA3695	1980	0.008	0.002	0.002	0.002	0.050	0.030	0.010	0.020	0.003
NA3696	NA4254	1980	0.006	0.002	0.002	0.002	0.050	0.030	0.010	0.020	0.003
NA4255	NA6000	1981	0.008	0.002	0.002	0.002	0.050	0.030	0.010	0.020	0.003
NA6001	NA6328	1981	0.008	0.003	0.002	0.002	0.020	0.030	0.010	0.010	0.003
NA6329	NA6543	1981	0.024	0.003	0.009	0.002	0.020	0.030	0.010	0.010	0.003
NA6544	NA6650	1981	0.009	0.003	0.002	0.002	0.020	0.030	0.010	0.010	0.003
NA6651	NA7299	1981	0.009	0.003	0.002	0.002	0.020	0.030	0.010	0.020	0.003
NA7300	NA7741	1981	0.009	0.003	0.003	0.002	0.020	0.030	0.010	0.020	0.003
NA7742	ND1937	1981-1985	0.009	0.003	0.003	0.003	0.020	0.030	0.010	0.020	0.003
ND1938	ND1938	1985	0.009	0.003	0.003	0.003	0.030	0.030	0.010	0.020	0.003
ND1939	ND2633	1985	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.003
ND2634	NF4630	1985-1987	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.010
NF4631	NH6700	1987-1989	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.020
NH6701	NM6824	1989-1993	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.020
NM6825	NS3700	1993-1998	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.003
NS3701	NU7200	1998-2000	0.009	0.003	0.003	0.003	0.005	0.010	0.010	0.020	0.003
NU7201	NW0218	2000-2001	0.009	0.003	0.003	0.003	0.005	0.010	0.010	0.020	0.009
NW0219	NZ9957	2001-2004	0.009	0.003	0.003	0.003	0.005	0.010	0.010	0.020	0.006
NZ9958	TA0214	2004	0.009	0.003	0.003	0.003	0.008	0.009	0.013	0.020	0.006
TA0215	TA0334	2004	0.002	0.001	0.001	0.003	0.008	0.009	0.013	0.020	0.006
TA0335	TB4169	2005	0.002	0.001	0.001	0.003	0.008	0.009	0.013	0.005	0.006
TB4170	TE3724	2006-2007	0.002	0.001	0.001	0.001	0.003	0.017	0.010	0.004	0.004
TE3725	TG9571	2007-2009	0.006	0.001	0.001	0.001	0.004	0.009	0.010	0.006	0.004
TG9572	TI2460	2009-2010	0.004	0.001	0.001	0.003	0.003	0.005	0.004	0.010	0.008
TJ5599	TM2704	2011-2013	0.005	0.003	0.002	0.002	0.009	0.010	0.010	0.009	0.005
TM2705	TN2615	2014	0.019	0.001	0.005	0.005	0.008	0.007	0.005	0.017	0.009
TN2616	TP0369	2015	0.009	0.002	0.002	0.006	0.005	0.005	0.005	0.016	0.005
TP0370	TQ4360	2016	0.009	0.004	0.002	0.003	0.005	0.005	0.004	0.019	0.005
TQ4361	TS9999	2017	0.006	0.002	0.002	0.002	0.003	0.005	0.005	0.018	0.006
TT0001	TT7317	2018	0.011	0.005	0.003	0.004	0.006	0.008	0.007	0.008	0.008
TT7318	TV0257	2019	0.023	0.005	0.006	0.010	0.018	0.018	0.018	0.017	0.010
TV0258	TW3112	2020	0.023	0.005	0.006	0.010	0.018	0.018	0.018	0.017	0.010
TW3113	TX6130	2021	0.010	0.006	0.006	0.008	0.020	0.020	0.020	0.014	0.010

10. AMoN MDLs

10.1. AMoN Lab MDL (MDL_L)

The AMoN lab MDL (MDL_L) is used for bench level QC (e.g. assessing blank acceptability, establishing low-level standard values, and identifying samples <10*MDL). The AMoN MDL_L is also used to flag travel blanks less than the MDL_L with a "d" flag and results in a QR of B.

10.2. AMoN MDL_L Calculations

In 2021, the AMoN lab MDL was calculated as the mean core blank + (t*stdev) for all available core blanks with results greater than zero. There were 126 valid core blank values from June 2018 – December 2020 and these were used to determine a mean of 0.010 mg/L NH_4 to be used as the MDL_L. See **Table 11** for other recent AMoN lab MDLs.

10.3. AMoN Network MDL (MDL_N)

The AMoN network MDL is used to flag data below the MDL_N with a "d" which automatically changes the sample QR code from "A" to "B". Other factors could further reduce the QR to a "C". AMoN data is reported with a QR code and is not "censored" at the MDL_N.

10.4. AMoN MDL_N Calculations

The AMoN network method detection limit (AMoN MDL_N) is calculated annually from valid travel blanks.

The 2021 AMoN MDL_N was calculated using all valid travel blanks from an approximate 12-month period of the most recent samples for which final data was available. Travel blanks are AMoN samplers prepared in the same manner as the deployed samplers that are shipped to individual sites but are not opened or deployed in the field. The AMoN MDL_N = mean valid travel blanks + (t*stdev).

See **Table 11** for AMoN network MDLs. See **Table 12** for a summary of the historical AMoN MDLs.

Table 11. Ammonia Monitoring Network Method Detection Limits, 2018-2021.

AMoN	2018 Lab MDL_L	2019 Lab MDL_L	2020 Lab MDL_L	2021 Lab MDL_L	2018 Network MDL_N	2019 Network MDL_N	2020 Network MDL_N	2021 Network MDL_N
mg/L NH_4	0.008	0.016	0.013	0.010	0.119	0.104	0.083	0.070

Note: The 2018 Lab MDL was based on NTN Lab MDL due to lack of data.

Table 12. Ammonia Monitoring Network Historical Method Detection Limits.

AMoN Historical Method Detection Limits					
Sample ID Range	**Year of Sample Receipt**	**AMoN Network MDL (MDL_N) mg/L NH_4**	**AMoN Lab MDL (MDL_L) mg/L NH_4**	Network MDL Basis	Lab MDL Basis
All Prior to N18005002	<2018	0.0469	0.0469	Established by ICAL	Established by ICAL
N18005002 - N18006407	2018	0.119	0.008	ISWS 2017 valid travel blank data	NTN Lab MDL due to lack of core data
N19000001 - N19002669	2019	0.104	0.016	All valid 2018 travel blanks	mean core blank value from June – December 2018
N20000001 - N20002856	2020	0.083	0.013	All valid TB for ~ 12 months most recent from 741 valid travel blanks with "end dates" (end of deployment period) from June 2018 to June 2019	mean core blank value for all available core blanks with results greater than zero. N =103 core blank values from June 2018 – December 2019
N21000001 - N21003101	2021	0.070	0.010	All valid travel blanks 2020 Deploy Jan - Nov 2020 = TB Mean + (SD*tvalue); n= 523	2 years data for detected Core blanks 12/2018-12/2020 Mean n=125 Mean prep blank 2 years (n-167) = 0.012 as reference - 0.01 represents background sampler level

It should be noted that the prior laboratory set the MDLs to 0.0469 mg/L in some unknown manner prior to 2018.

11. MDN and Litterfall (MLN) MDLs

11.1 MDL Establishment

When sufficient data points from daily MDL spike samples, analytical blanks, processed MDL spikes, and processed blanks have been generated (minimum of 7 but ideally 15 or more), MDLs can be calculated. Once data has been processed, usually two months into the year, the QA staff will calculate the lab detection limit for use in assessing data for the current year. MDLs are calculated and verified using a process based on the current EPA MDL procedures. No network detection limit currently exists for MDN.

The lab MDL is used primarily to validate instruments and as a tool for the QA staff to assess performance. The lab MDL, adjusted for dilution, is reported to the sites but is not currently associated with the data on the website. There is no flagging of samples that are below the lab MDL. The HAL will consider developing a network MDL that takes into account some of uncertainty in the sample handling and processing.

11.2 MDN and Litterfall LODs and LOQs

Calculations of MDN and Litterfall LODs and LOQs are completed according to EHD QA 116 SOP and 40 CFR Part 136, Appendix B, using spiked reagent solutions and blanks prepared in the laboratory. See **Table 13** below. The LOD and LOQ for MDN did not change from 2020.

Table 13. Network Limits of Detection (LOD) and Limits of Quantitation (LOQ) for the Mercury Deposition Network (MDN) and Mercury in Litterfall Network (MLN), 2020 – 2021.

Network	Analyte	2020 LOD	2021 LOD	2020 LOQ	2021 LOQ
MDN	THg	0.2 ng/L	0.2 ng/L	0.667 ng/L	0.667 ng/L
MDN	MeHg	0.1 ng/L	0.1 ng/L	0.3 ng/L	0.3 ng/L
MLN	THg	NA	0.1 ng*	NA	0.33 ng
MLN	MeHg	0.1 ng	0.1 ng	0.3 ng	0.3 ng

**Based on minimum of 10 mg well-homogenized sample.*

11.3 Ongoing MDL Verification

MDN MDLs are verified by analyzing a spiked solution, prepared with 0.5% HCl (v/v) and 1% BrCl (v/v), at a concentration between 1-5x (currently 2.5x) the initial MDL with every analytical run. Annually, these spiked samples and all of the batch method blanks are assessed. The lab MDL is calculated and compared to the previous MDL. The lab MDL may remain unchanged if all of the following criteria are met (per 40 CFR 136, Appendix B, Vol. 82, No. 165, Aug. 28, 2017, U.S. Environmental Protection Agency):

1) The new MDL is within 2x the current established MDL

2) Fewer than 3% of the method blanks are above the established MDL

3) Fewer than 5% of the spiked samples fail to meet recovery criteria

Litterfall network MDLs are verified by performing a complete MDL study annually because the instrument for this network is used infrequently.

11.4 MDN MDL Adjusted by Dilution

Mercury methods for waters involve a pre-concentration step, so the MDL is established based on a standardized (maximum) volume of 30mL. If a smaller volume is used, the MDL is multiplied by the dilution factor to define the MDL for an individual sample i.e. [(30.0/volume used)*MDL]. This is reported to the sites on the preliminary reports.

12. External Field QA Programs

Information for Section 12 is extracted from the USGS External Quality Assurance Project Report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network.

The CAL/HAL also participated in several external PT programs. Those programs and outcomes for 2021 are discussed in **Section 14**.

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

The USGS used two programs to provide external quality assurance monitoring for the NADP's NTN and MDN in 2021. The field audit program assesses the effects of onsite exposure, sample handling, and shipping on the chemistry of NTN and MDN samples. The inter-laboratory comparison program assesses the bias and variability of the chemical data from the CAL and HAL and other participating laboratories that analyze precipitation samples for major ions, nutrients, and mercury.

12.2. Field Audit Samples

The USGS Precipitation Chemistry Quality Assurance Project (PCQA) uses field collector equipment-rinse samples (bag and sample train) paired with corresponding deionized water or known concentration solutions to identify changes in chemical contamination levels in the networks. Sites process these samples on dry weeks and send them to the appropriate lab. These results are published in an official USGS publication every two years. **Figure 6** shows this data from 1997 to 2021. The most current data set, 2019-2021, is highlighted in red. There is consistent, but relatively minimal background contamination, at the field collectors. Calcium seems to be an increasing contaminant, but it is still below the network MDL value.

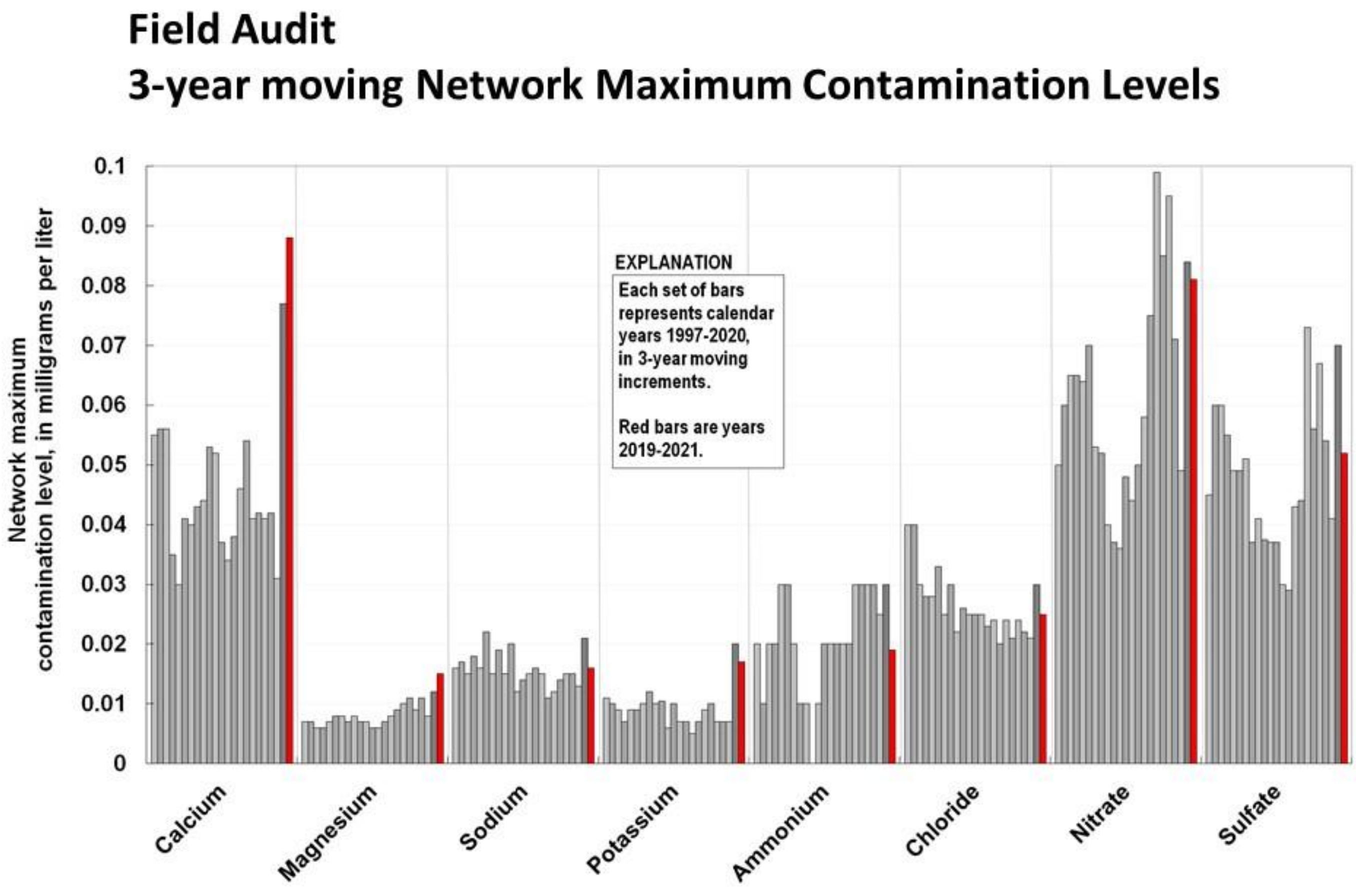

Figure 6. National Trends Network (NTN) Field Audit Results, 1997 – 2021 per USGS Precipitation Chemistry Quality Aassurance (PCQA) website.

12.3 Field QC System Blank Program

The MDN site operators normally receive system blank samples from the USGS PCQA project. When operators receive field system blanks from PCQA they wait until there is a week without wet deposition at their site. The operator then pours one-half of the volume of the system blank solution (reagent grade water) through the glass sample train. The glass sample train consists of the collector funnel, which collects the precipitation sample, and a thistle tube, which drains the precipitation into the sample bottle. This is called the system blank sample (also known as “DF”), and the solution remaining in the original sample bottle is called the bottle blank sample (also known as “DK”). Both system blank and bottle samples are sent to the HAL for total mercury (Hg) analysis. Reports of these data are prepared every two years by the USGS.

In 2021, USGS also sent two aliquots of system blank solution directly to the lab to ensure the original water used in the field blanks for analysis was not contaminated. Both blanks measured well below the established blank limit (<0.2ng/L). The 2021 data from the System Blank samples indicates some contamination in the field, but also some bottle blanks that were higher than might be expected. Occasionally, the reportedly processed sample is much lower than the unprocessed water. This fact, as well as reports from log in staff that sample identity is not always clear, casts some uncertainty on the validity of these results. In 2022, the HAL will be managing the shipment of the DF/DK bottles and hopes to improve the clarity on which sample has been processed.

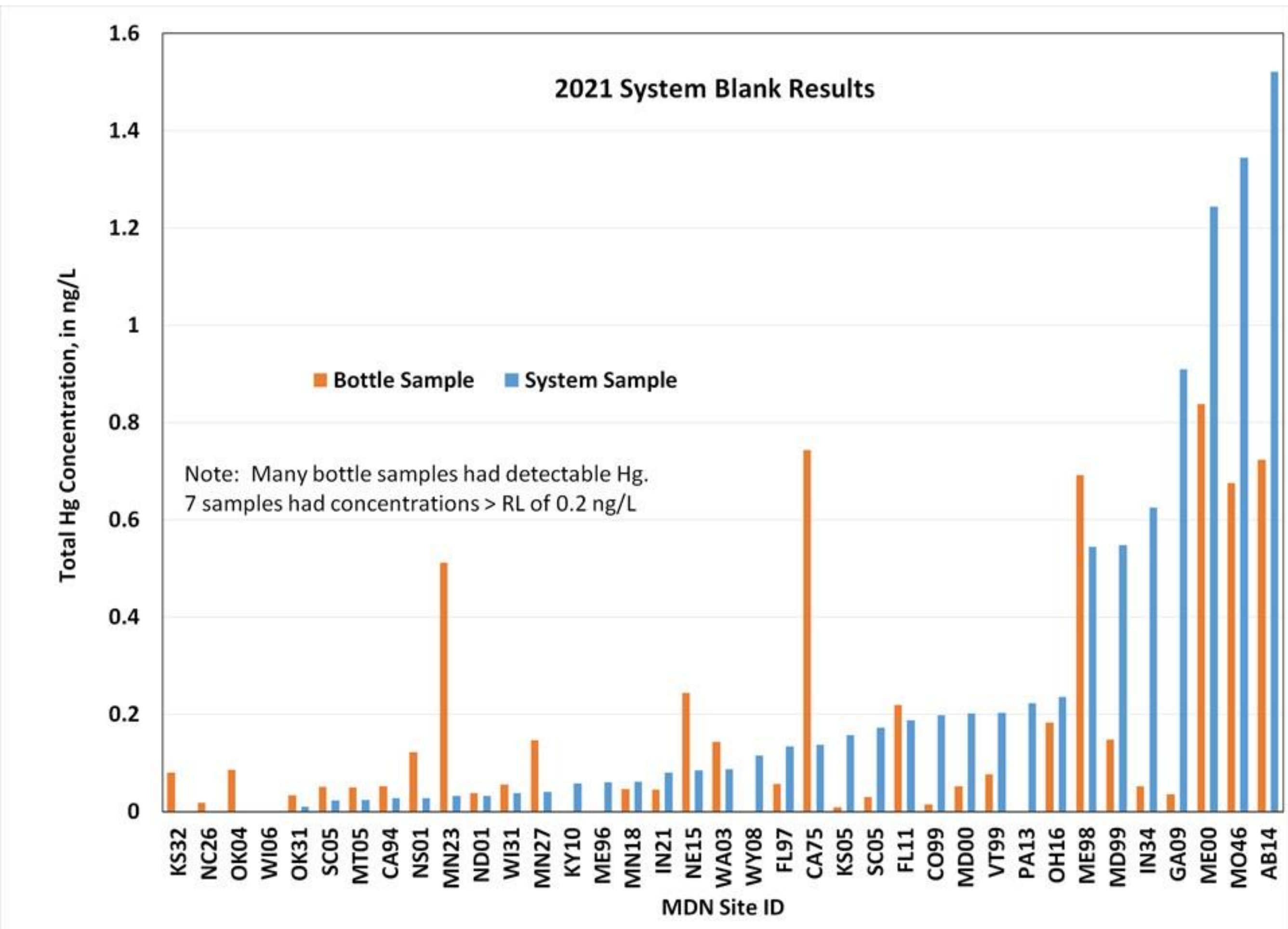

Figure 7. Results from 2021 MDN System Blanks per USGS Precipitation Chemistry Quality Assurance (PCQA) website in nanograms per liter (ng/L). The bottle sample is the DK and the system sample is the DF.

13. Internal Field QA Programs

13.1. AMoN Travel Blanks and Field Duplicates

In 2021, ~25% of the AMoN sites received travel blanks each deployment (2-week periods) and all sites received travel blanks at least several times per year. For deployments in 2020, the CAL switched from triplicate to duplicate samplers to assess precision (after approval from QAAG/Exec). Duplicate samplers were sent to approximately 15% of the sites each deployment, rotating to different sites with each subsequent deployment, beginning in January of 2020.

13.2. Travel Blanks

There were 573 travel blanks sent to sites and analyzed between January and December of 2021. Travel blanks >0.2 mg/L NH_4 (~0.4 µg/m^3 NH_3) exceed the established maximum blank criterion and are flagged. There was just one valid travel blank above 0.2 mg/L NH_4 during the reporting period. The mean/median travel blanks have remained very consistent and low under WSLH network operations. Refer to **Table 14** for the mean, median and maximum travel blank concentrations since the WSLH began operating the AMoN network. Refer to **Figure 8** for the 2021 AMoN travel blanks and **Figure 9** for the AMoN travel blanks since the beginning of the network.

Table 14. AMoN Travel Blank Results in milligrams per liter (mg/L) and micrograms per liter (µg/L), 2020-2021

	2020	**2021**	**2021**
	mg/L NH_4	**mg/L NH_4**	**µg/m^3 NH_3**
Mean	0.037	0.040	0.081
Median	0.033	0.037	0.080
Max	0.154	0.257	0.650
Number of Valid Travel Blanks	540	570	570
Number of Invalid (QR=C)Travel Blanks (not used)	0	3	3

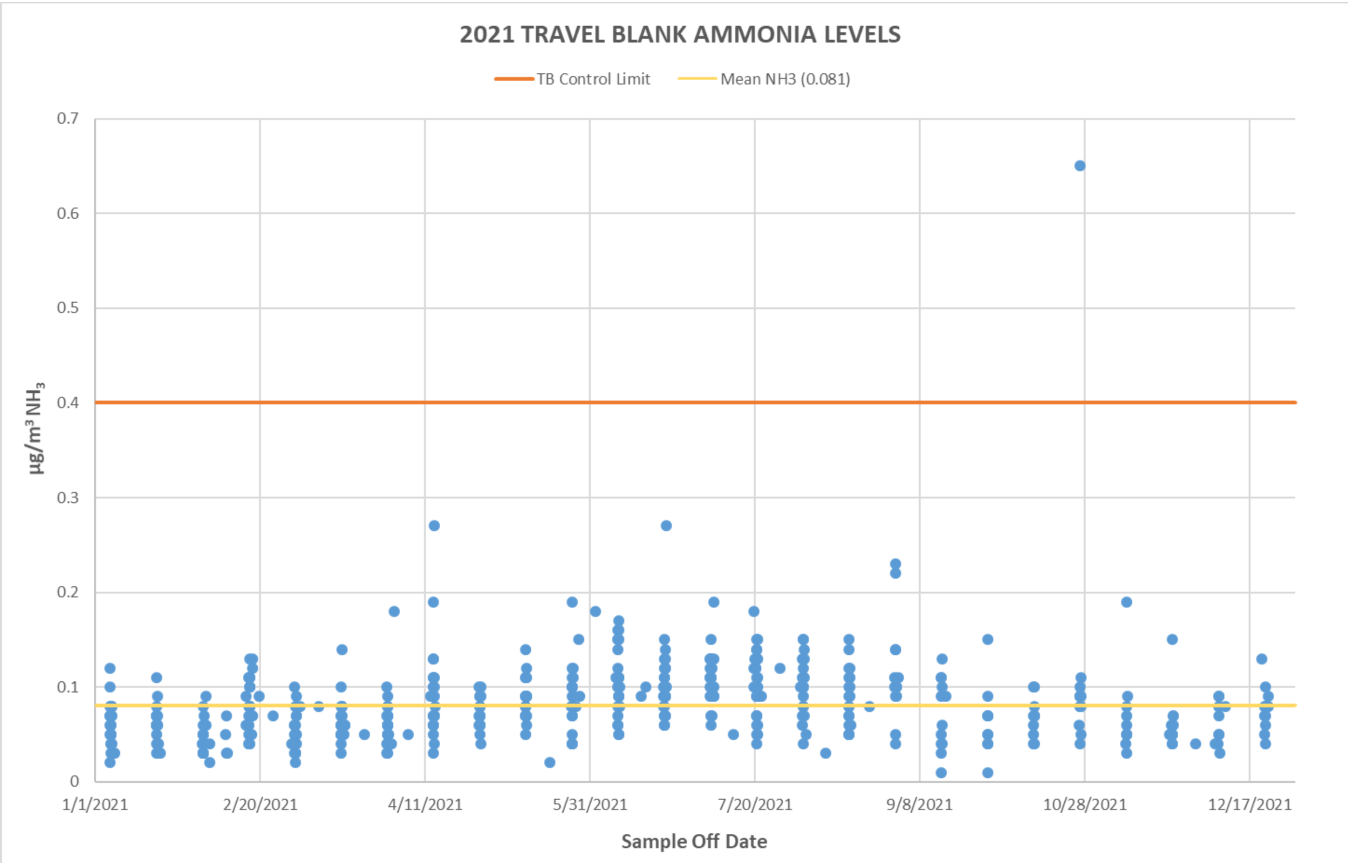

Figure 8. AMoN Travel Blank Ammonia (NH_3) Levels, in micrograms per cubic meter ($\mu g/m^3$), 2021.

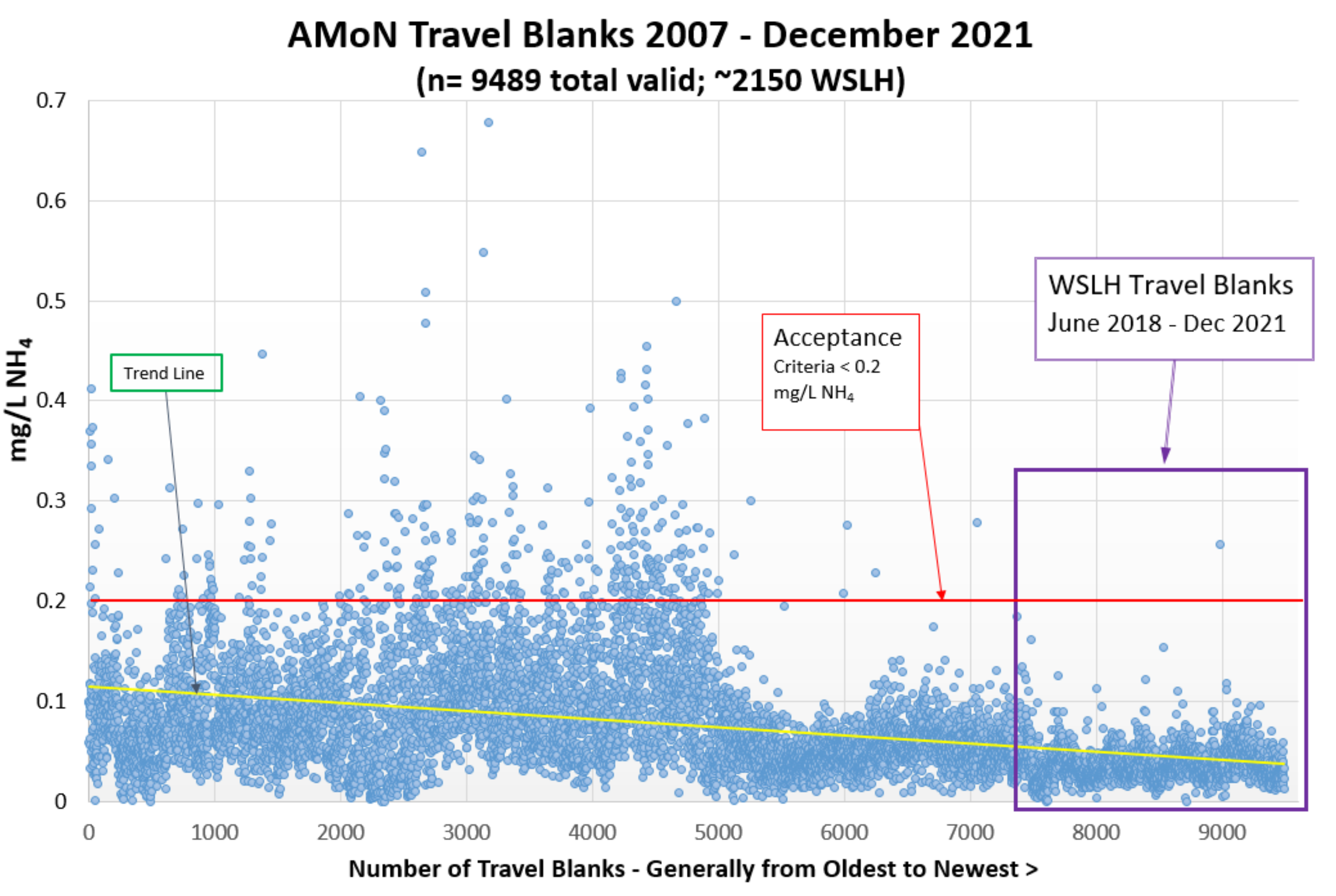

Figure 9. Ammonia Monitoring Network (AMoN) Travel Blank Historical Ammonium (NH_4^+) Levels, in milligrams per liter (mg/L), 2007 – 2021. [WSLH, Central Analytical Laboratory at Wisconsin State Laboratory of Hygiene]

13.2 AMoN Field Duplicates

Triplicates (2018 & 2019) and duplicates (2020-2021) that exceeded 15% RSD were retested to ensure that the differences did not indicate an analytical issue, and noted in the qualifiers spreadsheet. The disparate results were confirmed every time so we have discontinued this practice. In 2021, the CAL deployed and analyzed 393 duplicate sets.

In 2021, 90% of the replicate sets (across all ambient concentrations) had less than 13% RPD. All duplicate data sets were included in the average and median calculations. However, for assessing RPD it is apparent that the inclusion of low concentration sets skews the RPD data (as one would expect where the absolute difference (AD) is not a strong function of concentration.) This is conveyed in **Table 15** and **16**, and **Figures 10** and **11**. It is most appropriate to assess the AD in the concentration. The 95th percentile of the set AD was 0.43 µg/m^3 NH_3 and the 80th percentile was 0.09 µg/m^3 NH_3. This means that 95% of the sample and duplicate ammonia results were within 0.43 µg/m^3 NH_3 of each other.

As can be seen in **Figure 10** and **11**, AMoN duplicate differences are generally very small. Field duplicate differences that are extreme outliers are generally due to field error and have very high RPDs.

Table 15. Ammonia (NH_3) Monitoring Network (AMoN) Relative Percent Difference (RPD) and Absolute Difference (AD) percentiles, 2021. [%, percent; micrograms per cubic meter ($\mu g/m^3$).

AMoN Duplicate Sets 2021 - 393 Sets	2021	RPD %	AD $\mu g/m^3$ NH_3
	80th Percentile	7.93	0.09
	85th Percentile	10.31	0.12
	90th Percentile	13.01	0.18
	95th Percentile	25.77	0.43

Table 16. Ammonia (NH_3) Monitoring Network (AMoN) Average, Median, and Maximum values for Standard Deviation (SD), Relative Percent Difference (RPD), and Absolute Difference (AD) of Field Duplicates, in percent, 2021.

2021 Duplicates	SD	RPD	AD
Average	0.092	8.590	0.130
Median	0.021	3.636	0.030
Maximum	3.514	188.615	4.970

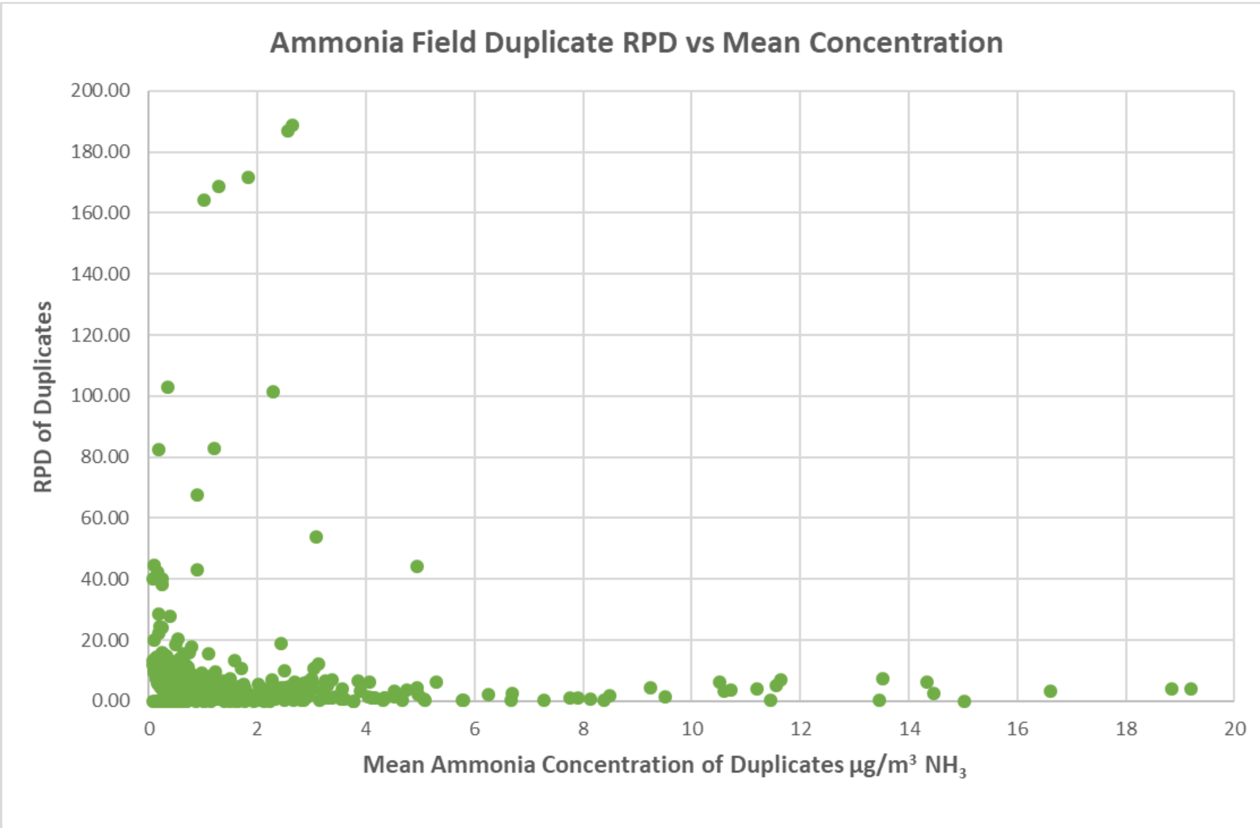

Figure 10. Relative percent difference (RPD) of 2021 AMoN field duplicate versus mean ammonia (NH_3) concentration (n=393 sets), in micrograms per cubic meter (µg/m^3).

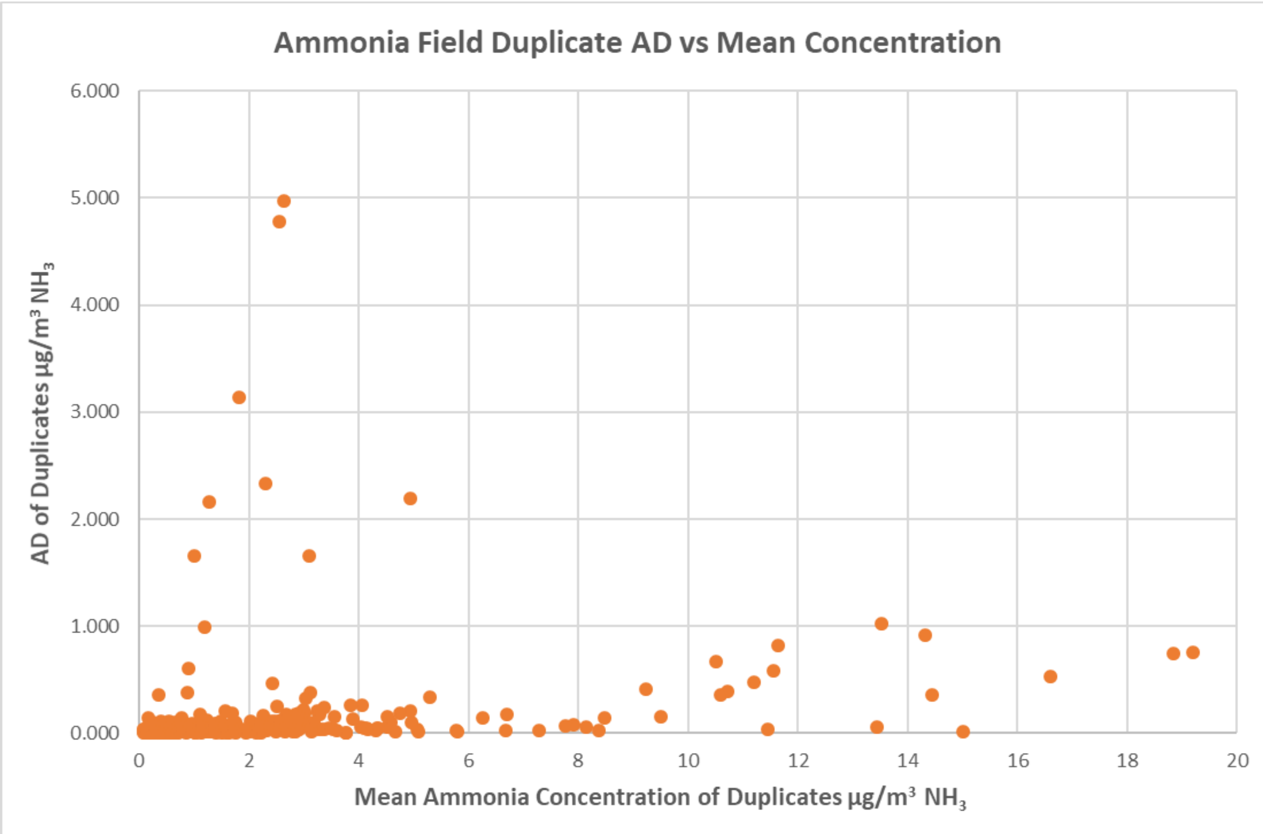

Figure 11. Absolute difference (AD) of 2021 AMoN field duplicates versus mean ammonia (NH_3) concentration (n=393 sets), in micrograms per cubic meter (µg/m^3).Proficiency Test results

In 2021, the NADP participated in and completed the following PT assessments:

- Two PT studies through the World Meteorological Organization (WMO)
- One study through Environment and Climate Change Canada (ECCC)
- Two studies through the USGS Standard Reference Solution (SRS)
- Monthly USGS Inter-laboratory Comparison samples

A summary of results are provided below.

Table 17. 2021 Proficiency Test Results Summary

[ECCC, Environment and Climate Change Canada; WMO, World Meteorological Organization; USGS, U.S. Geological Survey; Ca, calcium; NH4, ammonium; Hg, mercury; SO4, sulfate; NO3, nitrate; Cl, chloride; Na, sodium; Mg, magnesium]

PT Provider	PT Studies Completed	Results outside of Control Limits	Website Results
ECCC	ECCC 117 ECCC 118	ECCC 117 – started running samples on alternating days to better capture overall variability; no flags on any samples and overall rating of "good"; no Hg samples in this set. ECCC 118 – One Mg value above warning limit; Ca biased high but all passing; one low NH_4 value; all Hg were good.	Not on website - Refer to summary provided below
WMO Global Atmosphere Watch (GAW)	WMO 63 WMO 64	WMO 63 – Negative bias for pH; positive bias for SO_4 and NO_3 and smaller positive bias for Cl. WMO 64 – Slight positive bias for Ca, Na, and Mg.	https://www.qasac-americas.org/study-results?lab=700175&study=63&type= https://www.qasac-americas.org/study-results?lab=700175&study=64&type=
USGS	2021 - Full Year of Samples	Notes from Greg Wetherbee below	https://bqs.usgs.gov/PCQA/Interlaboratory_Comparison/graphOutput.php?page=start
USGS SRS (Standard Reference Samples)	P-76, N-149, Hg-72 (Spring) P-77, N-151, Hg-73 (Fall)	Spring – low recovery for SO_4 on P-76; there was a lot of variability among labs with this sample Fall – low recovery for SO_4 on P-77	Not on website - Available upon Request

13.3. ECCC Results

Table 18. Environment and Climate Change Canada (ECCC) Study 117 Performace Testing Results Assessment **[%, percent; Ca, calcium; Na, sodium; K, potassium; Mg, magnesium; Cl, choride; SO4, sulfate, NO3, nitrate; NH4, ammonium; NH3-N, ammonia as nitrogen]**

	ECCC 117 RN-1	ECCC 117 RN-2	ECCC 117 RN-3	ECCC 117 RN-4	ECCC 117 RN-5	ECCC 117 RN-6	ECCC 117 RN-7	ECCC 117 RN-8	ECCC 117 RN-9	ECCC 117 RN-10
pH	6.09	5.64	6.19	6.51	6.72	6.92	4.82	6.86	7.00	5.54
pH Study Mean	6.01	5.56	6.12	6.44	6.73	6.75	4.84	6.89	6.96	5.48
AD	0.08	0.08	0.07	0.07	0.01	0.17	0.02	0.03	0.04	0.06
% Recovery	101	101	101	101	100	103	100	100	101	101
Cond	6.2	26.9	16	10.7	23.9	15.3	11.5	43	26.4	5.5
Cond Study Mean	5.9	26.2	15.3	10.2	22.8	14.9	10.5	41.1	25.1	5.2
AD	0.30	0.7	0.7	0.5	1.1	0.4	1.0	1.9	1.3	0.3
% Recovery	105	103	105	105	105	103	110	105	105	106
Ca	0.3085	0.6845	1.4	0.6505	2.347	1.863	0.3345	2.344	1.583	0.1617
Ca Study Mean	0.321	0.696	1.421	0.676	2.301	1.831	0.334	2.333	1.586	0.162
% Recovery	96	98	99	96	102	102	100	100	100	100
Na	0.1521	3.124	0.6591	0.4518	0.4132	0.687	0.1155	4.028	0.9774	0.276
Na Study Mean	0.157	3.182	0.675	0.462	0.402	0.670	0.114	4.032	0.962	0.275
% Recovery	97	98	98	98	103	103	101	100	102	100
K	0.0617	0.2283	0.2947	0.063	0.1279	0.1932	0.0787	0.4418	0.2291	0.0186
K Study Mean	0.063	0.237	0.304	0.062	0.127	0.193	0.080	0.434	0.227	0.020
% Recovery	98	96	97	102	101	100	98	102	101	93
Mg	0.0899	0.4091	0.2182	0.2142	0.3435	0.1648	0.0646	0.782	0.2615	0.0385
Mg Study Mean	0.092	0.414	0.227	0.220	0.334	0.160	0.063	0.772	0.258	0.039
% Recovery	98	99	96	97	103	103	103	101	101	99
Cl	0.2178	5.1539	0.3662	0.7809	0.5531	0.300	0.0618	6.6816	0.3028	0.4732
Cl Study Mean	0.212	5.111	0.354	0.754	0.534	0.291	0.061	6.636	0.293	0.459
% Recovery	103	101	103	104	104	103	101	101	103	103
SO_4	0.6302	1.4245	2.505	0.688	2.7344	1.3288	0.6464	2.0813	2.6844	0.3039
SO_4 Study Mean	0.622	1.398	2.488	0.677	2.732	1.294	0.642	2.067	2.691	0.311
% Recovery	101	102	101	102	100	103	101	101	100	98
NO_3-N	0.1680	0.0033	0.2740	0.1926	0.2902	0.0702	0.1657	0.0831	0.2280	0.1446
NO_3-N Study Mean	0.164	0	0.266	0.187	0.281	0.07	0.162	0.082	0.224	0.144
% Recovery	102	N/A	103	103	103	100	102	101	102	100
NH_3-N	0.1923	0.0162	0.0523	0.1895	0.4264	0.0050	0.0484	0.0082	1.0497	0.0896
NH_3-N Study Mean	0.192	0.015	0.051	0.189	0.428	0.009	0.048	0.01	1.051	0.095
% Recovery	100	108	102	100	100	55	101	82	100	94

The analyte column is the reported value from the lab. The study mean is the expected value reported from ECCC. The percent recovery is the comparison of the lab value and the study value. The two low recovery values for NH_4 in study 117 are below our network MDL of 0.014 mg/L. As for study 118 (**Table 19**), Mg had a positive bias on the lower concentration samples. There are a few other outliers (Ca and NH_4), but no consistent bias.

Table 19. Environment and Climate Change Canada (ECCC) Study 118 Performance Testing Results Assessment for precipitation major ions (*A*) and mercury (Hg) (*B*) analyses at Central Analytical Mercury Analytical Laboratories at the Wisconsin State Laboratory of Hygiene. **[%, percent; Ca, calcium; Na, sodium; K, potassium; Mg, magnesium; Cl, choride; SO4, sulfate, NO3, nitrate; NH4, ammonium; NH3-N, ammonia as nitrogen, WSLH,; µg/L, micrograms per liter; ng/L, nanograms per liter; MDL, method detection limit; RDL, reporting limit]**]

	ECCC 118 RN-01	ECCC 118 RN-02	ECCC 118 RN-03	ECCC 118 RN-04	ECCC 118 RN-05	ECCC 118 RN-06	ECCC 118 RN-07	ECCC 118 RN-08	ECCC 118 RN-09	ECCC 118 RN-10
pH	7.18	7.1	7.15	5.58	5.68	5.62	4.7	5.69	5.42	5.78
pH Study Mean	7.05	6.88	6.96	5.45	5.63	5.55	4.72	5.62	5.38	5.71
AD	0.13	0.22	0.19	0.13	0.05	0.07	0.02	0.07	0.04	0.07
% Recovery	102	103	103	102	101	101	100	101	101	101
Cond	34.4	24.9	32	7.9	4.5	5.3	18	4.5	5.6	21.6
Cond Study Mean	33.2	24	30.8	7.7	4.4	5.2	17	4.3	5.4	21.2
AD	1.20	0.9	1.2	0.2	0.1	0.1	1.0	0.2	0.2	0.4
% Recovery	104	104	104	103	102	102	106	105	104	102
Ca	3.841	2.370	3.731	0.244	0.113	0.116	0.743	0.126	0.126	0.506
Ca Study Mean	3.782	2.259	3.586	0.235	0.107	0.110	0.702	0.114	0.120	0.490
% Recovery	102	105	104	104	106	106	106	111	105	103
Na	1.870	1.682	0.339	0.237	0.116	0.250	0.079	0.049	0.223	2.757
Na Study Mean	1.805	1.565	0.316	0.229	0.110	0.241	0.080	0.049	0.210	2.695
% Recovery	104	107	107	104	106	104	99	100	106	102
K	0.417	0.375	0.155	0.048	0.028	0.023	0.041	0.032	0.017	0.253
K Study Mean	0.425	0.372	0.152	0.045	0.025	0.025	0.045	0.033	0.019	0.259
% Recovery	98	101	102	106	113	91	92	98	90	98
Mg	0.646	0.607	0.502	0.051	0.027	0.039	0.288	0.026	0.037	0.318
Mg Study Mean	0.635	0.575	0.478	0.049	0.024	0.034	0.263	0.023	0.032	0.296
% Recovery	102	105	105	104	112	114	110	113	115	107
Cl	1.528	1.091	0.405	0.286	0.163	0.309	0.193	0.060	0.361	3.926
Cl Study Mean	1.432	1.102	0.398	0.291	0.175	0.298	0.195	0.062	0.350	3.770
% Recovery	107	99	102	98	93	104	99	96	103	104
SO_4	2.539	2.133	2.768	1.190	0.428	0.574	2.948	0.364	0.394	1.187
SO_4 Study Mean	2.429	2.015	2.669	1.123	0.417	0.551	2.885	0.350	0.384	1.131
% Recovery	105	106	104	106	103	104	102	104	102	105
NO_3-N	0.1766	0.0735	0.4004	0.2076	0.1350	0.1235	0.3266	0.1774	0.1570	0.0000
NO_3-N Study Mean	0.169	0.07	0.373	0.196	0.131	0.119	0.309	0.169	0.149	0
% Recovery	105	105	107	106	103	104	106	105	105	N/A
NH_3-N	0.0047	0.0043	0.6184	0.2569	0.1865	0.1575	0.0976	0.1756	0.1335	0.0587
NH_3-N Study Mean	0	0	0.606	0.252	0.183	0.158	0.099	0.207	0.134	0.064
% Recovery	N/A	N/A	102	102	102	100	99	85	100	92

A

WSLH Sample ID	ECCC Sample ID	Result ng/L	Converted to ug/L	Hg Study Mean ug/L	% Recovery	Analysis Date	Volume Analyzed (mL)	MDL ng/L	ug/L	RDL
21005354	HG02	71.6419	**0.0716**	0.072	100	10/1/2021	30	0.2	0.0002	0.67
21005355	HG03	1.3290	**0.0013**	0.001	NA	10/1/2021	30	0.2	0.0002	0.67
21005356	HG04	32.6679	**0.0327**	0.031	105	10/1/2021	30	0.2	0.0002	0.67
21005357	HG08	53.6692	**0.0537**	0.053	101	10/1/2021	30	0.2	0.0002	0.67
21005358	HG09	82.7238	**0.0827**	0.08	103	10/1/2021	15	0.2	0.0002	0.67

B

13.4. World Meteorological Organization (WMO) performance testing results for NADP Central Analytical Laboratory, 2021.

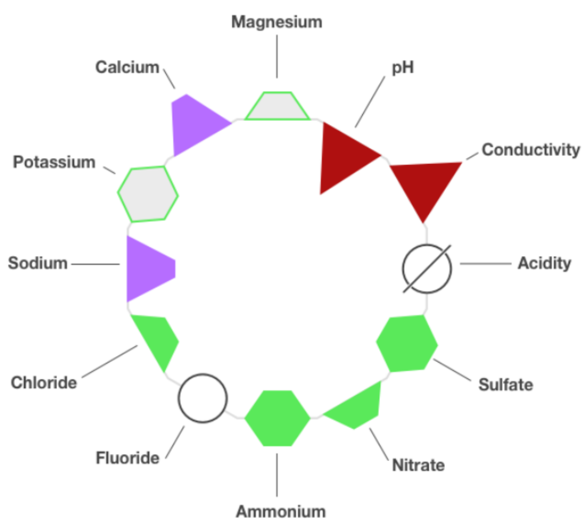

Figure 12. World Meteorological Organization Performance Testing Results Diagrams and Keys

Good - green hexagon - A good measurement is within the interquartile range (IQR), defined as the 25th to 75th percentile or middle half of the measurements (see sulfate). For a measurement within the IQR that fails to meet the DQO, the green hexagon has a gray fill (see potassium).

Satisfactory - green trapezoid - A satisfactory measurement is outside of the IQR but within the range defined by the median ± (IQR/1.349). The ratio, IQR/1.349, is the non-parametric estimate of the standard deviation, sometimes called the f-pseudosigma. A measurement that is outside of the median ±1 deviation-pseudosigma but meets the DQO is an exception to this definition. It is set automatically to satisfactory. Nitrate and chloride are satisfactory measurements that meet the DQOs. When a satisfactory measurement fails to meet the DQO, the green trapezoid has a gray fill (see magnesium).

Marginal - purple trapezoid - A marginal or marginally acceptable measurement is outside the range of satisfactory measurements but inside the range defined by the median ±2 (IQR/1.349). Marginal measurements fail to meet the DQOs. Examples are sodium and calcium.

Biased - red triangle - A biased measurement is outside the range of marginal measurements (>2 standard deviations from the median). Biased measurements fail to meet the DQOs. Examples are pH and conductivity.

Detection Limit - open circle - Measurement is below the detection limit of the laboratory's analytical method. Fluoride is an example.

No Measurement - circle with slash - Measurement was not reported. Acidity is an example.

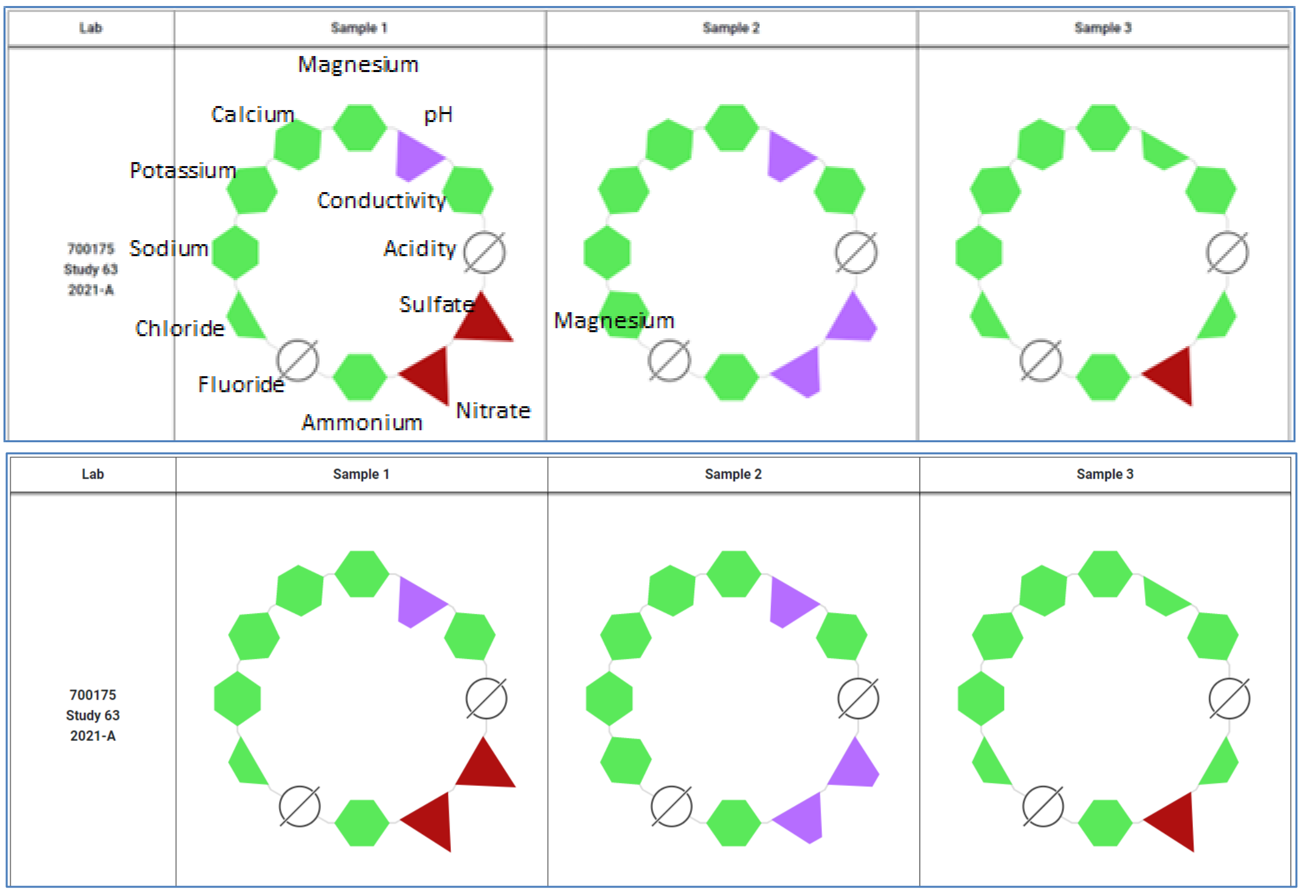

Figure 13. Results from World Meteorological Organization Performance Testing Study 63 – varied severity of positive bias on nitrate and sulfate for all three samples and a slight negative bias for pH on all samples.

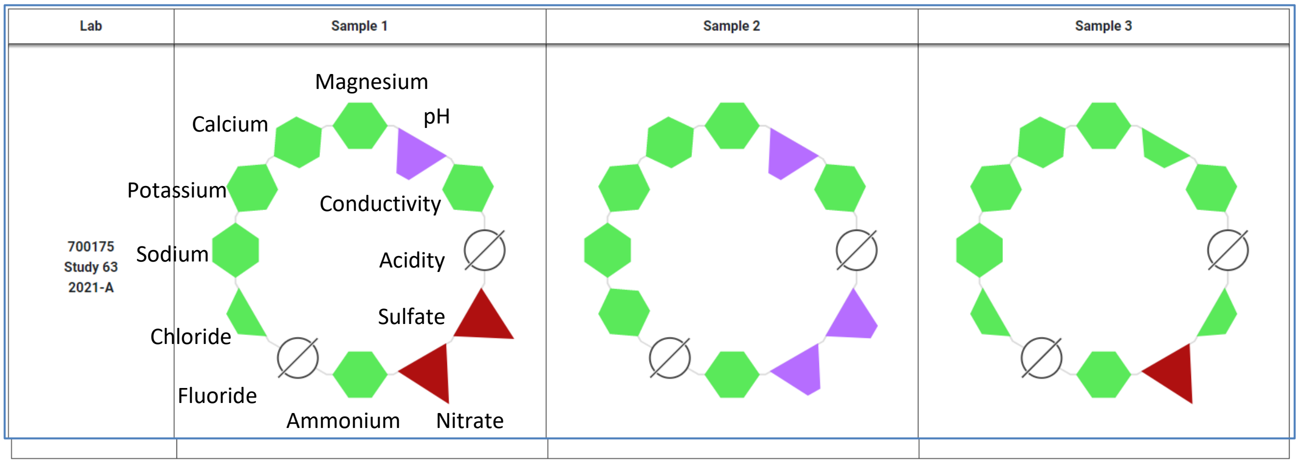

Figure 14. Results from World Meteorological Organization Performance Testing Study 64 – good consistent values with two positive bias for sulfate and nitrate on Sample 1 and one slight positive value for nitrate on Sample 3.

Table 20. World Meteorological Organization Study Performance Testing Study 63 Results Assessment – May 2021, showing no results of concern. [TV, target value; LIMS ID, Laboratory Information Management identifier; Cond, specific conductance; Ca, calcium; Na, socium; K, potassium; Mg, magnesium; Cl, chloride; SO4, sulfate; NO3, nitrate; NH4, ammonium; %, percent]

Date Received	Sample ID	LIMS ID	pH	Cond	Ca	Na	K	Mg	Cl	SO4	NO3	NH4
5/19/2021	WMO63-1	21002798	4.81	19.1	0.303	1.102	0.194	0.124	1.875	2.227	1.129	0.386
TV FINAL			4.89	19.1	0.302	1.109	0.187	0.123	1.751	2.104	1.052	0.387
% of TV			98	100	101	99	104	100	107	106	107	100
		Difference WSLH - TV	-0.08	0.0	0.002	-0.007	0.007	0.001	0.124	0.123	0.077	-0.001
5/19/2021	WMO63-2	21002799	4.62	12.6	0.129	0.092	0.023	0.026	0.138	1.122	1.045	0.214
TV FINAL			4.72	12.4	0.129	0.092	0.022	0.027	0.137	1.054	0.986	0.217
% of TV		AD for pH cond	98	102	100	100	106	98	101	106	106	98
		Difference WSLH - TV	-0.10	0.3	0.000	0.000	0.001	-0.001	0.001	0.068	0.059	-0.003
5/19/2021	WMO63-3	21002800	4.65	22.2	0.398	0.662	0.144	0.126	1.101	2.758	2.129	0.663
TV FINAL			4.72	22.0	0.397	0.656	0.141	0.123	1.028	2.650	2.001	0.660
% of TV		AD for pH cond	99	101	100	101	102	103	107	104	106	100
		Difference WSLH - TV	-0.07	0.20	0.001	0.006	0.003	0.003	0.0733	0.108	0.128	0.003

Table 21. World Meteorological Organization Performance Testing Study 64 Results Assessment – November 2021. [TV, target value; LIMS ID, Laboratory Information Management identifier; Cond, specific conductance; Ca, calcium; Na, socium; K, potassium; Mg, magnesium; Cl, chloride; SO4, sulfate; NO3, nitrate; NH4, ammonium; %, percent]

Date Received	Sample ID	LIMS ID	pH	Cond	Ca	Na	K	Mg	Cl	SO4	NO3	NH4
11/10/2021	WMO64-1	21006200	5.28	6.5	0.206	0.114	0.029	0.040	0.164	0.667	0.742	0.250
TV Final			5.33	6.5	0.194	0.108	0.032	0.038	0.175	0.664	0.747	0.247
% of TV			99	100	106	105	91	106	94	100	99	101
		Difference WSLH - TV	-0.05	0.0	0.012	0.006	-0.003	0.002	-0.011	0.003	-0.005	0.003
11/10/2021	WMO64-2	21006201	5.79	8.8	0.343	0.226	0.060	0.073	0.432	0.971	1.178	0.492
TV Final			5.75	8.8	0.327	0.215	0.060	0.066	0.433	0.954	1.164	0.482
% of TV		AD for pH cond	101	100	105	105	100	110	100	102	101	102
		Difference WSLH - TV	0.04	0.0	0.016	0.011	0.000	0.007	-0.001	0.017	0.014	0.010
11/10/2021	WMO64-3	21006202	4.58	22.5	0.361	0.425	0.126	0.109	0.777	2.497	1.858	0.616
TV Final			4.63	21.7	0.339	0.412	0.128	0.099	0.764	2.499	1.837	0.600
% of TV		AD for pH cond	99	104	107	103	99	110	102	100	101	103
		Difference WSLH - TV	-0.05	0.80	0.022	0.013	-0.002	0.010	0.0129	-0.002	0.021	0.016

Mg is biased high, but not out of range.

13.5. USGS Inter Comparison Results (per Greg Wetherbee – Quality Assurance Advisory Group, April 2021)

- Positive, statistically significant bias for H^+ and NO_3. Low variability for Ca, Na, K, NH_4, SO_4 and specific conductance, higher for Mg, Cl, NO_3, and pH (as compared to labs participating).
- April samples for H^+ were out of statistical control (i.e. outside $\pm$ 2 f-pseudosigma from most probable (median) values).
- Negative bias for the HAL, possibly corrected in November. High variability (~200% higher than other labs). Hg network maximum contamination of 0.09 ng/sample (which is well within the acceptable range).

  Note – Christa Dahman stated that the HAL was removing an aliquot from the bottle and brominating for MDN PT samples. In November, the lab started brominating in the bottle to resolve the issue of high variability. There are still implications for MeHg, but the lab is optimistic that it didn't impact MDN samples which are brominated in the bottle.

13.6. USGS Standard Reference Sample Results

Table 22. USGS Standard Reference Sample (SRS) Spring Results Assessment, 2021.

[Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; Cl, chloride; SO_4, sulfate, NO_3-N, nitrate as nitrogen; NH_3-N, ammonia as nitrogen; OPO_4, orthophosphate; THg, total mercury; %, percent]

USGS SRS Spring 2021				
Sample ID	**Analyte**	**Reported Value**	**True Value**	**% Recovery**
P-76	pH	7.69	7.8	99
	Conductivity (uS/cm)	93.5	93	101
	Ca (mg/L)	2.01	1.84	109
	K (mg/L)	0.097	0.091	107
	Mg (mg/L)	11.2	10.3	109
	Na (mg/L)	0.872	0.81	108
	Cl (mg/L)	3.61	3.44	105
	SO_4 (mg/L)	0.138	0.21	66
N-149	NO_3-N (mg/L)	0.416	0.3892	107
	NH_3-N (mg/L)	0.154	0.154	100
	OPO_4 (mg/L)	0.161	0.16	101
Hg-72	THg (μg/L)	0.0295	0.028	105

P-76 was prepped by USGS incorrectly and is very high in some analytes unlike “normal” precipitation. Also, this SRS was quite variable for SO_4 when looking at all lab responses.

Table 23. USGS Standard Reference Sample Fall Results Assessment, 2021.

[Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; Cl, chloride; SO_4, sulfate, NO_3-N, nitrate as nitrogen; NH_3-N, ammonia as nitrogen; OPO_4, orthophosphate; THg, total mercury; %, percent]

USGS SRS Fall 2021				
Sample ID	**Analyte**	**Reported Value**	**True Value**	**% Recovery**
P-77	pH	3.94	3.97	99
	Conductivity (uS/cm)	59.9	58.1	103
	Ca (mg/L)	0.129	0.128	101
	K (mg/L)	0.519	0.528	98
	Mg (mg/L)	0.036	0.036	100
	Na (mg/L)	0.699	0.699	100
	Cl (mg/L)	1.805	1.75	103
	SO_4 (mg/L)	0.088	0.115	77
N-151	NO_3-N (mg/L)	0.337	0.337	100
	NH_3-N (mg/L)	0.061	0.064	95
	OPO_4 (mg/L)	0.067	0.073	92
Hg-73	THg (µg/L)	0.024	0.023	104

Much more consistent results in the fall study, with values more reflective of “normal” precipitation. Still a low bias for SO_4, which only seems to occur with the SRS samples.

14. Analytical Quality Assurance

14.1. Analytical Sample Duplicates

Duplicate sample analysis is performed to assess analytical precision under routine laboratory operations. A second aliquot of a sample is analyzed in the same batch of 10 samples and the precision of two results is evaluated. Duplicates are chosen at random and must be performed at a frequency of 10%. Refer to **Table 24** for the duplicate acceptance criteria for the ICP, IC and FIA platforms. Criteria for pH and conductivity duplicates is within ± 0.2 pH units and ± 1 µS/cm, respectively. Exceedance metrics for 2021 are provided in **Table 25** and show remarkably good precision for a large number of duplicates. Note – the exceedances listed below are failures based on the criteria in **Table 24**, and that the IC and ICP-OES analytical platforms each have multiple analytes, each subject to the acceptance criteria. All duplicates that fail to meet **Table 24** criteria are rerun if possible.

Table 24. Sample and Duplicate Scenarios and Criteria. [MDL, method detection limit]

Sample Result	Duplicate Result	Calculation	Criteria
MDL to 10x MDL	MDL to 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 ≤ 10%
>10x MDL	>10x MDL	RPD	RPD must be ≤ 10%

Table 25. Analytical Duplicates and Percent Exceedances of quality criteria in 2021.

[#, count of; %, percent]

Platform	# Replicates in 2021	# Failures in 2021	% Exceedance (prior to reanalysis)	# Reanalyzed successfully
FIA AMoN	546	4	0.73%	4
FIA NTN	1354	3	0.22%	3
ICP-OES	1313	23	1.75%	23
IC	1354	4	0.30%	4
pH/Conductivity	1110	28	2.52%	28

Note: Some platforms have more duplicates in a year due to more frequent re-runs of samples, which therefore requires additional duplicates to be analyzed. All reanalyzed samples met quality criteria.

NOTE –The duplicate graphs below show duplicates above 10% RPD which are not technically QC failures if the sample concentration is at or below 10X MDL. In the lab, those are assessed as pass/fail based on the absolute difference being within the MDL per **Table 24**.

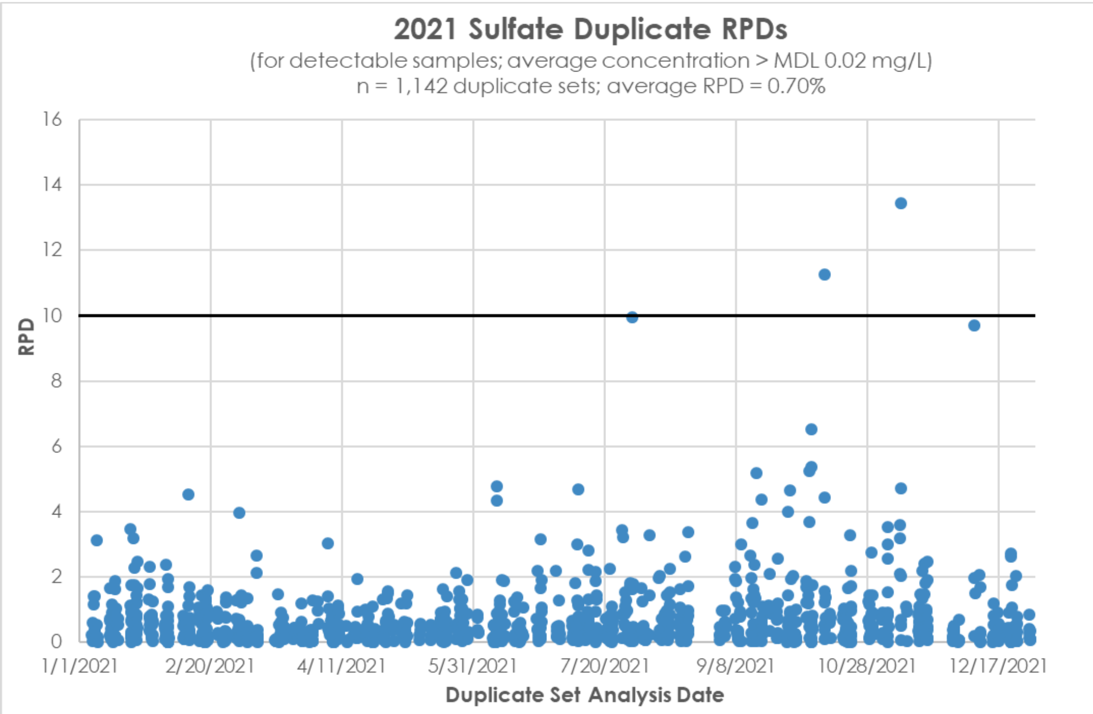

Figure 15. Sulfate (IC) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

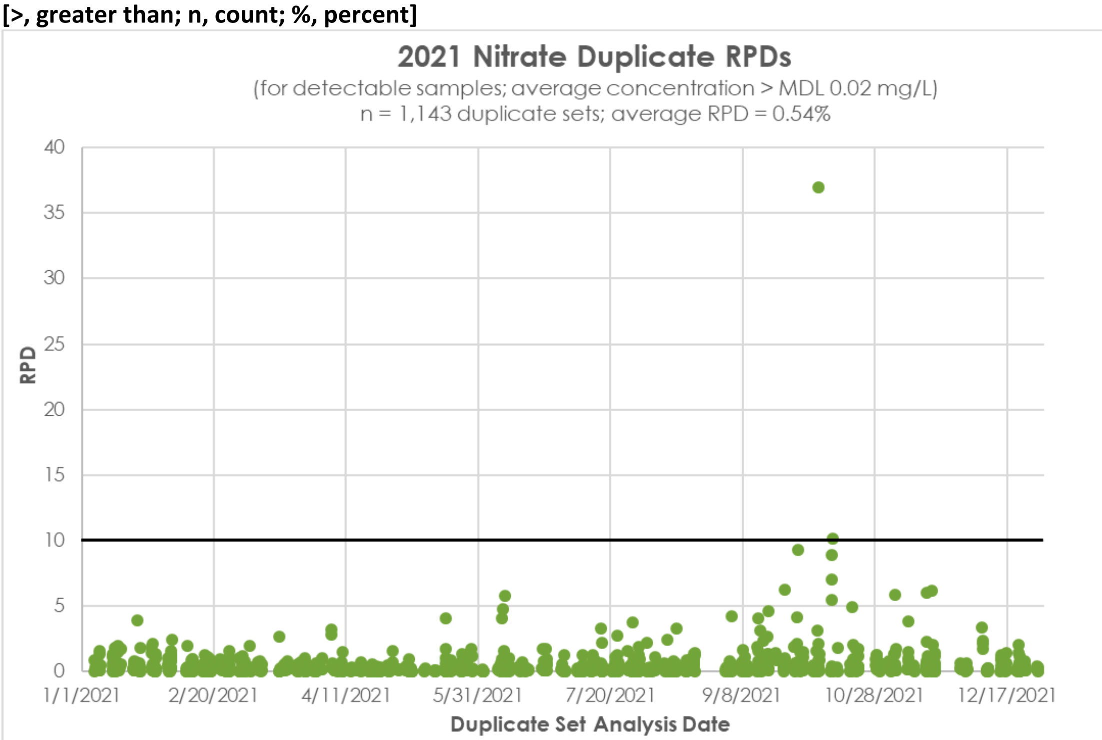

Figure 16. Nitrate (IC) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

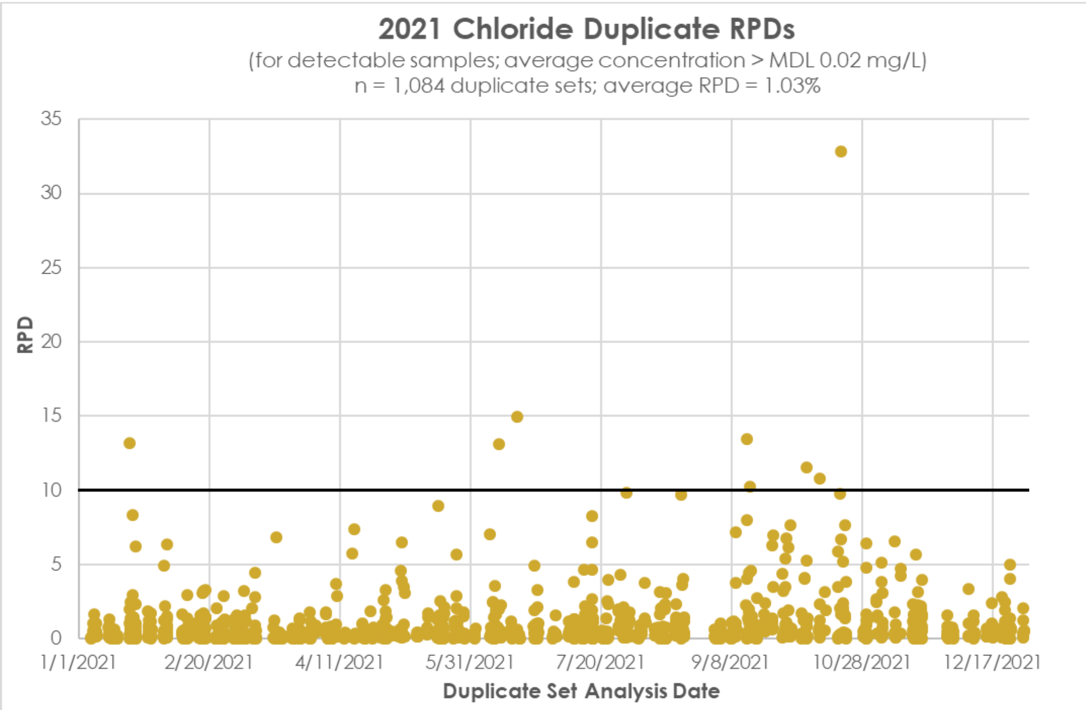

Figure 17. Chloride (IC) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

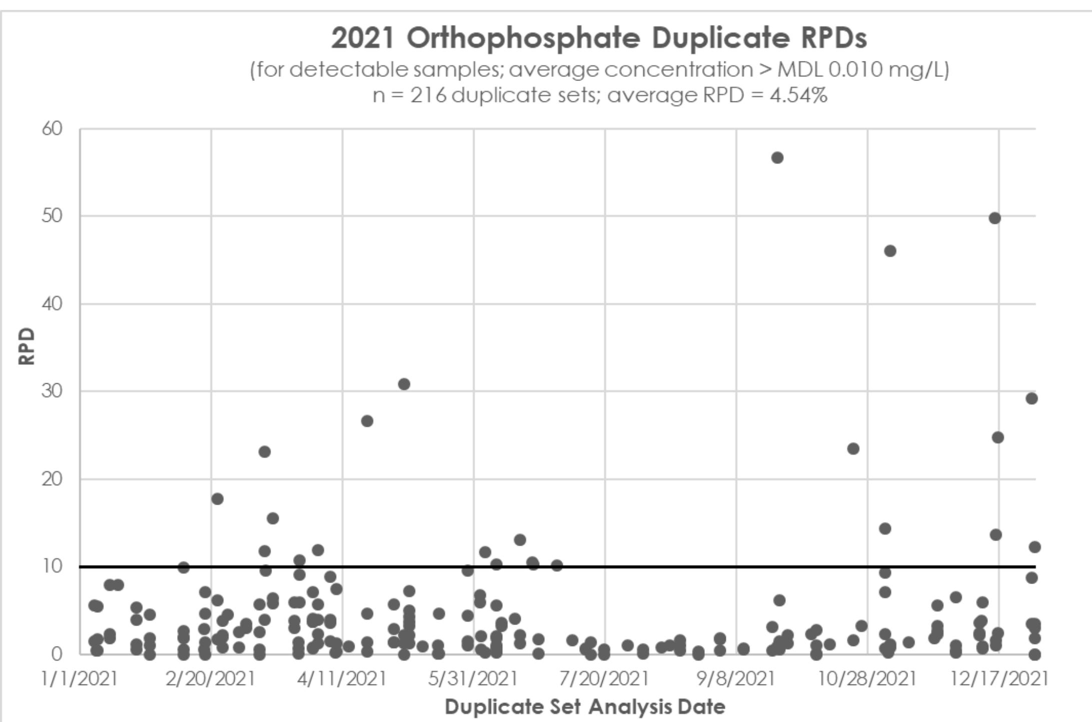

Figure 18. Orthophosphate (FIA) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

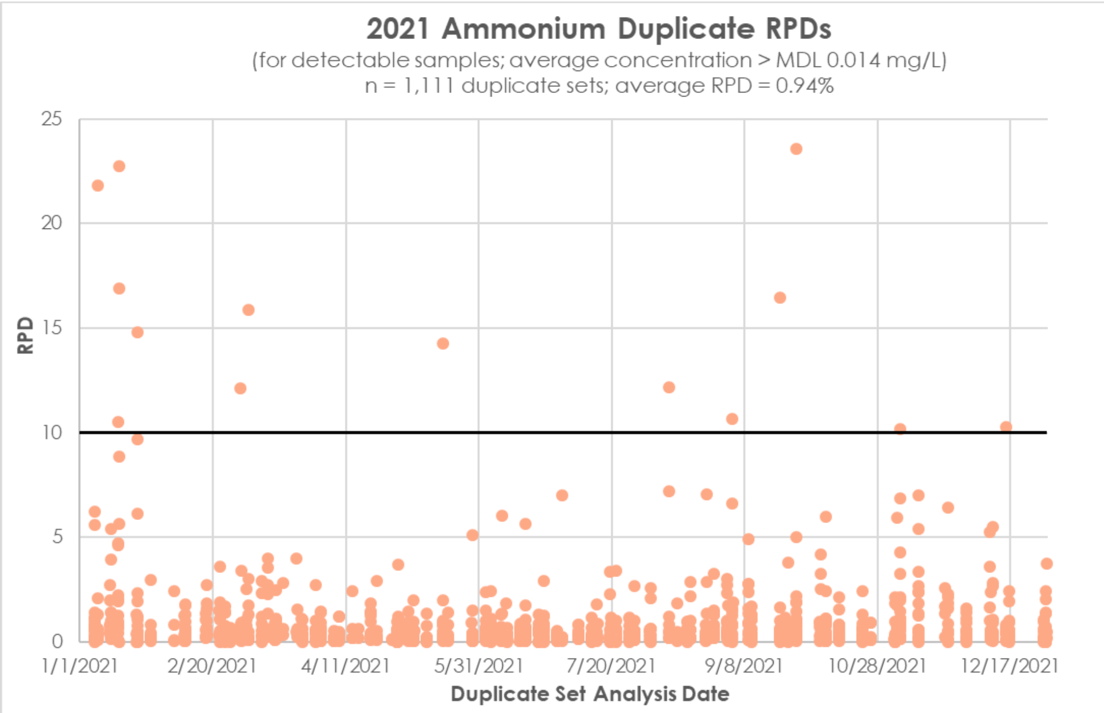

Figure 19. Ammonium (FIA) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

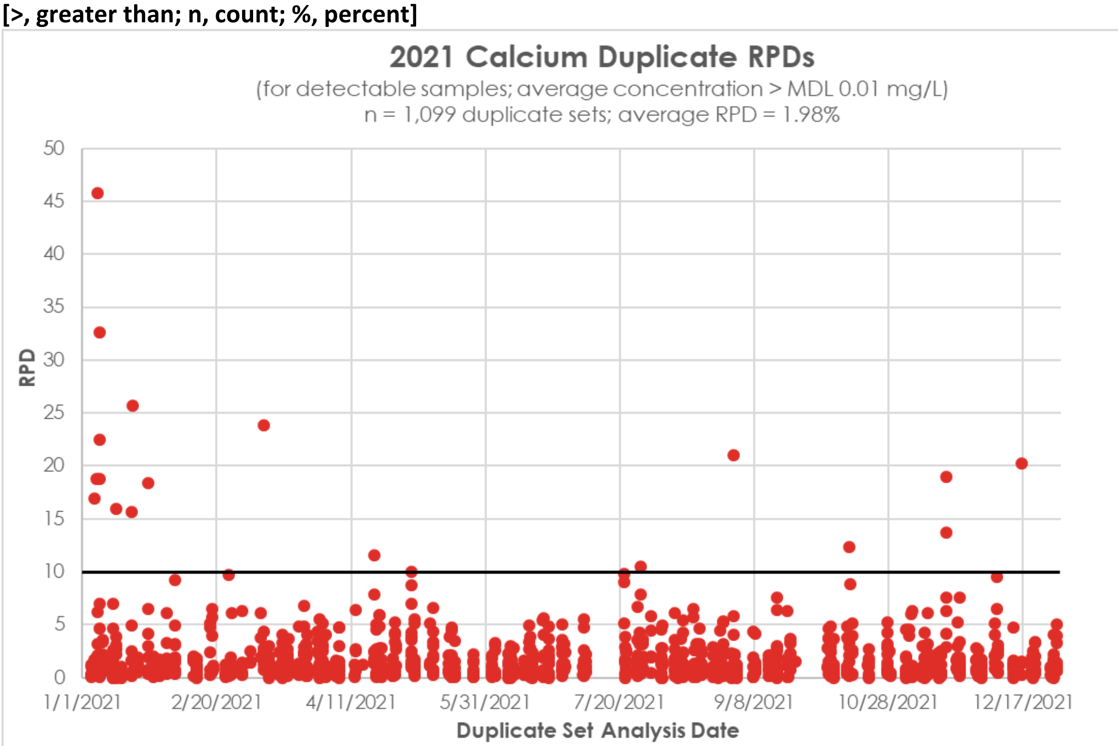

Figure 20. Calcium (ICP) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

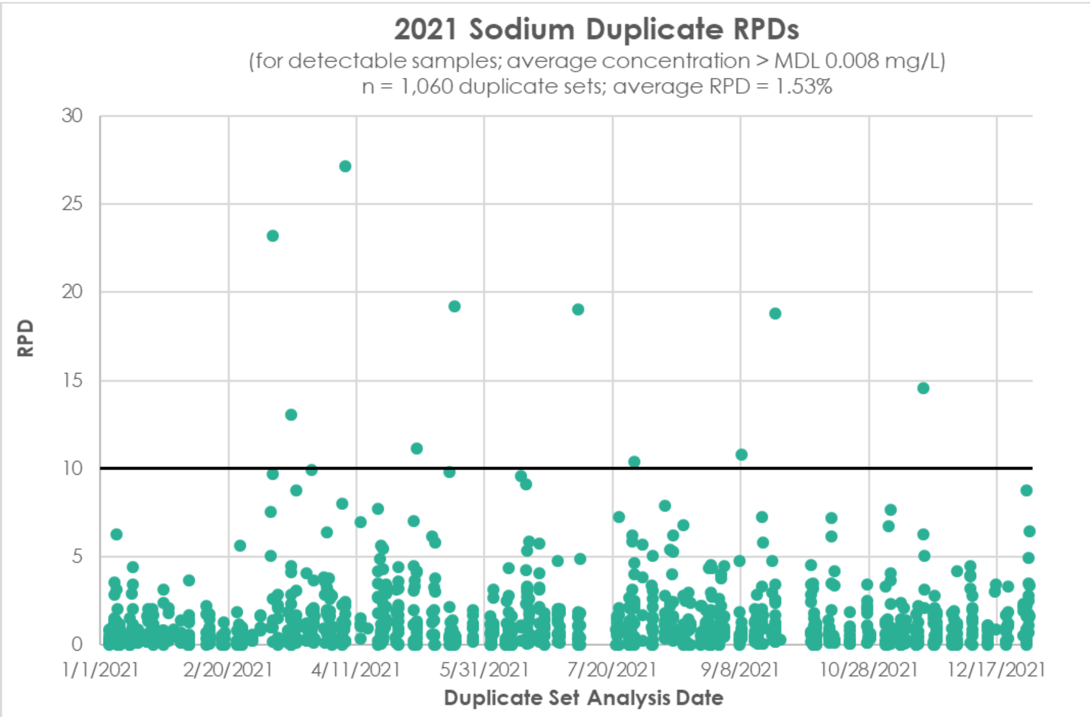

Figure 21. Sodium (ICP) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

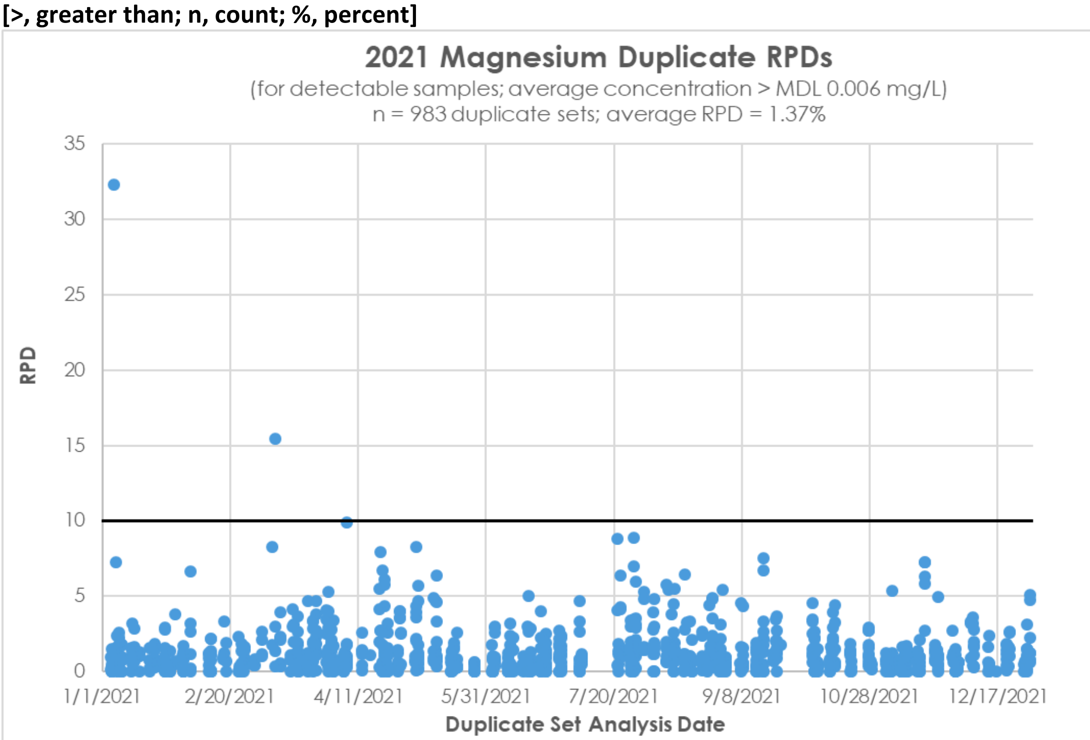

Figure 22. Magnesium (ICP) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

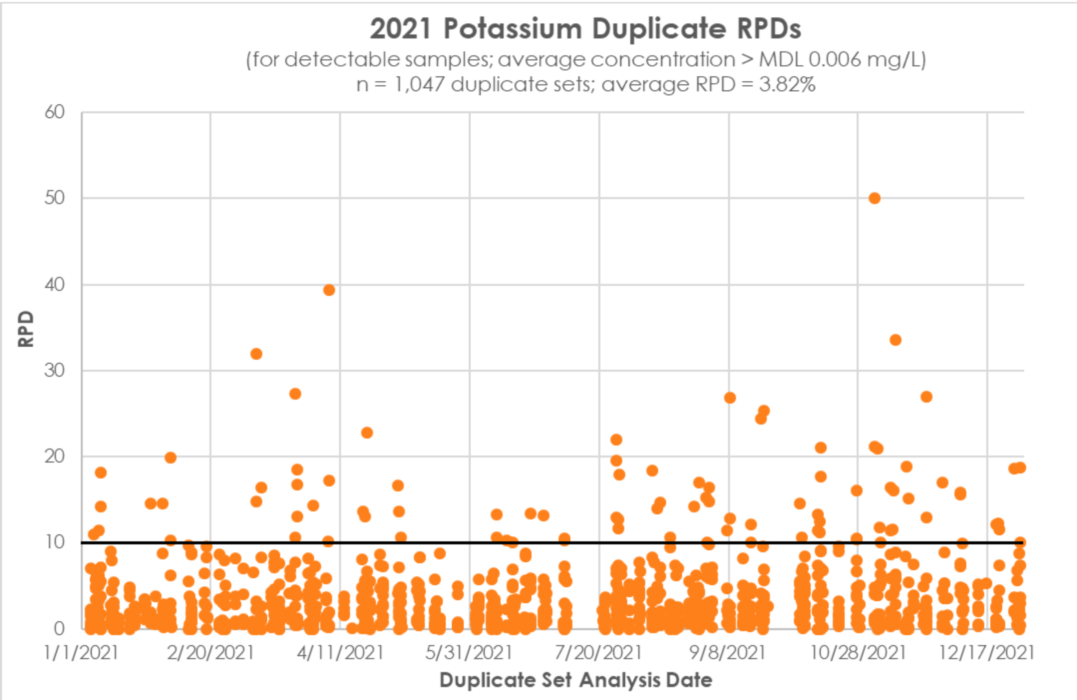

Figure 23. Potassium (ICP) sample and analytical duplicate relative percent differences (RPD) for sets with concentrations at or above the National Trends Network Method Dectection Limit.
[>, greater than; n, count; %, percent]

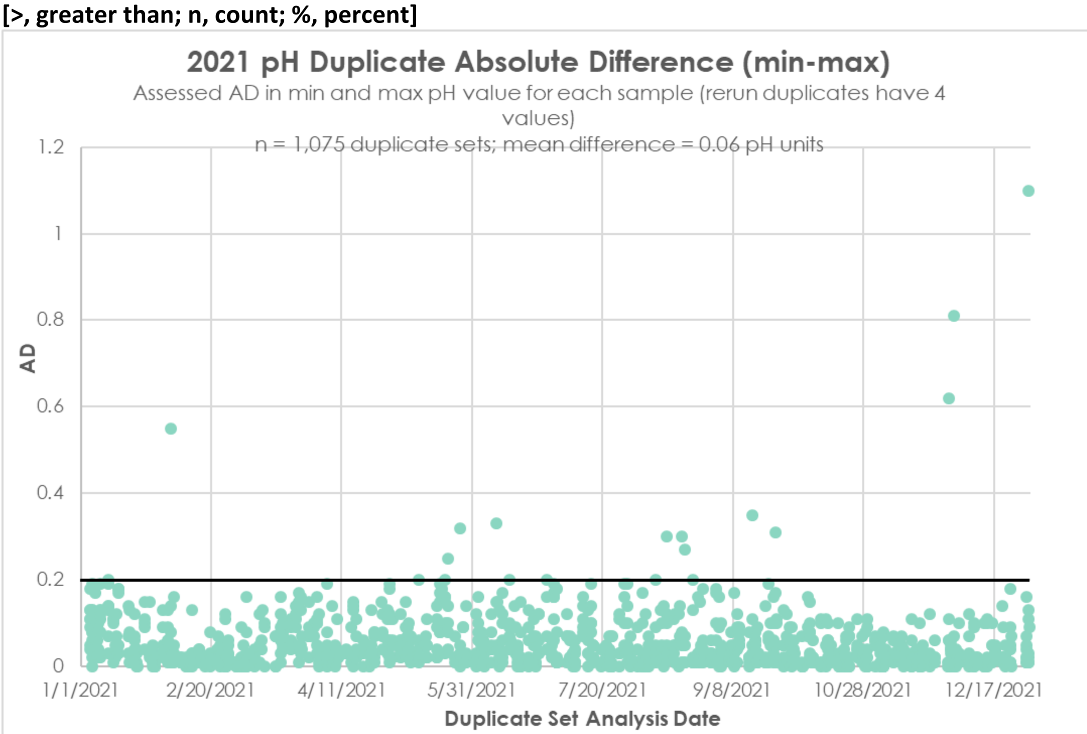

Figure 24. Absolute differences between minimum and maximum pH values from duplicate analyses.

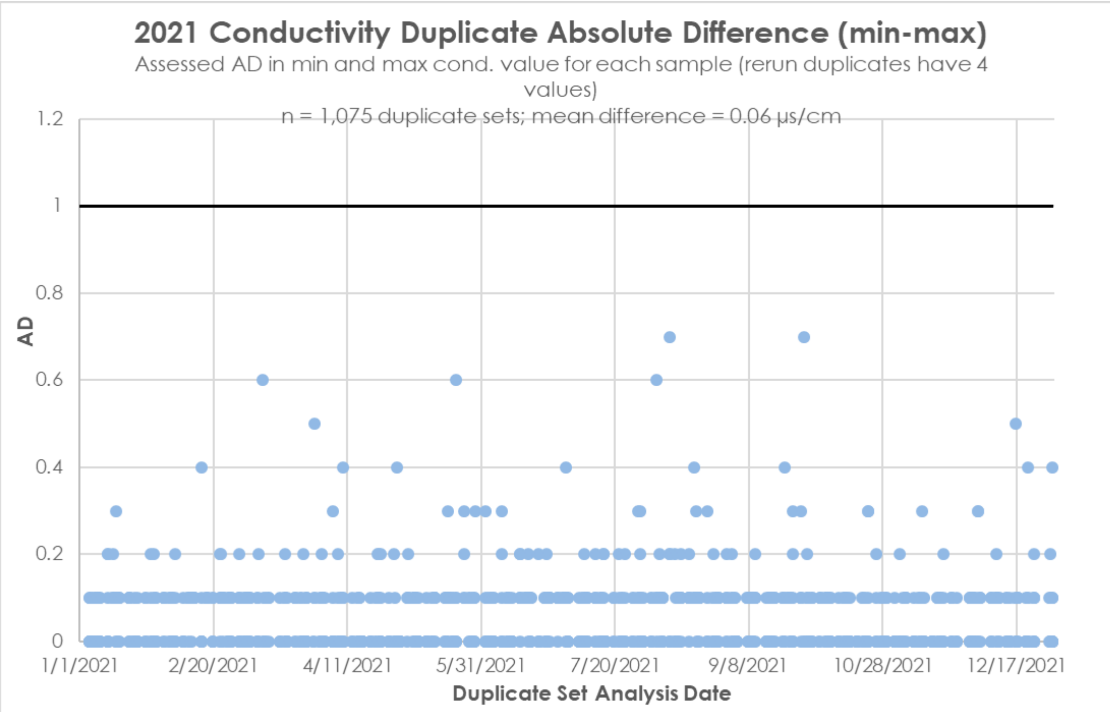

Figure 25. Absolute differences between minimum and maximum conductivity duplicate values.

14.2. Analytical Sample Matrix Spikes and Duplicates for Mercury Analytical Laboratory

A second and third aliquot from a randomly chosen MDN sample (>400 mL sample volume) are analyzed with a spike level of 15 ng/L and the precision between the two results is evaluated. A matrix spike (MS) and matrix spike duplicate (MSD) pair are prepared for every group of 10 or fewer samples. Therefore, approximately 10% of samples are spiked. Matrix spikes must recover between 75%-125% and the two spike results must have an RPD <24% (per EPA Method 1631). Refer to **Table 27** for all HAL QA/QC samples and associated criteria.

For Litterfall, a duplicate and matrix spike are analyzed every 10 samples or fewer. Samples are chosen at random. Duplicates must have an RPD <20%. Litterfall samples are analyzed with a spike of 5 ng. The spike recovery must be within 80-120%. For each analysis date, one sample must be randomly selected for triplicate analysis at three different masses (20 mg, 30 mg, and 40 mg). The percent RSD (of the ng/g data) must be within 10%. Daily calibration is not required; a check standard must be recovered 80-120% and a blank must measure below the MDL. Please refer to **Table 28** for all Litterfall QA/QC samples and associated criteria.

14.2.1. 2021 MS/MSD Results

In 2021, there were no MS recovery failures and no MS/MSD failures associated with reported samples for MDN or Litterfall. Infrequent failures may occur due to instrument instability, matrix interference, or analyst errors. In such a case, all samples in the control group are promptly reanalyzed and documented.

The mean recovery for accepted matrix spikes was 101.12% for MDN; the mean RPD was 1.72%. All matrix spikes met criteria for Litterfall in 2020.

14.3. Digested Lab Reagent Blanks (DLRB)

Every batch of MDN samples that are prepared together are accompanied by three digested lab reagent blanks. The blanks are prepared with acidified Type I reagent water, weighed into bottles, oxidized with the same BrCl lot used in the samples, and analyzed alongside the samples to ensure that no contamination is introduced by the preparation procedure. DLRBs must be less than the method detection limit for the run to be considered within control limits. Annually, DLRBs are assessed (as well as low-concentration spikes) in the ongoing verification of the method detection limit.

14.3.1. DLRB Results

In 2021, results for 241 DLRBs were reported. No LRBs measured above the method detection limit (MDL) of 0.2 ng/L in 2021. The average of all LRB results was 0.007 ng/L.

14.4. Digested Quality Control Standards (DQCS)

Every batch of MDN samples that are prepared together are accompanied by a spiked control sample (8 ng/L), using a standard different from the calibration standard. The DQCS sample is prepared with acidified Type I reagent water, weighed in bottles, oxidized with the same BrCl lot used in sample processing, and analyzed alongside the samples to confirm the calibration to ensure that the sample preparation and analytical procedures produce reliable results. The DQCS recoveries between 80%-120% result in a run within control limits.

Each Litterfall batch is analyzed with a certified reference material as the control standard, NIST 1515 SRM (Apple Leaves). The recovery must be within 80-120% of the certified value to be considered acceptable (TV = 43.2 ng/g).

14.4.1. DQCS Results

In 2021, 85 DQCS samples were reported for MDN. None of the samples exceeded the control limits, and the average recovery was 98.3%. All NIST 1515 samples for Litterfall met criteria in 2020.

14.5. 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.). Criteria are further detailed in the CAL/HAL QAP.

Table 26. Analytical Limits for Internal QC Solutions for National Trends Network (NTN) and Ammonia Monitoring Network (AMoN).

[Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; Cl, chloride; SO_4, sulfate, NO_3-N, nitrate as nitrogen; NH_3-N, ammonia as nitrogen; OPO_4, orthophosphate; %, percent; LDR, linear dynamic range; ~, approximately; mg/L, milligrams per liter]

NADP Combined NTN/AMoN Control Limits ~ Target Values (Acceptable Range)					
Version 30	12/27/2021	Round to 3 decimal places per rounding rules below			
ID	Criteria	Ca	Na	K	Mg
FBFB2101	±MDL	0.000 (-0.010 to 0.010)	0.000 (-0.008 to 0.008)	0.000 (-0.006 to 0.006)	0.000 (-0.006 to 0.006)
FR50210#	±MDL	0.130 (0.120 to 0.140)	0.060 (0.049 to 0.065)	0.022 (0.016 to 0.028)	0.023 (0.017 to 0.029)
FLFL2101	80-120%	0.050 (0.040 to 0.060)	0.050 (0.040 to 0.060)	0.050 (0.040 to 0.060)	0.050 (0.040 to 0.060)
FMFM2101	90-110%	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)
ID	Criteria	NH_4 (NTN ONLY)	OPO_4		
FBFB2101	±MDL	0.000 (-0.014 to 0.014)	0.000 (-0.010 to 0.010)		
FR50210#	90-110%	0.250 (0.225 to 0.275)	NA		
FLFL2101	80-120%	0.050 (0.040 to 0.060)	0.030 (0.024 to 0.036)		
FMFM2101	90-110%	0.600 (0.540 to 0.660)	0.200 (0.180 to 0.220)		
ID	Criteria	Cl	SO_4	NO_3	
FBFB2101	±MDL	0.000 (-0.020 to 0.020)	0.000 (-0.020 to 0.020)	0.000 (-0.020 to 0.020)	
FR50210#	90-110%	0.100 (0.090 to 0.110)	0.960 (0.864 to 1.056)	0.900 (0.810 to 0.990)	
FLFL2101	80-120%	0.025 (0.020 to 0.030)	0.025 (0.020 to 0.030)	0.025 (0.020 to 0.030)	
FMFM2101	90-110%	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)	
ID	Criteria	NH_4 (AMoN ONLY)			
FBFB2101	±MDL	0.000 (-0.010 to 0.010)			
FR50210#	90-110%	0.250 (0.225 to 0.275)			
FLFL2101 (low FL)	80-120%	0.050 (0.040 to 0.060)			
FMAM2101	90-110%	0.750 (0.675 to 0.825)			
QC ID	Description			LDR/Carryover	
FBFB2101	Calibration Blank - Type 1 Water.			AMoN LDR= **10** mg/L; No Carryover up to **9** mg/L	
FR50210#	Faux Rain Solution - ~50% NTN Concentration.			NTN Lachat PO4 LDR=N/A (2nd order); No Carryover up to **2.829** mg/L (2nd order) NTN Lachat NH4 LDR= **10** mg/L and no carryover up to **10** mg/L (linear curve)	
FLFL2101	Quality control sample at low level - second source.			ICP LDR= Mg=**10** mg/L, K,Ca, Na = **20** mg/L ; No carryover up to **15** mg/L	
FMFM2101	Quality control sample at mid level - same source as curve.			IC LDR= **12** mg/L (quadratic), **15** mg/L (Linear). No carryover to **12** mg/L (quadratic)	
FMAM2101	Quality control sample at mid level - for AMoN (NH_4 only no PO_4) -			Round to 3 decimal places using even/odd rounding rules	
				FMDL Criteria is +/- 30% FCRM is +/- 15% but neither are used for run acceptanc	
Rounding: Last digit < 5 round down; > 5 round up; IF = 5 use EVEN down/ODD Up rounding i.e. 0.255 = 0.26 and 0.245 = 0.24					

Table 27. Mercury Deposition Network Analytical Limits and Batch Run Sample Sequence

[<, less than; ng/L, nanograms per liter; %, percent; RSD, relative standard deviation; MDL, method detection limit; Std., standard; DLRB, digested lab reagent blank; RPD, relative percent difference]

Sequence #	Sample/Control Type	Criteria
1	Calibration Blank 1	<0.5 ng/L
2	Calibration Blank 2	<0.5 ng/L
3	Calibration Blank 3	<0.5 ng/L
4	Std 0.5 ng/L	Recovery 85%-115%; Calibration Factor RSD<15%
5	Std 1.0 ng/L	Calibration Factor RSD<15%
6	Std 5.0 ng/L	Calibration Factor RSD<15%
7	Std 25.0 ng/L	Calibration Factor RSD<15%
8	Std 100.0 ng/L	Calibration Factor RSD<15%
9	Continuing Calibration Blank	<MDL
10	Ongoing Precision and Recovery Check (5 ng/L)	Recovery 80%-120%
11	DLRB 1	<MDL
12	DLRB 2	<MDL
13	DLRB 3	<MDL
14	DQCS (8.0 ng/L)	Recovery 80%-120%
15	MDL Verification Sample (0.5 ng/L)	Recovery 80%-120%; Criterion not assessed for run control, used only for ongoing MDL study
16	Sample 1	<highest standard
17	Sample 2	<highest standard
18	Sample 3	<highest standard
19	Sample 4	<highest standard
20	Sample 5	<highest standard
21	Sample 6	<highest standard
22	Sample 7	<highest standard
23	Sample 8	<highest standard
24	Sample 9	<highest standard
25	Sample 10	<highest standard
26	Sample 10 Matrix Spike (15 ng/L)	Recovery 75%-125%; RPD<24%
27	Sample 10 Matrix Spike Duplicate (15 ng/L)	Recovery 75%-125%; RPD<24%
28	Ongoing Precision and Recovery Check (5 ng/L)	Recovery 80%-120%
29	Continuing Calibration Blank	<MDL

Table 28. Mercury in Litterfall Analytical Limits and Batch Run Sample Sequence

[<, less than; RSD, relative standard deviation; MDL, method detection limit; Std., standard, ng, nanograms; %, percent; NIST, National Istitute of Standards and Technology; RPD, relative percent difference]

Sequence #	Sample/Control Type	Criteria
1	Calibration Blank 1	<MDL
2	Calibration Blank 2	<MDL
3	Calibration Blank 3	<MDL
4	Std. 0.100 ng	Recovery 75%-125% r≥0.998
5	Std. 0.250 ng	Recovery 75%-125% r≥0.998
6	Std. 0.500 ng	Recovery 75%-125% r≥0.998
7	Std. 1.000 ng	Recovery 75%-125% r≥0.998
8	Std. 5.000 ng	Recovery 75%-125% r≥0.998
9	Std. 8.000 ng	Recovery 75%-125% r≥0.998
10	Std. 10.00 ng	Recovery 75%-125% r≥0.998
11	Check Standard (1 ng)	Recovery 80%-120%
12	Continuing Calibration Blank	<MDL
13	NIST 1515 (TV = 43.2 ng/g)	Recovery 80%-120%
14	Sample 1	<highest standard
15	Sample 2	<highest standard
16	Sample 3	<highest standard
17	Sample 4	<highest standard
18	Sample 5 – 20 mg (one set/batch)	<highest standard; %RSD<10%
19	Sample 5 – 30 mg (one set/batch)	
20	Sample 5 – 40 mg (one set/batch)	
21	Sample 6	<highest standard
22	Sample 7	<highest standard
23	Sample 8	<highest standard
24	Sample 8 Duplicate	RPD<20%
25	Sample 8 Matrix Spike (5 ng)	Recovery 80%-120%
26	Check Standard (1 ng)	Recovery 80%-120%
27	Continuing Calibration Blank	<MDL

14.6. Analytical Accuracy

As seen in **Table 26**, many QC standards are analyzed with each batch of AMoN and NTN samples. All of these QC standards can be viewed in the Benchem LIMS to assess issues with accuracy and potential bias. When bias is suspected, all the standards and QC samples (i.e. PTs) will be assessed for similar patterns. In order to demonstrate examples of accuracy assessment, most of the following graphs **Figures 26 – 39** are for the faux rain water mix (FMDL) that is prepared in the lab from Type I water and clean spikes at concentrations of approximately 2-10 times the MDL level. This solution is made multiple times within a year and each is given a unique numerical ID. One graph is associated with each ID, which produces the shortened time frame on the x-axis. In some cases, low or mid-level standards are also displayed as indicated in the titles. The y-axes are in units of concentration for each graph (mg/L).

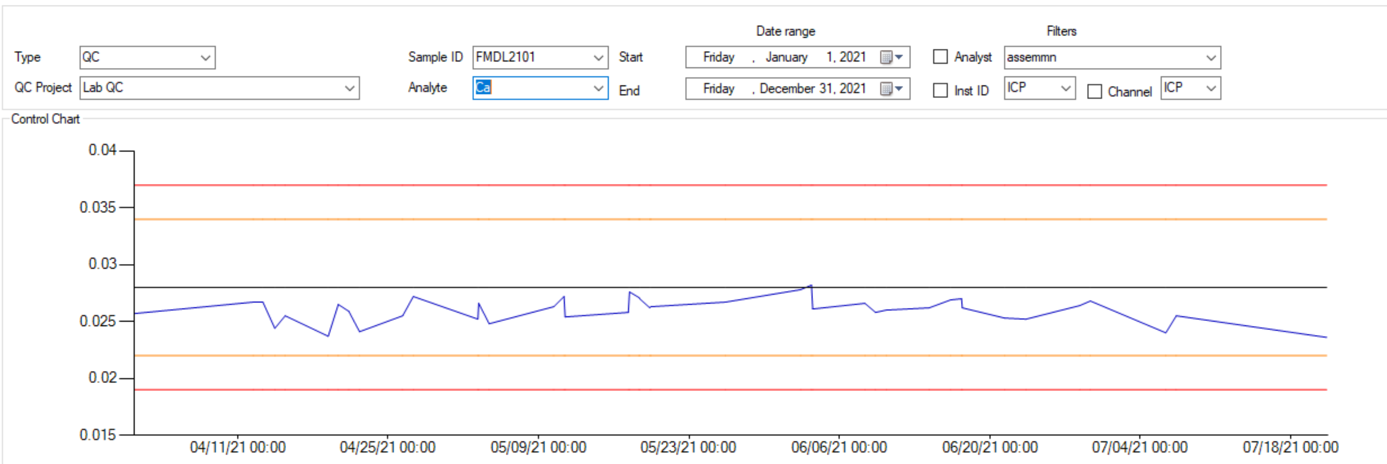

Figure 26. Calcium FMDL2101 solution recoveries.

Figure 27. Potassium FMDL2101 solution recoveries.

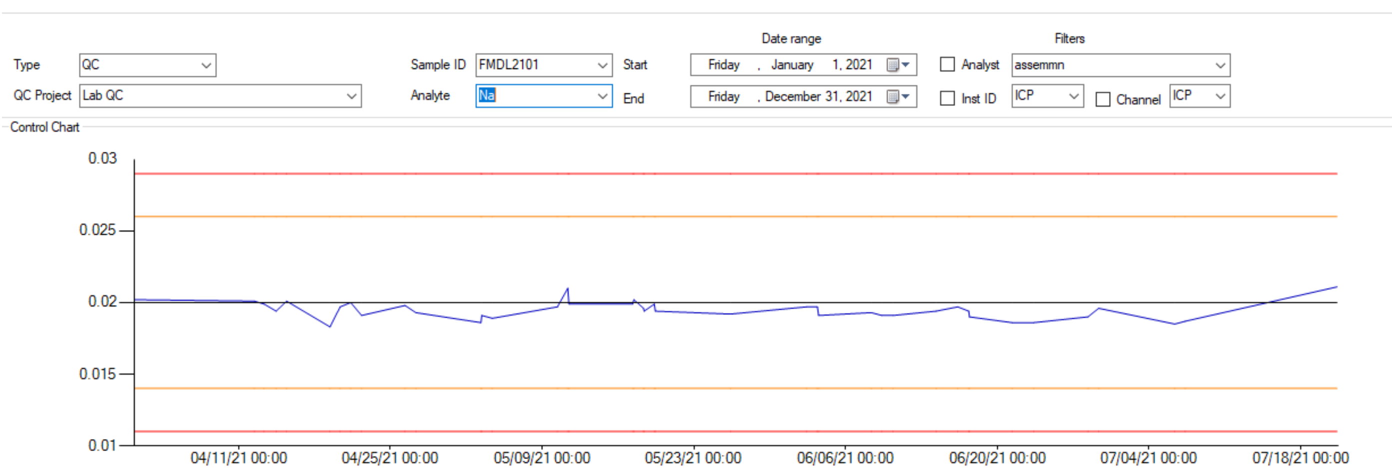

Figure 28. Sodium FMDL2101 solution recoveries.

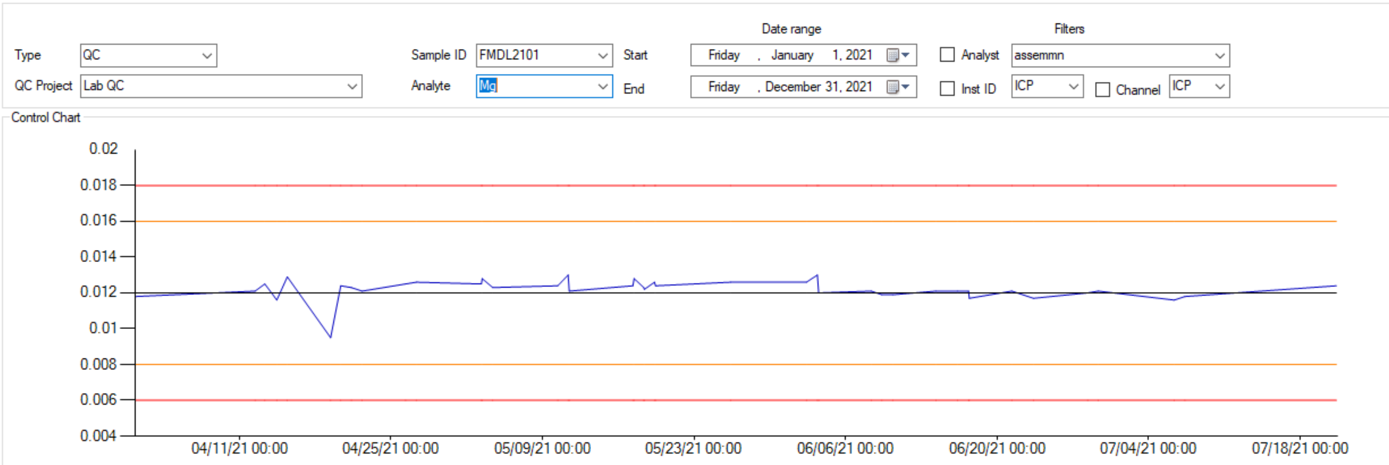

Figure 29. Magnesium FMDL2101 solution recoveries.

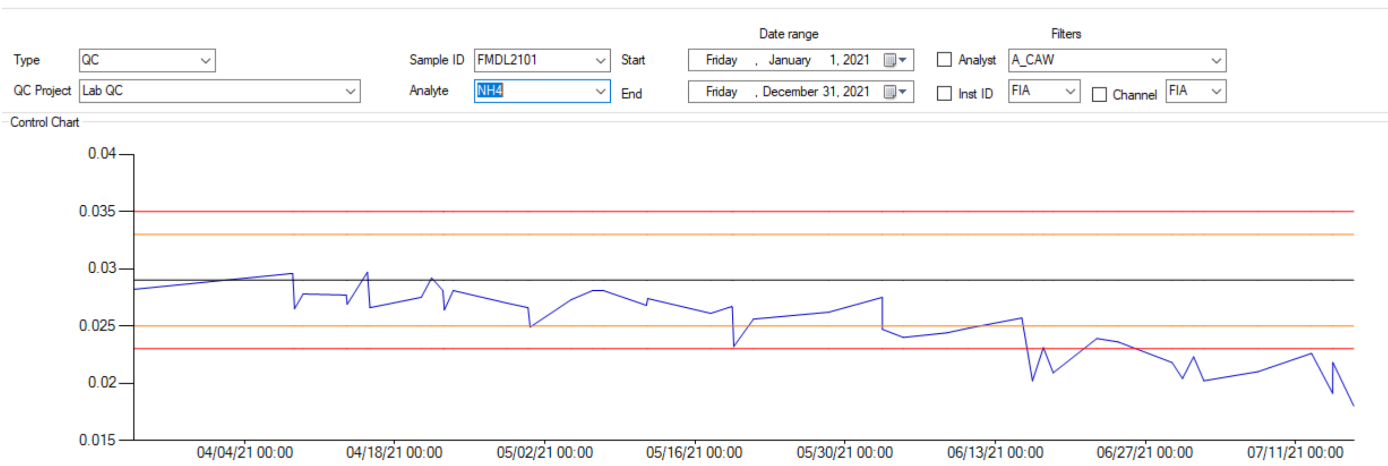

Figure 30. Ammonium AMoN and NTN FIA FMDL2101 solution recoveries. NOTE: recoveries tend to trend down for NH4 when the solution volume gets low.

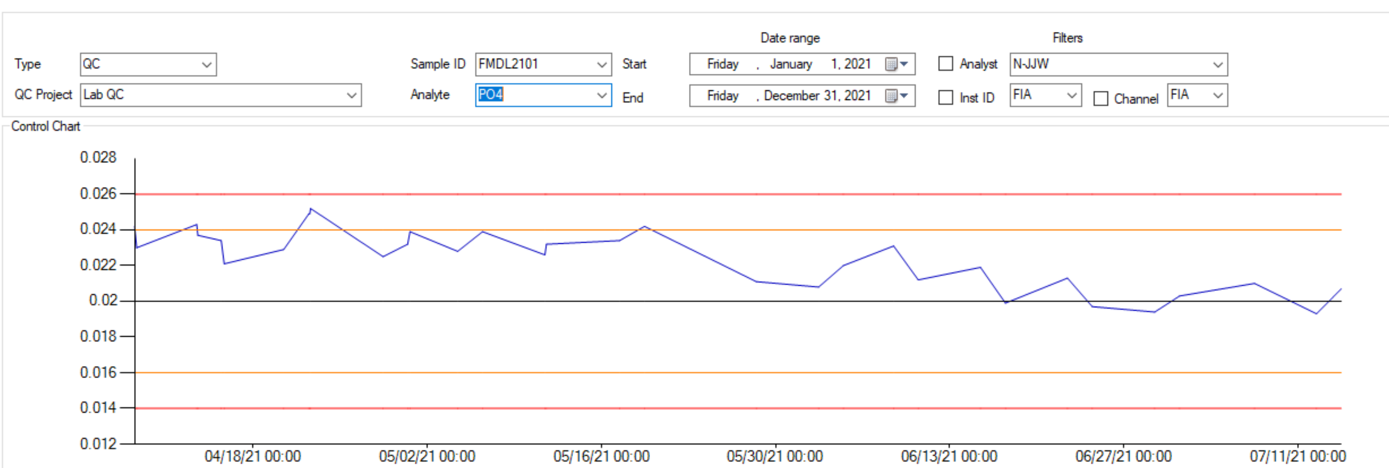

Figure 31. Ortho phosphate FMDL2101 solution recoveries.

Figure 32. Chloride FMDL2101 solution recoveries.

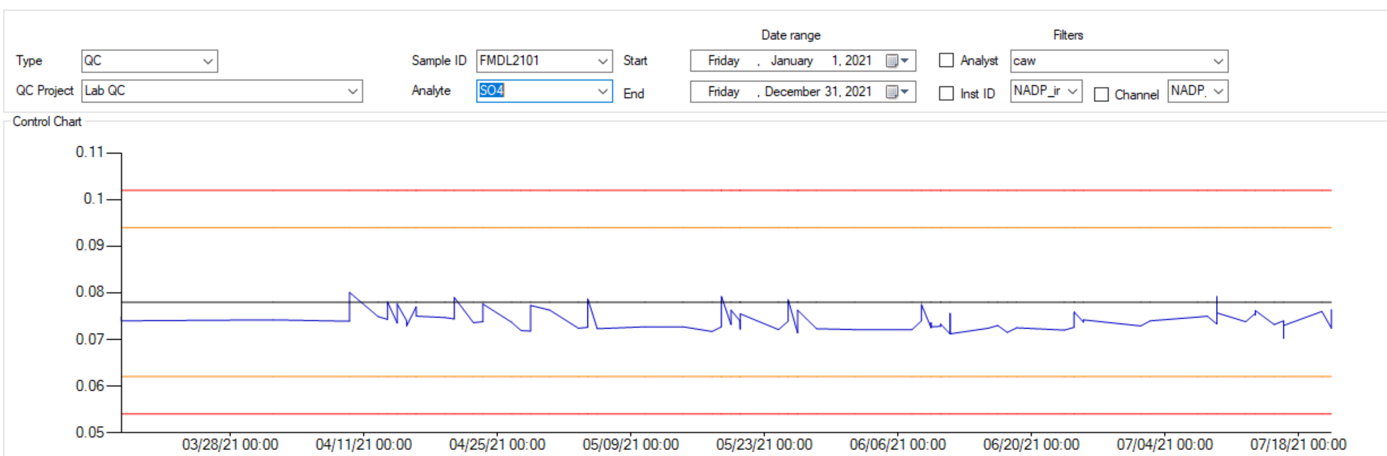

Figure 33. Sulfate FMDL2101 solution recoveries.

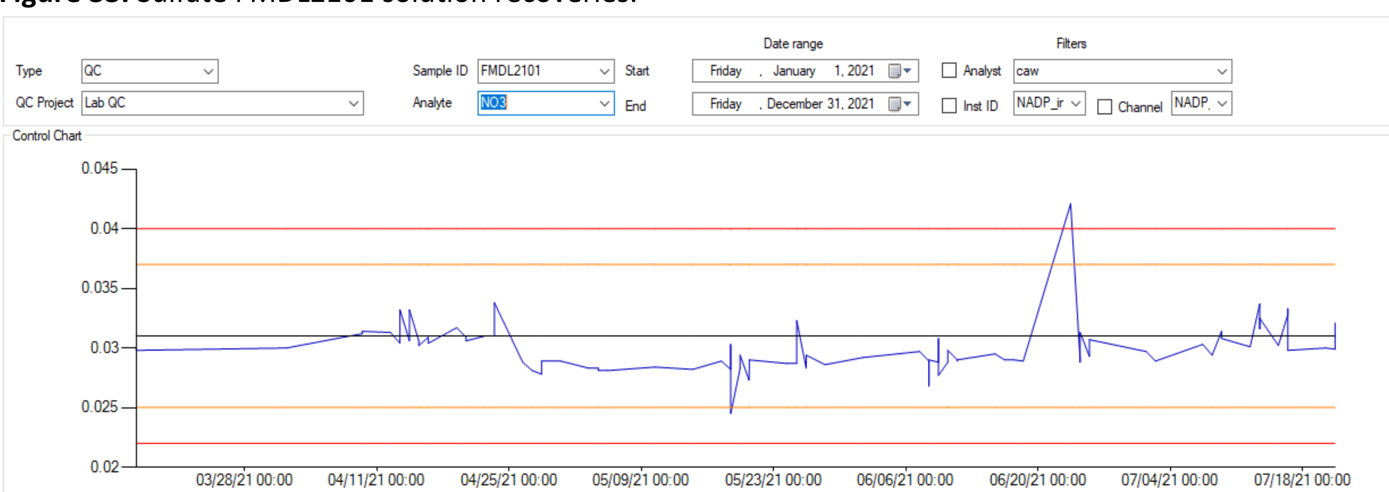

Figure 34. Nitrate FMDL2101 solution recoveries.

Figure 35. pH low-level (FL) standard recoveries. The outlier was due to issues during calibration of the probe which were resolved within that run day. There is a slight high bias until 8/30/2021 when a new stock of the reagent was received.

Figure 36. The time frame of the graph was shortened to provide a closer look at the data after the new stock was received.

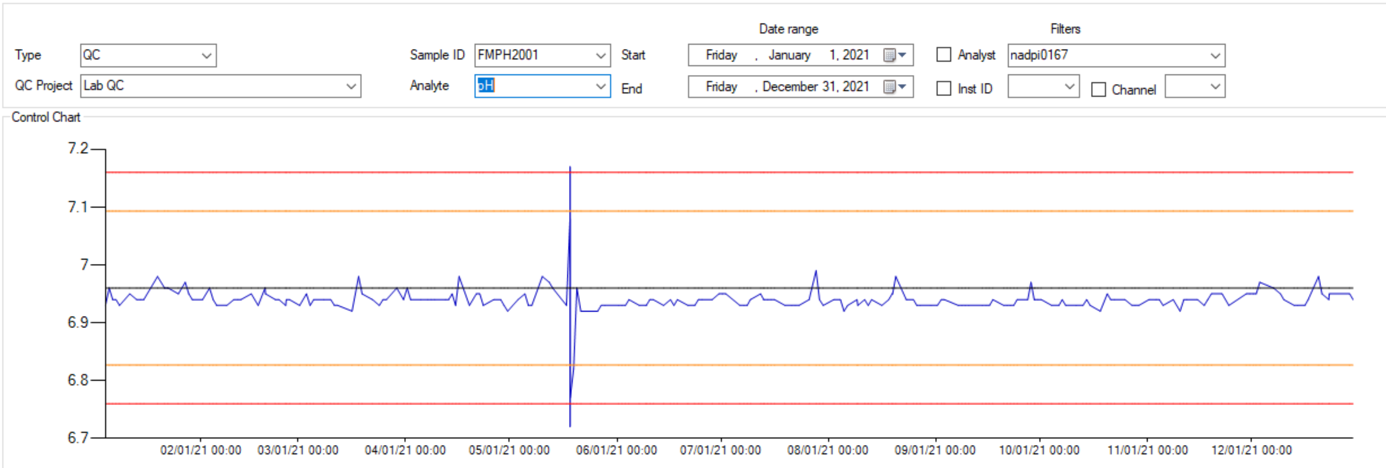

Figure 37. pH mid-level (FM) standard recoveries.

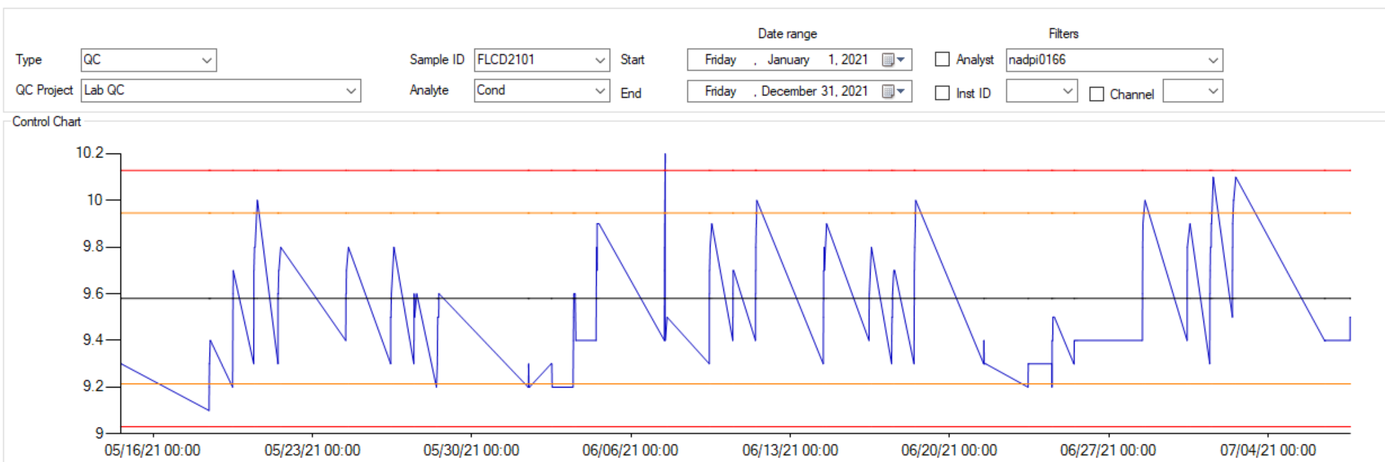

Figure 38. Conductivity low level (FL) standard recoveries. This standard's true value changes slightly between lots. A new numerical ID is given when the true value changes to keep the graphs accurate. One graph is associated with each ID, so this is the cause for the shortened time frame on the x-axis.

Figure 39. Conductivity mid-level (FM) standard recoveries.

15. Supply QC

15.1. Overview of Supply QC

Each network within the NADP long-term monitoring program requires very specific sampling and processing supplies, which are all cleaned and prepared using established specialized protocols to maintain data consistency throughout the networks. The NADP must supply materials of identical quality to those being replaced at the sites. The laboratory cleans and provides supplies for NTN, MDN, and AMoN. In order to verify that supplies are adequately clean, supply blanks are measured as outlined in **Table 29** and **Table 32**.

15.2. New Supply Assessment

New lots of bottles, test tubes, filters, and bucket 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.

15.3. 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 and end of each filter day and weekly syringe filter blanks.

15.4. New Bottle, Bag, and Test Tube Testing

<u>New</u> bottles, sampling bags, and test tubes are <u>lot tested</u> prior to use per the protocols in **Table 29.**

Table 29. New Lot Supply QC Sampling Protocols for National Trends Network (NTN) and Mercury Deposition Network (MDN).

[mL, milliliters; MQ, ultrapure (Type 1) deionized water; <, less than; mm, millimeters; HPDE, high density polyethylene; PETG; polyethylene terephthalate glycol]

NADP Supply Lot Approval QC Frequency and Log In (Revision 09/01/2021)						
Item	**Solution**	**Amount & Frequency**	**Project LOG IN**	**Client Number***	**LIMS Description**	**Rinse Collection Bottle?****
BAG LOTS						
NTN Sample Bags	~150 mL MQ	20/new lot (unless <500 then 10)	**New Sampling Bag Lot Check**	Date Prepared & Preparer Initials	Bag Type, Lot #, Bag# (i.e. NTN Sample Bag Lot X 1of20)	Y
NTN Bucket or Lid Bags	~150 mL MQ	5/new lot	**Bag Blank Study**	Date Prepared & Preparer Initials	Bag Type, Lot #, Bag# (i.e. NTN Bucket Bag Lot X 1of5)	Y
BOTTLE LOTS						
NTN 60mL HDPE Bottles	~60mL MQ	10/new lot (unless <100 then 5)	**NADP New Bottle Blanks**	Date Prepared & Preparer Initials	Bottle Type, Lot #, Bottle# (i.e. 60mL NTN LotX 1of10)	N
NTN 1 Liter HDPE (New)	~150 mL MQ	10/new lot (unless <100 then 5)	**NADP New Bottle Blanks**	Date Prepared & Preparer Initials	Bottle Type, Lot #, Bottle# (i.e. 1L NTN LotX 1of10)	N
MDN 125 mL, 250 mL, 1L or 2L PETG	20 mL 1% HCl + 100mL MQ	10/new lot (unless <200 then 2%)	**MDN Bottle Blanks**	Date Prepared & Preparer Initials	Bottle Type, Lot #, BottleID, Bottle# (i.e. 250mL MDN LotX; 1of10)	N
FILTER LOTS						
NTN 47mm Disc Filters	60 mL MQ	20/New Lot min 2 boxes from lot	**Filter Blank Lot Testing**	Date Prepared & Preparer Initials	Lot, Box#, Filter #, Brand, filter type	Y
NTN Syringe Filters	20 mL MQ	5 per lot of 150	**Filter Blank Lot Testing**	Date Prepared & Preparer Initials	Lot, Box#, Filter #, Brand, filter type	Y
TUBE LOTS						
NTN Test Tubes	2-10 mL MQ	10/New Lot ICP/FIA	**Test Tube QC Blank**	Date Prepared & Preparer Initials	Brand, Test tube type, lot # & tube # (i.e. Fisher, ICP, Lot 3434, 2 of 10)	Y
OTHER LOTS						
MDN Acid Preservative	30 mL (15 mL analyzed)	1/Batch of Acid Preservative	**Acid Checks**	Date Prepared & Preparer Initials	"Acid Preservative Blank", Acid Lot # and Batch ID	Y
Must Meet LOT Approval Before Use of these Supplies						
* Date Prepared should be the date the sample is collected into the final bottle for analysis.						
**Collection bottle should be rinsed with either the sample being collected or Type I						

15.5. Lot Testing Criteria

The NADP lot testing criteria states that the mean of at least 10 samples per lot must be < MDL_N and none of the supply blanks in the batch tested may exceed 3 times the MDL_N for any analyte the supply is used for (for HAL supplies we only assess total mercury for example). 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 the 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 protocols are listed in **Table 30**, and results for the numbers of samples in 2021 are shown in **Table 31**.

Table 30. National Trends Network Lot Approval QC Samples and Failures, 2021.

Item tested	# of 2021 QC Samples	Number Individual Samples Failed	Lots Tested	Lots Rejected	Lots Approved
Bottles	100	7	14	0	14
Large NTN Disk Filters	46	0	3	0	3
Syringe Filter	41	0	1	0	1
Syringes Only	37	4	2	0	2
Test Tubes - ICP and FIA	154	0	16	0	16
Total	378	11	36	0	36

Table 31. Mercury Deposition Network Lot Approval QC Samples and Failures, 2021.

Bottle Size Tested	# of 2021 QC Samples	# of Individual Exceedances	Lots Tested	Lots Rejected	Lots Approved
PETG 1L	28	1	3	0	3
PET 1L	6	0	1	0	1
PETG 2L	3	3*	1	0	1
PETG 250 mL	3	0	1	0	1
PETG 60 mL	3	0	1	0	1
Total	44	4	7	0	7

*Due to a supply shortage, the 2L PETG bottles were accepted for use. The values were slightly over the MDL_N.

15.6. New Acid Preservative Testing

Acid preservative is prepared by MDN sample receiving staff. Acid preservative is 1% v/v HCl (~1.2M, Trace Metal Grade), prepared in 2.5L batches. All MDN 1L bottles are pre-charged with 20 mL of acid preservative and all 2L bottles are pre-charged with 40 mL of preservative before being shipped to sites for field use (**Table 32**). Acid preservative must have total Hg concentrations <0.4 ng/L in order to be approved for official use. All acid preservative batches prepared in 2021 met criteria.

15.7. Litterfall Collector QC

The collector materials that are used for capturing, storing, and transporting Litterfall samples were extracted in a solution of bromine monochloride and analyzed to ensure that the materials do not contaminate samples. Included in this test were sample bags, collector bags, and collector netting. All materials were below the detection limit.

15.8. Litterfall Process Blanks

Litterfall process blanks were prepared at a rate of one blank per five sites for the 2020-2021 Litterfall season samples. Process blanks consisted of running ~50 mg of dry milk powder through the grinder used for all Litterfall samples. All process blanks measured below the MDL in 2021.

15.9. Ongoing Supply Assessment

Data from the ongoing supply QC program (**Table 32**) is assessed, at a minimum, on a quarterly basis. Trends in potential contamination or supply issues are investigated and corrective action taken, as needed. Analysts are 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) supplies are assessed for blank values above the supply criteria which are set to the MDL_N. Results for 2021 ongoing supply QC testing are shown in **Table 33** and **Figure 40**. Overall, these data demonstrate that cleaning and supply/lot protocols are clearly in control, with few exceedances. There were no ongoing supply QC exceedances for MDN.

Table 32. Ongoing Supply QC Types and Frequencies for National Trends Network (NTN) and Mercury Deposition Network (MND).

[MQ, ultrapure deionized water; Hg, mercury; mL, milliliters; mm, millimeters]

NADP Ongoing Supply QC Frequency/Log In (Revision 09/01/2021)

Item	Project Log In	Amount/Frequency	Solution	Rinse Collection Bottle?**	Client Number*	LIMS Description
TYPE I WATER						
MDN Type 1 Water	MQ Water System Blanks	1/purifier/week	100 mL MQ	Y	Date Prepared & Initials	"Hg Type 1 Water Blank", BLDG, Lab # (i.e. Type 1 Blank, AG 200, HM135)
NTN Type 1 H_2O Blanks	MQ Water System Blanks	1/purifier/week	60 mL MQ	Y	Date Prepared & Initials	"Type 1 Water Blank", BLDG, Lab # (i.e. Type 1 Blank, AG 200B, HM135)
NTN SUPPLIES						
NTN 47mm Disc Filters	Filter Blanks DI	2/ Filter Day	60 mL MQ	Y	Date Prepared & Initials	"Start/End Filter" & Sample Range
NTN Syringe Filters	Weekly Syringe Filter Blank	1 per week	20 mL MQ	Y	Date Prepared & Initials	"Syringe Filter Blank", Syringe and Filter Lot#
NTN Sample Bags	Bag Blank Study	1/week	~150 mL MQ	Y	Date Prepared & Initials	Bag Type, Lot#
NTN 1 Liter HDPE	Bottle Blanks	1/wash day	~150 mL MQ	Y	Date Prepared & Initials	"1L NTN Washed"
NTN Buckets	Bucket Blanks	1/wash day	~150 mL MQ	Y	Date Prepared & Initials	"New" or "Used" "Bucket"
NTN LIDS	Lid Blanks	1/wash day /per type	~100 mL MQ	Y	Date Prepared & Initials	Lid Type
MDN SUPPLIES						
MDN Sample Train	Sample Train Blanks	1/week in bag ≥2 days	~ 100 mL MQ	N	Date Prepared & Initials	"Sample Train Preparation Week"
MDN Acid Bath	Acid Checks	1/Acid Bath/month	10 mL	N	Date Prepared & Initials	"Acid Bath Blank", BathID
USGS System Blanks (NOT DF/DKs)	USGS System Blanks	2/Quarter	MQ	N	Date Logged & Initials	USGS ID for blanks, Blank 1 of 2
MDN Travel Blanks	MDN Travel Blanks	Up to 4 a month	acid preservation in bottle	N	Date Logged & Initials	Site ID shipped from, approximate time in the field (i.e. 4 weeks)

*Date Prepared should be the date the sample is collected into the final bottle for analysis.

**Collection bottle should be rinsed with either the sample being collected or Type I water if sample volume is too low.

Table 33. National Trends Network Ongoing Supply QC Exceedances, 2021.

Item Tested	Ca	Na	K	Mg	Cl	SO_4	NO3	NH4	PO4
Used Buckets (n=20)	0	0	0	0	0	0	0	0	0
Used Lids (n=207)	16	3	5	0	20	0	0	0	0
New Lids (n=65)	6	1	2	0	6	0	0	1	0
MQ H20 (n=242)	0	0	0	0	1	0	0	0	1
Disc Filters (n=406)	5	15	3	0	1	0	1	0	2
Syringe Filters (n=51)	4	0	1	0	4	0	0	0	0
Used 1L Bottles (n=211)	0	0	1	0	0	0	0	0	0
Bags(n=31)	0	1	1	0	3	0	0	0	0

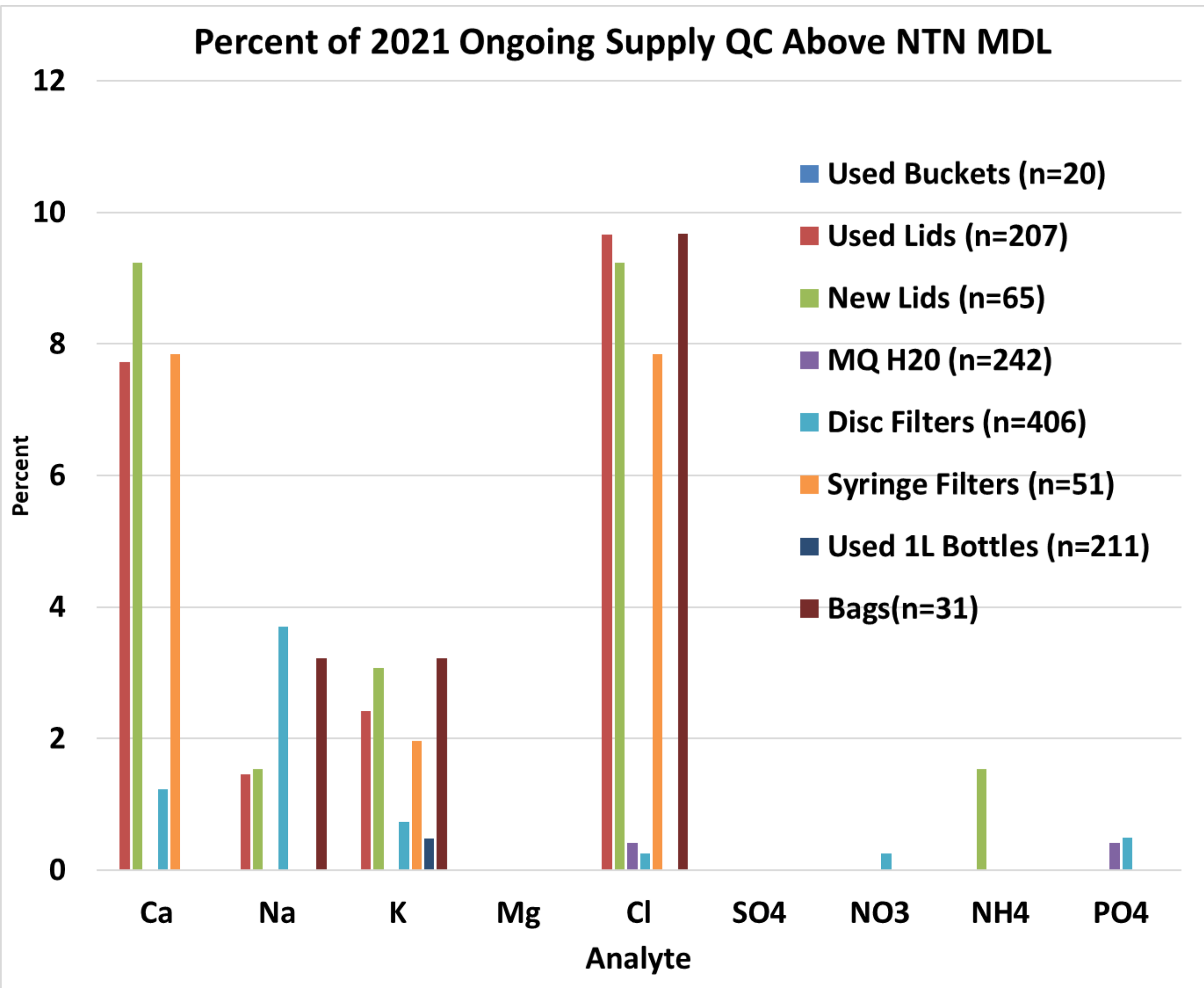

Figure 40. Percent of 2021 Ongoing Supply QC Tests that Exceeded National Trends Network - Network method detection limits (MDL_{NS}).

16. AMoN Supply QC

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

As outlined in **Table 34**, "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 laboratory AMoN processing suite.

Table 34. AMoN Supply Quality Control Protocols, 2021.

[mL, milliliters; MQ, high-purity deionized water; H2O, water;

NADP AMoN Supply QC Frequency and QC Log In to LIMS (Rev 7/27/2021)

Item	Solution	Amount & Frequency	Project LOG IN	Client Number	LIMS Description
Jars					
Glass Jar – NEW	10 mL MQ	1/wash batch	**AMoN QA Samples**	Date Washed and Initials	**"GJ New", Batch letter (A or B or C) and Lot # if available**
Glass Jar – USED	10 mL MQ	1/wash batch	**AMoN QA Samples**	Date Washed and Initials	**"GJ Used", batch letter**
Blanks With Cores					
Core Blanks	10 mL MQ	2 per NEW lot **only for new lots on arrival**	**AMoN QA Samples**	Date Extracted and Initials	**"Core Blank" and Core lot**
Prep Blanks (body+core+jar)	10 mL MQ	1/sampler prep batch per sonicator	**AMoN QA Samples**	Date Extracted and Initials	**"Preparation Blank", Samper batch ID & Core lot**
Water Only Blanks					
Sonicator Blank	10 mL Sonicator H2O	1/sampler prep batch at end of prep	**AMoN QA Samples**	Date Prepped and Initials	**"Sonicator Blank", Sampler batch**
Method Blank (extraction water)	10 mL MQ	1/extraction day	**AMoN QA Samples**	Date Prepped and Initials	**"Method Blank", water source - (from dispenser)**
Hood/Room Blanks					
2 Week Blank Sonicator Hood	10 mL MQ	1/two week period	**AMoN QA Samples**	Date Extracted and Initials	**"AIR Sonic Hood", Deployment Minutes**
2 Week Blank Extraction Hood	10 mL MQ	1/two week period	**AMoN QA Samples**	Date Extracted and Initials	**"AIR Extraction Hood", Deployment minutes**

Each preparation week, a number of AMoN QC samples are also prepared and tested to monitor potential background contamination. The most significant indicator of overall cleanliness are the preparation blanks and none of those exceeded criteria. All details are provided in **Table 35.**

Table 35. Ammonia Monitoring Network Supply QC Summary 2020-2021 and ammonium concentration results in milligrams per liter (mg/L) NH_4.

QC Type	2020 Mean	2021 Mean	2020 # Tested	2021 # Tested	Number of exceedances in 2020	Number of exceedances in 2021	Criteria for 2021
Preparation Blanks	0.006	0.009	69	59	0	0	0.036 mg/L NH4
Core Blanks	0.005	0.004	74	64	2	0	0.036 mg/L NH4
2 Week Hood Blanks	0.070	0.096	50	54	0	0	0.4 mg/L NH4
Room Blanks	0.749	0.792	27	16*	1	0	1.2 mg/L NH4
Hood Extraction Blanks	0.010	0.012	54	30*	0	0	0.2 mg/L NH4
Water Blanks	0.002	0.000	164	131*	5	1	0.010 mg/L NH4
Jar Blanks	0.003	0.005	120	130	6	22**	0.010 mg/L NH4
Total			**558**	**484**	**14**	**23**	
					2020 % Exceedance		**2.50%**
					2021% Exceedance		**4.75%**

*The room blank, hood extraction blank, and type I water blank (part of the water blanks) were stopped in late July due to continued low results.

**Glass jars are QC'd by filling a clean jar with 10 mL of Type I water and placed upside down in the hood overnight and poured off. This process does not really depict the use of the glass jars within the network and other options are being considered.

17. Occurrence Management

The NADP uses a WSLH 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. Details from 2021 can be viewed in the Annual Management Review **Table 6** above. A summary of metrics is provided in **Table 36**.

Table 36. Summary of Occurrences for Central Analytical Laboratory (CAL), 2021

Number of Recorded CAL Occurrences	Category of Issue
2	Recording Protocol Deviation/Change
1	Sample Handling
10	Analytical QC
5	Supply QC
10	Data/Reporting
4	Instrumentation/Equipment
32	**Total**

18. Method Improvement Projects

The NADP Laboratories have continued to test and assess new techniques and supplies that might improve outcomes and efficiencies of the networks. Some of the initiatives pursued in 2021 include:

- Finished the evaluation and roll-out of sample collection bags into the NTN (reduction in costs for shipping, bucket washing)
- Began recycling our gloves and bags with an offsite company
- Moved the ICP from two to one calibration curve (saves chemist's time at the bench/software)
- Ongoing five-year archive preservation study (112 samples preserved frozen and refrigerated) - robust evaluation of the impacts of long-term storage (both refrigeration and freezing) on NTN analytes. Critical information for the precipitation and water quality community, in general, is being collected to determine if reliable archiving is viable?
- Started stirring pH samples during measurement (improve data quality)
- Method development of Litterfall MeHg analysis by distillation and CVAFS
- Method development of Litterfall THg analysis by Thermal Decomposition, Gold Amalgamation and AAS
- Exploration and testing of alternative Litterfall processing procedures (oven drying, subsampling, etc.)
- MDN field spiking experiments to determine if Hg loss is occurring

19. Special Studies

The NADP mission includes efforts to maximize the scientific impact of the network infrastructure and analytical capabilities at the WSLH. It is through these studies that the NADP program will ultimately grow and continue to be relevant. The primary vehicle through which this mission goal is being addressed is via special studies with either external or internal scientists. 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 2021 are shown in **Table 37**. Fees are incurred for special study requests and NADP data needs are always the first priority.

Table 37. NADP Samples Provided to Outside Research Groups (all for National Trends Network) January 2021 through December 2021.

Cooperator and Affiliation	Network	# of Samples Provided	Notes
David Clow (USGS)	NTN	10 filtered water samples	Estimate water residence times in the Loch Vale research watershed.
Ty Coplen (USGS)	NTN	2000 filtered water samples	Measure stable hydrogen and oxygen isotopic abundances to generate a historic time line of these data in the subject area.
Monica Ramirez-Andreotta, Project Harvest (Univ. of Arizona)	NTN	64 unfiltered water samples	Samples will be analyzed to compare results from sample collected from rooftop systems for home agriculture purposes.
Drew Spear/Stephen Monroe (Mesa Verde National Park)	NTN	43 filtered water samples	Develop a conceptual model of GW flow and potential vulnerability of selected springs to effects of climate change or anthropogenic contamination including WW/runoff from developed areas in park.
James Ranville (Colorado School of Mines)	NTN	7 unfiltered water samples	Determine the nature of nanoparticulate and colloidal particles in rainwater and examine urban and wildfire influences.
Carl Bern (USGS)	NTN	48 filtered water samples	To use the isotopic composition of water (^{18}O and ^{2}H) from precipitation and surface water to better understand the controls on water availability in the Upper Colorado River Basin.
Erik Pollock/Jimmy Fox (University of Kentucky/University of Arkansas)	NTN	137 filtered water samples	Examine the changes in stable water isotopes for samples from a karst watershed; compare a shift in water isotopes for a record wet year in comparison with more normal years to understand the causes of the shifts in rainfall and karst aquifer flows.
Dane Blanchard (Trent University)	NTN	27 filtered water samples	Investigations have suggested gaseous organic pollutants sourced from the Athabasca Oil Sands (AOS) are entering the surrounding environment at elevated rates. Analysis of precipitation samples collected at NADP monitoring stations will provide valuable insight regarding the magnitude and composition of organic matter deposition in the Athabasca Oil Sands Region (AOSR).

20. Data Review

20.1. Analytical Data Review

CAL chemists and supervisors implement multiple protocols to ensure that data are accurate and properly qualified before moving to the data review stage. These include:

a. Peer review – a second analyst reviews all data packets prior to results being uploaded to the NADP LIMS and released to the sites in monthly reports.
b. 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.
c. Possible Qualifiers spreadsheet – record of all anomalies with samples during preparation/analysis.
d. Duplicate Failures spreadsheet – record of all duplicate failures even those corrected by rerun to assess trends.
e. LIMS Compare – monthly data packet review per platform compared to LIMS analytical data. Extra checks on duplicates and dilutions.
f. QC Login Error spreadsheet – record minor issues/login errors for QC samples that can then be edited by the data team.

20.2. Network Data review

Prior to releasing reports to sites or publishing data to the PO, the CAL or HAL 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 review

NTN, AMoN, and MDN-THg samples are all analyzed within respective target holding times (3 weeks from receipt for NTN, 3 weeks from date off for AMoN, and 4 weeks from receipt for MDN-THg). Data are then peer reviewed within 1-3 weeks of analysis and then uploaded to the NADP LIMS. Therefore, most data are uploaded to the NADP LIMS within 4 weeks of sample receipt. CAL data turnaround time is calculated from the end of the month in which a sample was received to when the data were released to a site (in the form of monthly preliminary data report) and published to the PO. Publishing on the website is the responsibility of the PO. In 2021, our turnaround times (TAT) have come down to around 90 days and are holding steady. This improvement resulted from the completion of the MDN integration and changing from a linear data review approach to a multi-faceted parallel approach. Refer to **Figure 41** for Data Review TATs.

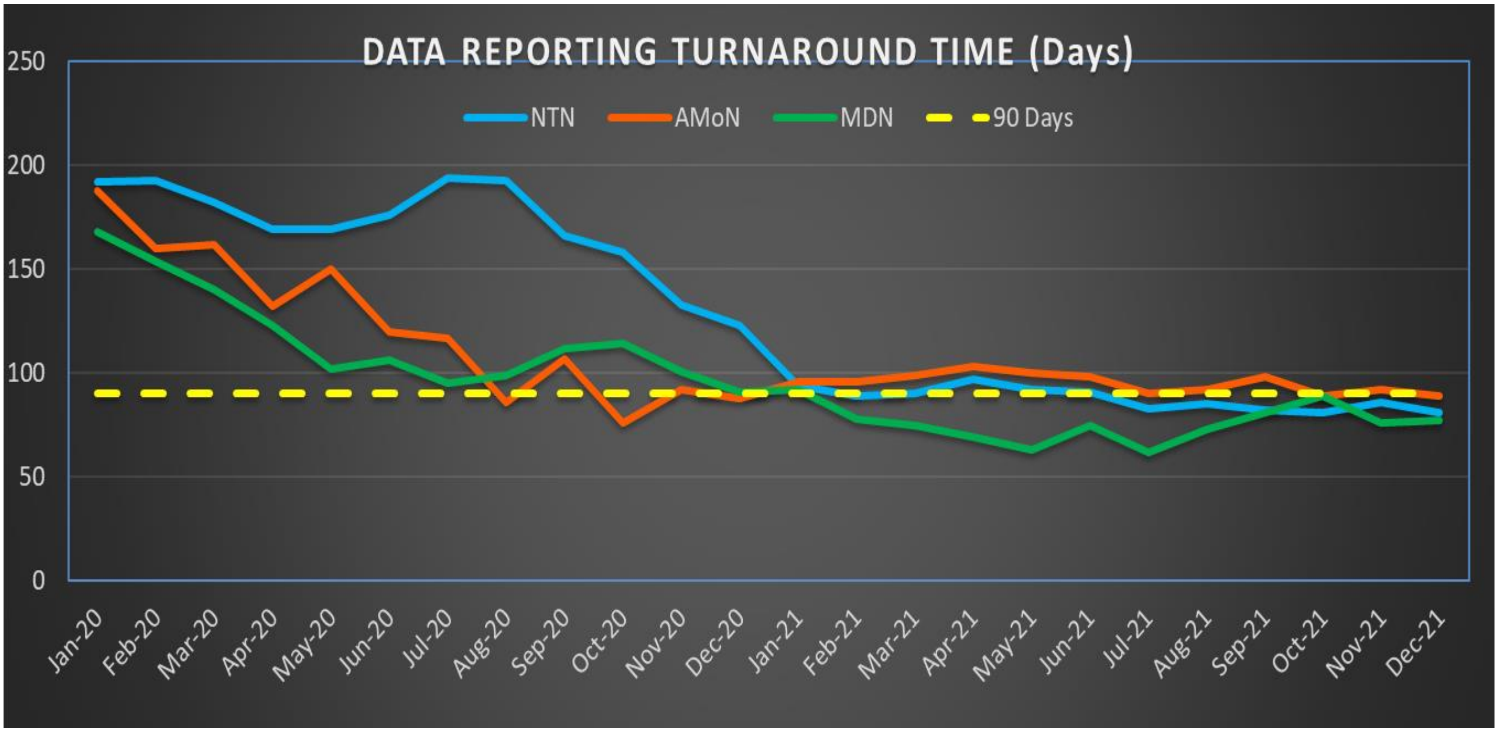

Figure 41. Wisconsin State Lab of Hygiene, Central Analytical Laboratory/Mercury Analytical Laboratory Data Deliverables: Preliminary Reports to Sites and Data Delivered to the NADP Program Office by Network as of Month and Year. Note: 90 days is the target turnaround time.

22. References

- Applicable NADP SOPs for instrumentation and laboratory procedures and requirements via OnBase
- National Atmospheric Deposition Program Laboratory Quality Assurance Plan, Mercury and Central Analytical Laboratories
- USGS Precipitation Chemistry Quality Assurance Project (PCQA) https://bqs.usgs.gov/pcqa/

23. Approvals

- 2021 CAL QAR Prepared by Nichole Miller, Laboratory QA Specialist; Christa Dahman, HAL Analytics/ TECL Supervisor; Amy Mager, Lab Director, Environmental Survey Programs ; Zac Najacht, Assistant Data Manager on: 3/21/2023
- Shared with NADP Management for review as draft on: 3/21/2023
- Reviewed and revised by Systems QA and Special Projects Manager Martin Shafer on: 4/28/2023
- Approved by the NADP Laboratory Director Amy Mager on: 5/16/2023
- Shared with the QAAG for review on: 5/16/2023
- Approved by QAAG by vote: 6/1/2023