2022 Quality Assurance Report

January 01 – December 31, 2022

National Atmospheric Deposition Program

Analytical Laboratory (NAL)

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National Atmospheric Deposition Program

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National Atmospheric Deposition Program (NADP) Analytical Laboratory (NAL) Quality Assurance Report (QAR)

January 1 – December 31, 2022

1. Overview

The NAL provides field-sampling supplies, sample processing, chemical analysis, and data validation services for: (a) precipitation samples collected by the NADP/National Trends Network (NADP/NTN), (b) the passive ambient air ammonia samplers for the NADP/Ammonia Monitoring Network (NADP/AMoN), (c) the precipitation samples collected by the NADP/Mercury Deposition Network (NADP/MDN), and (d) leaf litter samples collected by the NADP/Mercury in Litterfall Network (NADP/MLN). The 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.

2022 NADP Staff

- Systems QA and Special Projects Manager - Martin Shafer
- CAL Laboratory Manager – Chris Worley (until March 2022)
- Chemist Supervisor – Katie Blaydes, Christa Dahman
- EHD Environmental Survey Programs Director – Amy Mager (as of September 2022)
- QA Manager – Camille Danielson (until July 2022)
- Laboratory QA Specialist – Nichole Miller (as of October 2022 – in place of QA Manager position)
- Assistant Data Manager – Zac Najacht, Dana Grabowski
- NTN/AMoN Chemists – Katie Blaydes, Nichole Miller (until October 2022), Marie Assem (until March 2022), Chris Bauknecht (as of February 2022), Abby Carr (as of July 2022)
- Mercury Chemists – Kirsten Widmayer, Chris Lepley
- Environmental Health Technologists – Colin Kelly, Kat McKinnon, Anita Peterson, Cami Ritonia (as of January 2022)

See section 4.2.1. for detailed explanation of staffing changes.

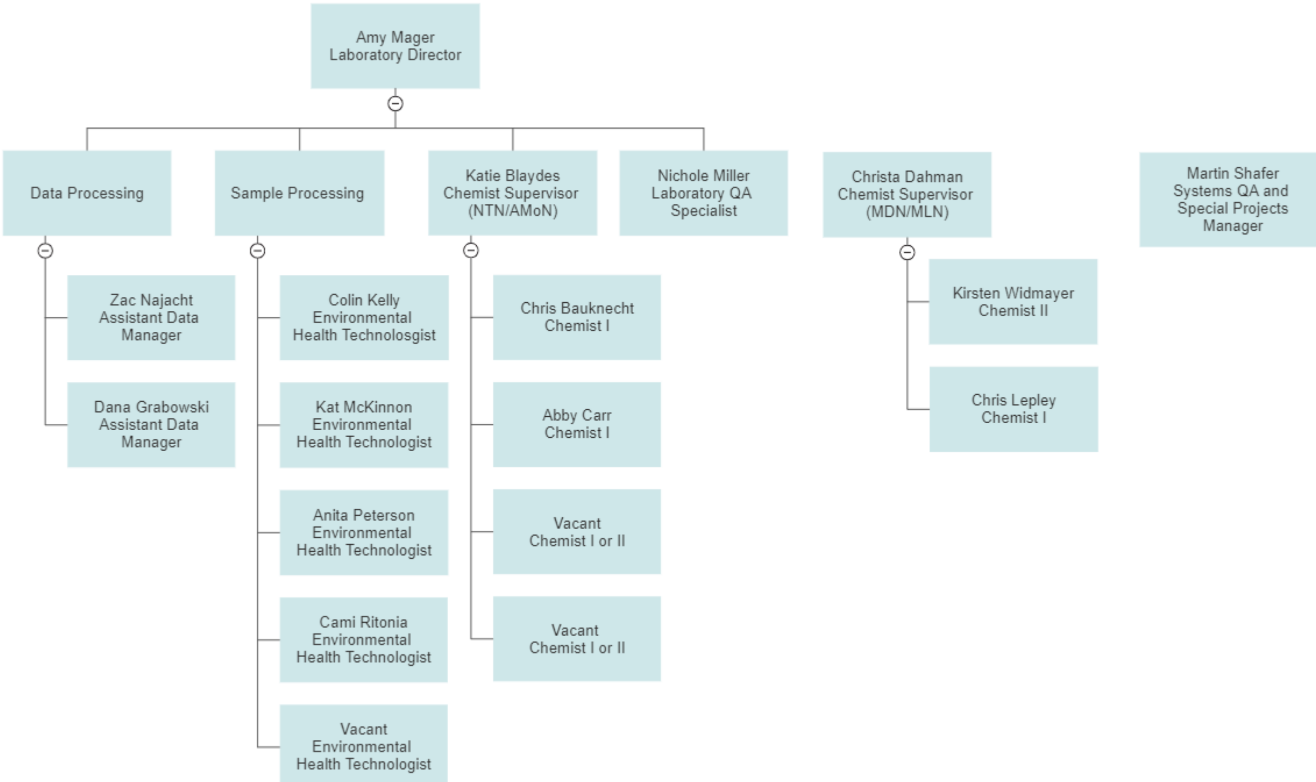

Figure 1. Organizational chart of laboratory staff as of December 2022.

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 reviewed and published by the Program Office (PO). Valid samples include all samples that received a Quality Rating (QR) of "A" (valid data) or "B" (valid data with minor problems). While a quality rating of "C" is invalid data. 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 Observer Report Form (FORF) is submitted to the NAL. Trace and dry samples are not analyzed in the lab. Low volume sample weights are confirmed gravimetrically as the difference between the 1L collection bottle tare weight and the sample + bottle weight in the lab prior to analysis to code them accordingly.

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

- W ("Wet") = ≥ 27.51 mL
- WD ("Wet Dilute") = 13.51-27.50 mL
- WI ("Wet Incomplete") = 4.01-13.50 mL
- T ("Trace") = ≤ 4 mL
- D ("Dry") = 0 mL

Table 1. NTN Total Sample Counts 2018-2022

Year	Total Samples	Wet Samples		Trace Samples		Dry Samples		Valid Samples	
		Number	Percent	Number	Percent	Number	Percent	Number	Percent
2018	13107	9912	75.6	413	3.2	1882	14.4	10337	78.9
2019	12945	10363	80.1	142	1.1	1878	14.5	10426	80.5
2020	12791	9796	76.6	231	1.8	2173	17.0	10430	81.5
2021	12937	10518	81.3	229	1.8	2190	16.9	10691	82.6
2022	12897	10434	80.9	199	1.5	2164	16.8	10291	79.8

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 is 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. MDN Total Sample Counts 2018-2022

Year	Active Sites	Total Samples	Wet Samples		Dry Samples		Valid Samples	
			Number	Percent	Number	Percent	Number	Percent
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
2022	81	4074	3598	88.3	476	11.7	3519	86.4

*EFGS – Eurofins Frontier Global Sciences – analyzed all MDN samples prior to May 2019.

Very few AMoN samples are invalidated (QR of C) given current field and lab criteria, as can be seen in **Table 3. Figure 2** shows total NTN sample numbers and valid and invalid counts for the past 5 years. **Figure 3** depicts these same metrics for MDN and **Figure 4** for AMoN.

Table 3. AMoN Total Sample Sets Count 2018-2022

Year	AMoN Sites	# of Sample Sets	Valid Samples	
			Number	Percent
2018	103	2579	2551	98.9
2019	107	2665	2643	99.2
2020	111	2760	2735	99.1
2021	115	3100	3072	99.1
2022	90	2545	2512	98.7

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.

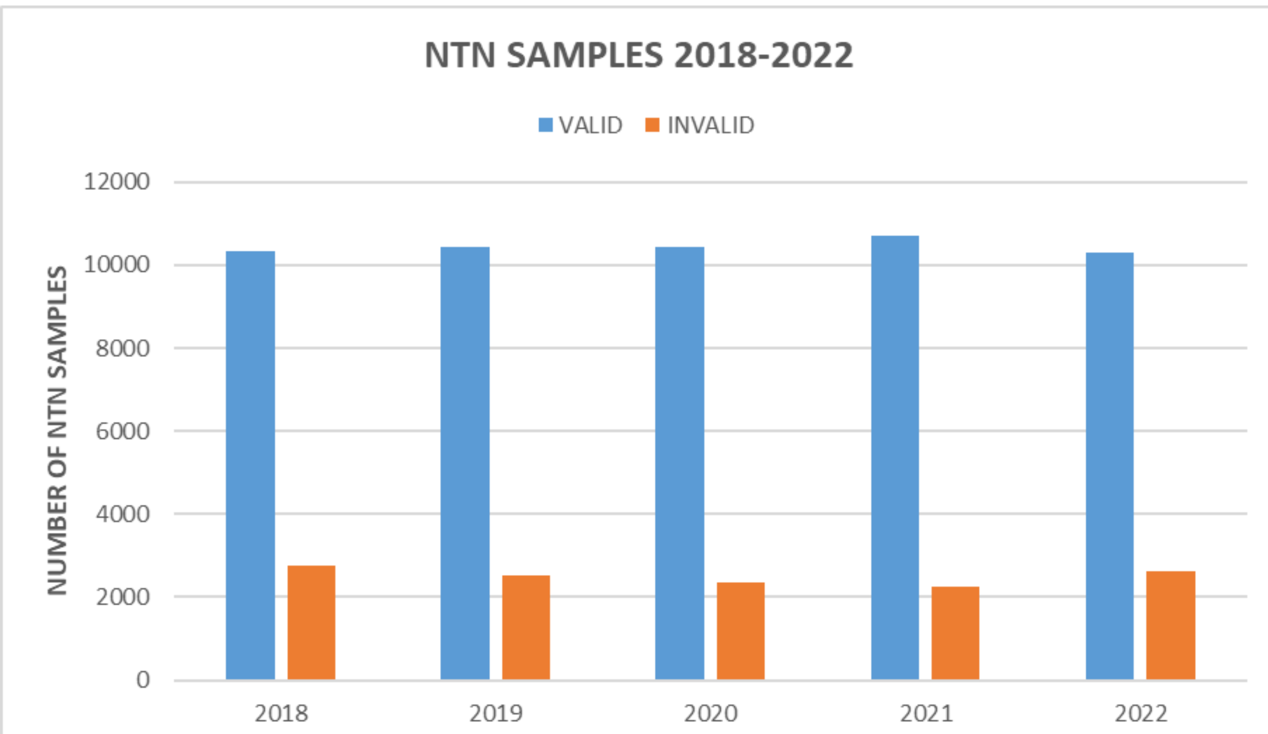

Figure 2. Total Valid and Invalid NTN Samples from January 2018 - December 2022.

The number of NTN valid samples has remained constant over the past 5 years.

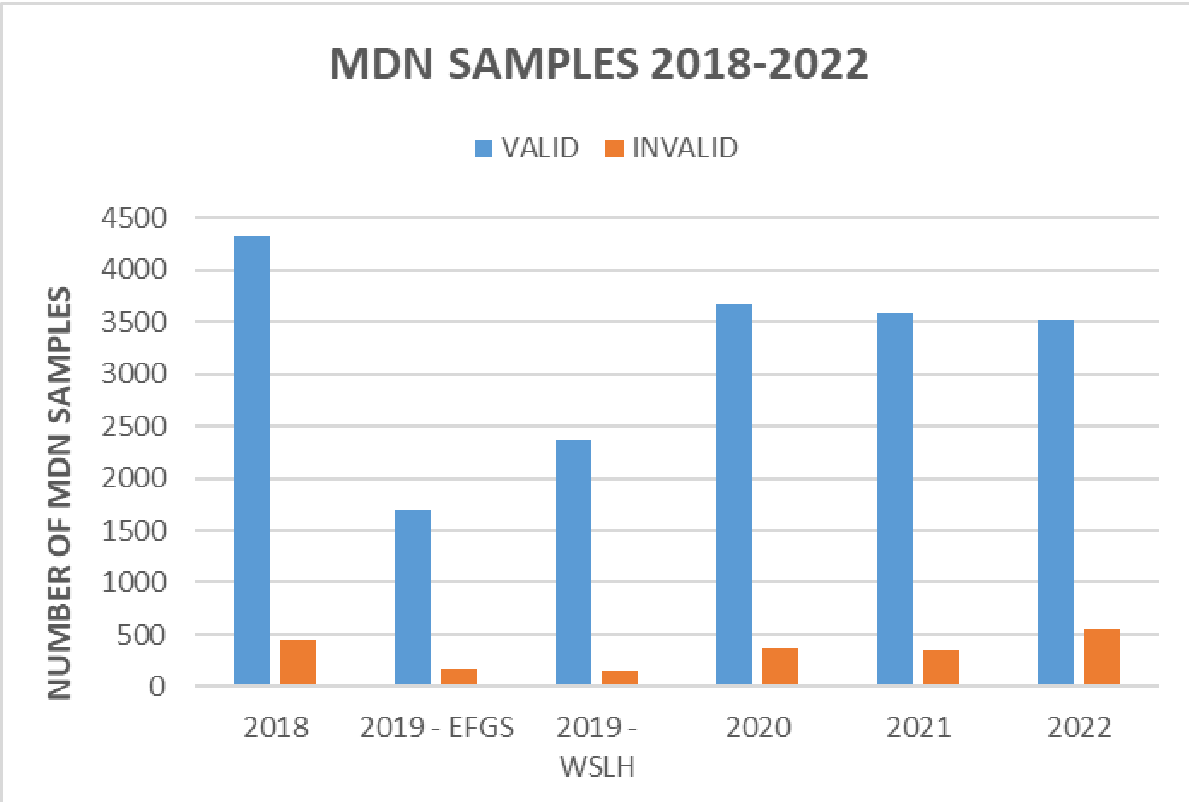

Figure 3. Total Valid and Invalid MDN Samples from January 2018 - December 2022.

The number of MDN valid samples has also remained constant. Results indicate a slight increase of invalid samples in 2022 with a corresponding slight decrease of valid samples.

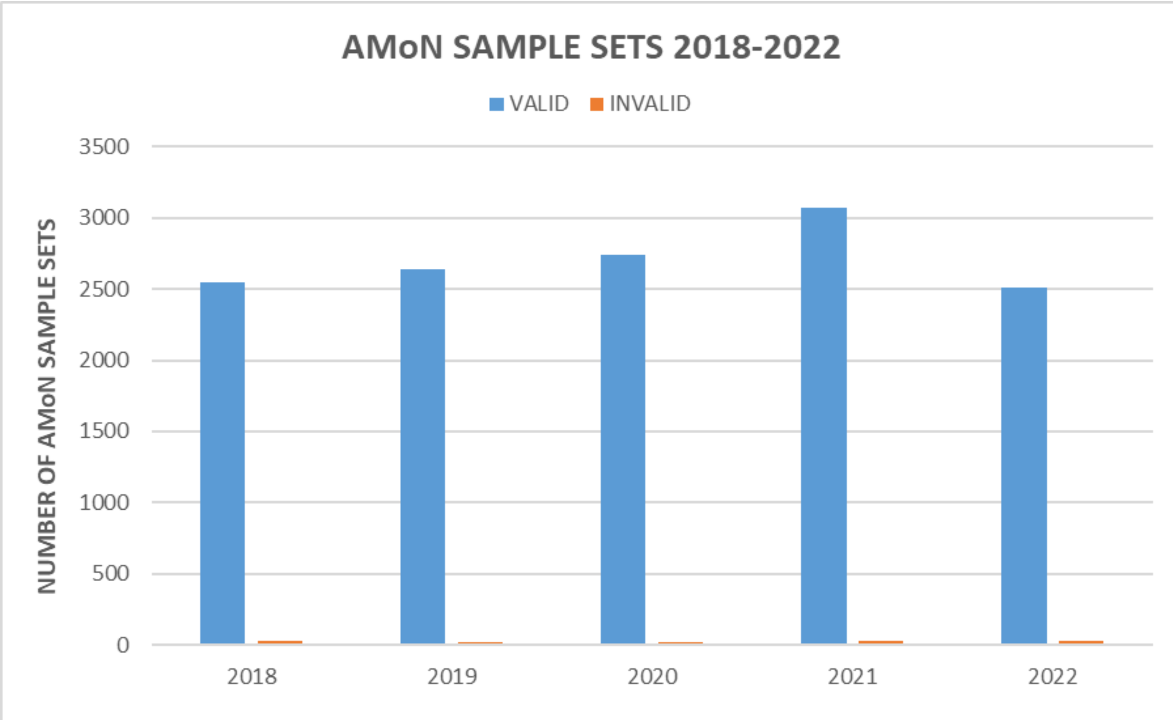

Figure 4. Total Valid and Invalid AMoN Samples from January 2018 - December 2022.

The decrease of AMoN valid samples is due to site closures and less sample received by the lab, not an increase of invalid samples.

In 2022, seven MDN sites requested methylmercury (MeHg) analysis on their MDN samples. MeHg was discontinued as an analyte for MDN sites effective May 2022 after several data evaluations that demonstrated that results were biased by aliquoting and contamination.

The Litterfall Initiative was transitioned to the Mercury Litterfall Network in the 2021-2022 litterfall season. There were 21 sites contributing samples for the 2021-2022 season. Each site consists of four collectors and at least two retrievals (typically one-month duration) are submitted from each collector every season (under normal circumstances). There were 278 individual samples submitted for the 2021-2022 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 0.15% - 1.5% of the total mercury measured.

3. Network Operations

The NTN has been in operation for 44 years, MDN for 26 years, and AMoN has been operating for 15 years. The AIRMoN ended operation in September of 2019. **Table 4** shows the total number of samples (including dry and trace) received through December 2022 since inception of the networks. **Figure 5** 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 (Samples Received prior to 1/2023)

Network	Date Network Began	Date Network Ended (if applicable)	Number of Years in Operation	Total Sample
NTN	7/5/1978	Continuing	44	503,077
AMoN	10/29/2007	Continuing	15	45,751
AIRMoN	9/23/1992	9/1/2019	27	7,709
MDN - THg	2/27/1996	Continuing	26	117,388
MLN	8/1/2021	Continuing	1	278
TOTAL				**673,925**

3.1. Active Sites

The number of active field sites in each network has varied from year to year. Over the last decade, the number of NTN sites has remained relatively constant. AMoN had steady growth, although due to EPA budget cuts, many sites were put on long term hold in 2022. MDN sites have steadily declined since 2016, attributed primarily to site sponsor budget cuts and changes in regulatory rulemaking. The Litterfall Initiative (now MLN) had minor fluctuations in active sites since its beginnings in 2007.

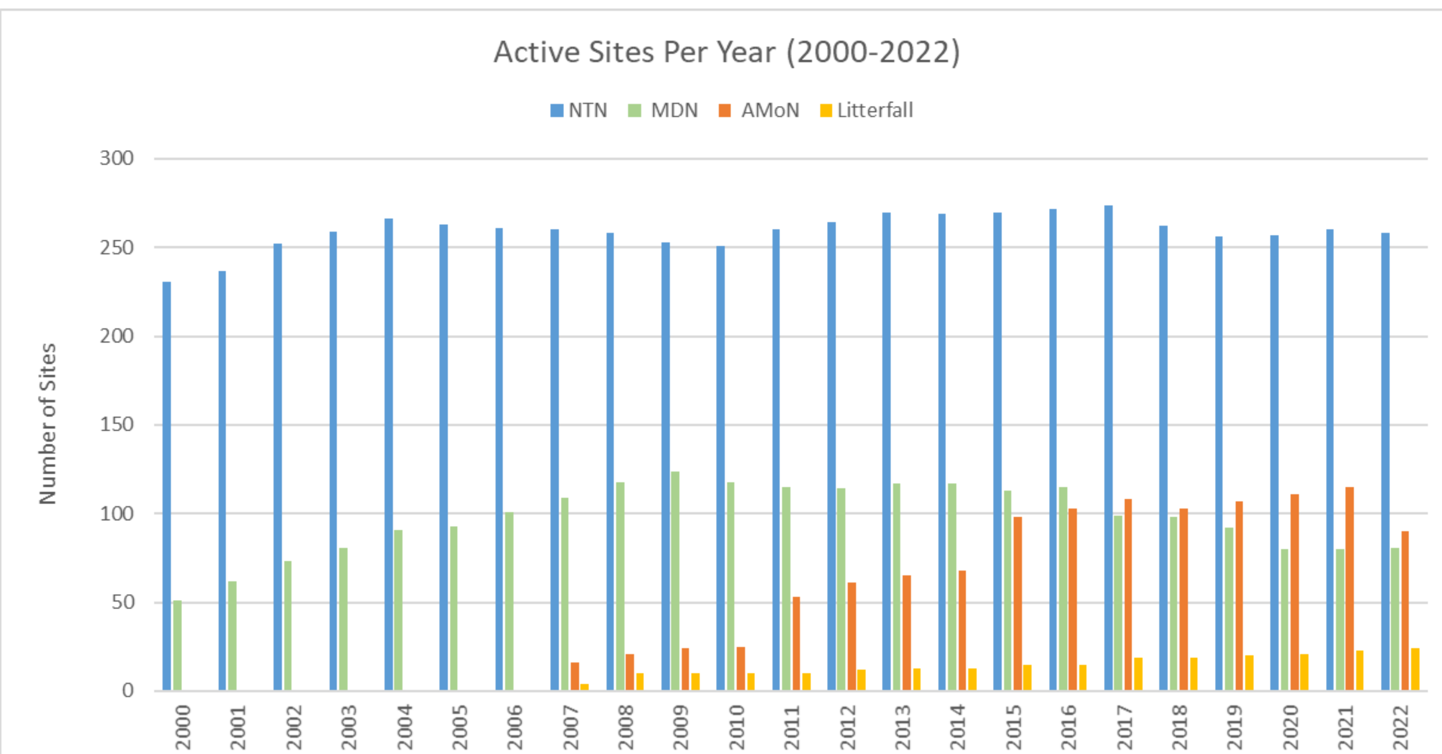

Figure 5. Active sites per network from 2000-2022.

4. Annual Management Review Summary

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

Dates covered by review: January 1, 2022 to December 31, 2022
Department: NADP
Person responsible for department's review: Amy Mager, Christa Dahman, Katie Blaydes, and Nichole Miller
Note: this summary was condensed from original report

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

4.1.1. 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 2022**).

4.1.2. 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.

4.1.3. Reviews and edits of all NADP SOPs in OnBase (the WSLH electronic system for management of SOPs) will be completed in 2023. This was partially completed during the transition into OnBase. SOPs in development into 2023 are MDLs, NADP Data Management/Backup, Internal Systems and Method Audits, Check Standard Preparation, and Field Audit/System Blanks.

4.1.4. Mercury Litterfall Network (MLN) SOP for supply shipment is under development with a goal to have it in place before the 2023-2024 Litterfall season. The login SOP was completed in 2022.

4.1.5. Updates are needed for Data Review SOPs to incorporate changes to several Field and Lab hold time parameters. Our goal is to have these completed by October 1, 2023.

4.1.6. Procedures for Field Audit and System Blank preparation and shipping have been prepared. These are currently not official SOPs, due to uncertainty if these activities will stay with NADP. While documents are not official SOPs at the moment, document control has been added. A decision on whether or not these activities will stay with NADP will be made by June 1, 2023.

4.2. Reports from managerial and supervisory personnel:

4.2.1. **Staffing.** At the end of 2021, two Chemists left the sample receiving group. These positions were replaced in December 2021 with two Health Technician – Environmental positions (Anita Peterson and Kathryn McKinnon). In January 2022, an additional Health Tech-Environmental was hired to serve as a floater between the receiving and field operations departments – Cameron Ritonia. Chris Worley (Laboratory Manager) retired in March. This combined with Jesse Wouters departure in September, 2021, resulted in the creation of a new working Chemist Supervisor position that was filled by Katie Blaydes (Chemist II) in December 2021. This allowed her to cross train with Chris before his departure. Chris Bauknecht was hired as a Chemist I (internal hire from WSLH-LID) in February to fill Katie's vacancy as a full time chemist. Marie Assem vacated a Chemist II position in March. Abby Carr (Chemist I) transitioned from the sample receiving group at HM to fill this chemist role at Ag Drive. This transition was complete in July. As of early 2022, Cameron Ritonia's focus switched primarily to the sample receiving group. Amy Mager (Sample and Data Processing Manager) accepted a new role as EHD Environmental Survey Programs Director in September. Two Lab Supervisor positions will be put into place to cover Sample Receiving and Field Operations in early 2023. Camille Danielson (QA Manager) accepted a new role as EHD Environmental Chemistry Program Director in July. Nichole Miller (Chemist II) accepted the new role of Laboratory QA Specialist to cover these responsibilities in October. Kat McKinnon (Health Technologist) has been hired as a Chemist I to fill the Chemist II position vacated by Nichole Miller. Kat will be transitioning from her role with the sample and receiving team in February 2023. See **Figure 1** on page 4.

4.2.2. Audits. An internal method audit for mercury analysis was performed by Na Zhang in December of 2022. An extensive external audit of the NADP Program Office was performed from October 4-6, 2022 by Douglas Burns, U.S. Geological Survey (lead); Catherine Collins, U.S. Fish and Wildlife Service; Kristi Morris, U.S. National Park Service; and Christopher Rogers, WSP.

4.2.3. Major Network Changes.

4.2.3.1 Reduced some supply QC for NTN, AMoN, and MDN, due to long term data sets showing little to no contamination, to improve efficiency.
4.2.3.2 Changed use of AMoN bodies to a maximum of 8 uses before removal from use.
4.2.3.3 Ended MeHg aliquoting from THg samples due to high bias on THg measurements.
4.2.3.4 Switched back to sending Degage NTN sample bags in supply boxes.

4.3. Changes in the scope/scale and type of work during 2022:

4.3.1. In total, 26 AMoN sites were inactivated during this year; 22 of them were due to loss of EPA funding. However, one of the EPA sites has been restarted.

4.3.2. Methylmercury was discontinued as an analyte for those MDN sites where MeHg was previously quantified. Overall, fewer than 120 samples per year were discontinued.

4.3.3. Implementing MLN as an official network temporarily increased our effort dedicated to SOP and data systems development.

4.4. Recommendations for improvement from the NADP Executive Committee and NADP Subcommittees:

4.4.1. Restart the process of working on data quality objectives and how data is presented to end users.

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

4.4.3. Start comparison studies with the ALPHA ammonia samplers.

5. Staff Training

Existing 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.

6. Instrumentation

Table 5. NADP Dedicated Major Analytical Equipment

Analysis	Type	Species	Instrument
Inductively Coupled Plasma – Optical Emission Spectrometry (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 in-vial sparging sample introduction (IVS)
Automated Cold Vapor Atomic Fluorescence (CVAFS) with Chromatographic separation	CVAFS	Methyl Hg	Tekran 2700 with in-vial sparging sample introduction (IVS)
Thermal Decomposition, Gold Amalgamation, and Atomic Absorption Spectroscopy (AAS)	AAS	Total Hg (solids)	Nippon MA-3000

7. 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 3 March 2022) and is revised every three years. The NADP QAP contains detailed QA information on all aspects of the NADP laboratories. An Annual Management Review (summarized above) was completed in 2022 and is saved in the following folder O:\Teams\EHD QC Team\Team Access Only\Management Reviews EHD.

7.1. Standard Operating Procedures

The NADP protocols are documented in an extensive series of standard operating procedures (SOPs). A list of these SOPs is available on the NADP website (NADP-SOP-list-2023.pdf (wisc.edu)). 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.

8. NTN Method Detection Limits (MDL)

8.1. 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 over several days) of spiked samples in the matrix of concern (at a concentration of approximately 2-5 times the MDL).

8.2. NTN MDL_L Blank calculations

A minimum of seven matrix 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 blank-based MDL_L is used as the analytical lab MDL_L if the result is greater than the spiked lab MDL_L result.

8.3. NTN MDL_L Usage

Analytical laboratory MDLs are an important data quality indicator and are reviewed annually and revised by the QA staff as warranted (e.g. 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 staff to assess the network MDLs validity. It is not used for qualifying NTN data.

8.4. 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 (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.

8.5. 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 sample IDs for a calendar year are also documented in the Historical MDL table to indicate which MDLs apply to specific samples each year. The NTN sample results that are less than the MDL_N for a given 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 include the less than MDL_N values (such data are italicized if less than the NTN MDL_N for the calendar year).

Table 6. NTN Historical Network MDLs 1987-2022

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
TX6131	TY9103	2022	0.010	0.006	0.004	0.008	0.020	0.020	0.020	0.014	0.010

9. AMoN MDLs

9.1. 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 with values less than the MDL_L with a "d" flag, which results in assigning a Quality Rating (QR) of B. Definitions of flags can be found on the website:
https://nadp.slh.wisc.edu/wp-content/uploads/AMoN_Metadata_v2_1.pdf

9.1.1. AMoN MDL_L Calculations

In 2022, the AMoN lab MDL was calculated as the mean sampler core blank + (t*stdev) for all available core blanks with results greater than zero. There were 138 valid core blank values from January 2020 – December 2021 and these were used to determine a mean of 0.010 mg/L NH_4 to be used as the MDL_L.

9.1.2. AMoN Network MDL (MDL_N)

The AMoN network MDL is used to flag data that is 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.

9.1.3. AMoN MDL_N Calculations

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

The 2022 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).

Table 7. AMoN Historical MDLs

AMoN Historical MDLs Version 2/2023			
AMoN Sample Set ID Range	Year of Sample Receipt	AMoN Network MDL (MDL_N) mg/L NH_4^+	AMoN Lab MDL (MDL_L) mg/L NH_4^+
All Prior to N18005002	<2018	0.0469	0.0469
N18005002 - N18006407	2018	0.119	0.008
N19000001 - N19002669	2019	0.104	0.016
N20000001 - N20002856	2020	0.083	0.013
N21000001 - N21003101	2021	0.070	0.010
N22000001 - N22002743	2022	0.080	0.010

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

10. MDN and Litterfall (MLN) MDLs

10.1 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 have 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 QA staff and management is considering developing a network MDL that takes into account some uncertainty in the sample handling and processing.

10.2 MDN and Litterfall MDLs

Calculations of MDN and MLN MDLs 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 8** below. The LOD and LOQ for MDN did not change from 2020. The LOD and LOQ for MeTHg decreased by approximately a factor of 3 since 2020.

Table 8. Network MDLs

Year/Limit type	MDN (THg) ng/L	MDN (MeTHg) ng/L	MLN (THg) ng	MLN (MeHg) ng
2020 LOD	0.20	0.10	NA	0.1
2021 LOD	0.20	0.10	0.1*	0.1
2022 LOD	0.20	0.029	0.096	
2020 LOQ	0.67	0.30	NA	0.3
2021 LOQ	0.67	0.30	0.33	0.3
2022 LOQ	0.67	0.096	0.32	

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

10.3 Ongoing MDL Verification

MDN MDLs are verified by analyzing a spiked solution, prepared with the same reagents as a sample, at a concentration of 0.5 ng/L (2.5x the current MDL) <u>with every analytical run</u>. 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.

10.4 MDN MDL Adjusted by Dilution

Mercury methods for waters involve a pre-concentration step, so the reference 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.

11. External Field QA Programs

Information for Section 11 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 NAL also participated in several external PT programs. Those programs and outcomes for 2022 are discussed in **Section 13**.

11.1. 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 2022. The Field Audit and System Blank programs assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of NTN and MDN samples, respectively. 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 chemical contamination levels and concentration biases in the networks. The inter-laboratory comparison program assessed the bias and variability of the chemical data from the NAL and other participating laboratories that analyze precipitation samples for major ions, nutrients, and mercury.

11.2. Field Audit Samples

For the 2022 season, the NAL took over the preparation and shipping of NTN field audit samples to the sites. This was done to reduce costs as the NAL already ships to sites on a regular basis. On a dry week, sites process these samples by having the operator pour 75% of the volume of the field audit solution into the sample collection bag and then treat it as a normal weekly sample by pouring it off into the sample collection bottle. This sample (DF), along with the 25% of the field audit solution that remains in the original container (DK), is shipped back to the NAL for analysis. These results are published in an official USGS publication every two years. The most current data set can be found at the following link https://www.sciencebase.gov/catalog/item/6476195dd34e4e58932d9d0e

11.3 Field QC System Blank Program

Historically, the MDN site operators received system blank samples from the USGS PCQA project, but in 2022, the NADP took over the preparation and shipping of the samples. Operators who received system blank samples from NADP waited to process their samples after a week without wet deposition at their sites. The operators then poured one-half of the volume of the system blank solutions (reagent grade water) through their installed glass sample trains. 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 by sample type "DF"), and the solution remaining in the original sample bottle is called the bottle blank sample (also known as sample type "DK"). Both system blank and bottle samples are sent to the NAL for total mercury (Hg) analysis. Reports of these data are prepared every two years by the USGS. The most current data set can be found at the following link https://www.sciencebase.gov/catalog/item/6476195dd34e4e58932d9d0e

12. Internal Field QA Programs

12.1. AMoN Travel Blanks and Field Duplicates

In 2022, all AMoN sites received travel blanks and duplicates at least three times per year. These don't always necessarily align to the same deployment date. This means a sample set can consist of a single A sampler, a duplicate pair (A and B sampler), a single A sampler with a travel blank TB sampler, or a full set of a duplicate pair (A and B sample) with a travel blank TB sampler.

12.2. Travel Blanks

There were 367 travel blanks sent to sites and analyzed between January and December of 2022. 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 9** for the mean, median and maximum travel blank concentrations since the WSLH began operating the AMoN network. Refer to **Figure 6** for the 2022 AMoN travel blanks and **Figure 7** for the AMoN travel blanks since the beginning of the network.

Table 9. AMoN Travel Blank Results 2021-2022

	2021	**2022**	**2022**
	mg/L NH_4	**mg/L NH_4**	**µg/m^3 NH_3**
Mean	0.040	0.042	0.085
Median	0.037	0.039	0.080
Max	0.257	0.224	0.45
Number of Valid Travel Blanks	570	364	364
Number of Invalid (QR=C) Travel Blanks (not used)	3	3	3

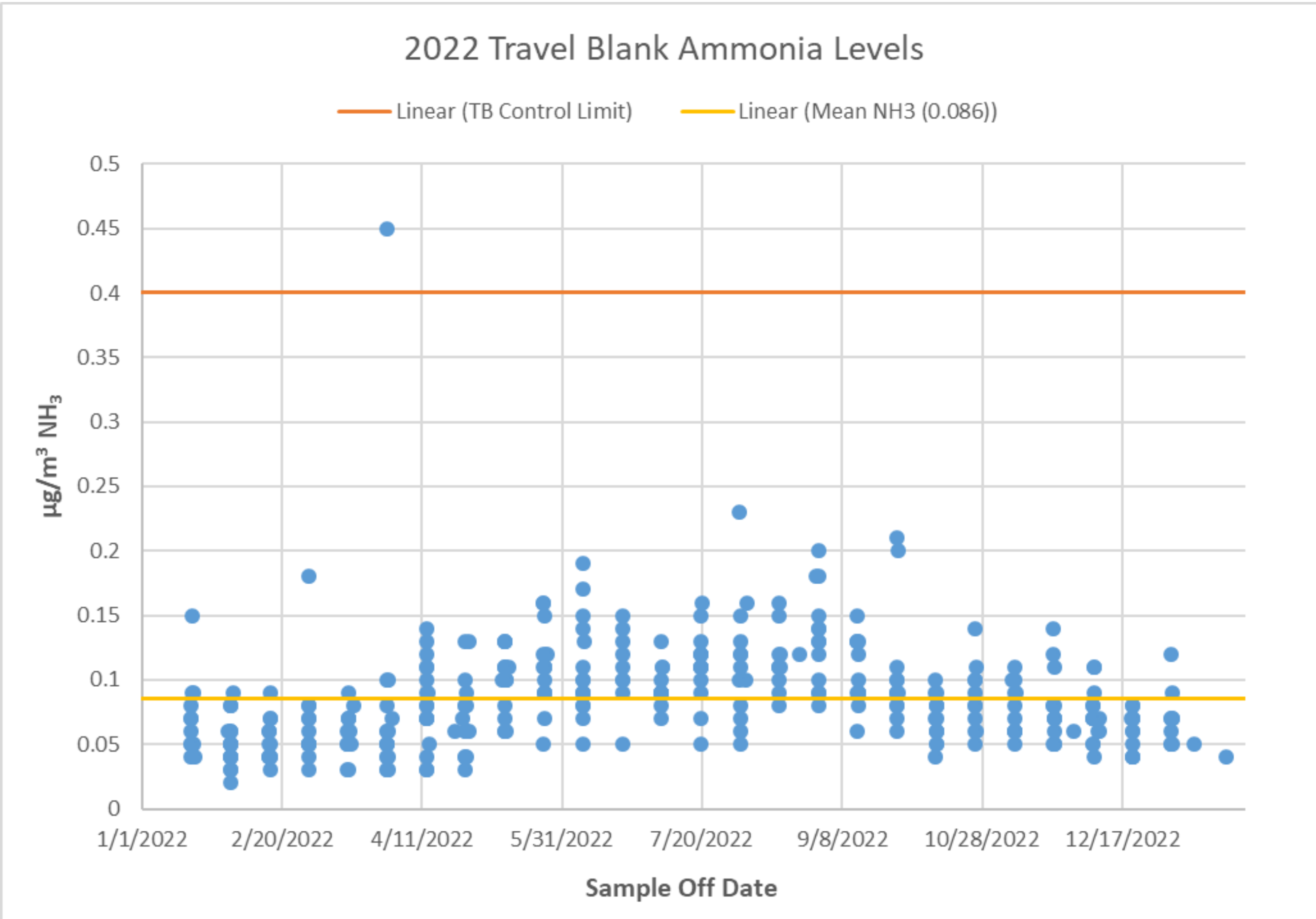

Figure 6. AMoN Travel Blank Ammonia Levels 2022

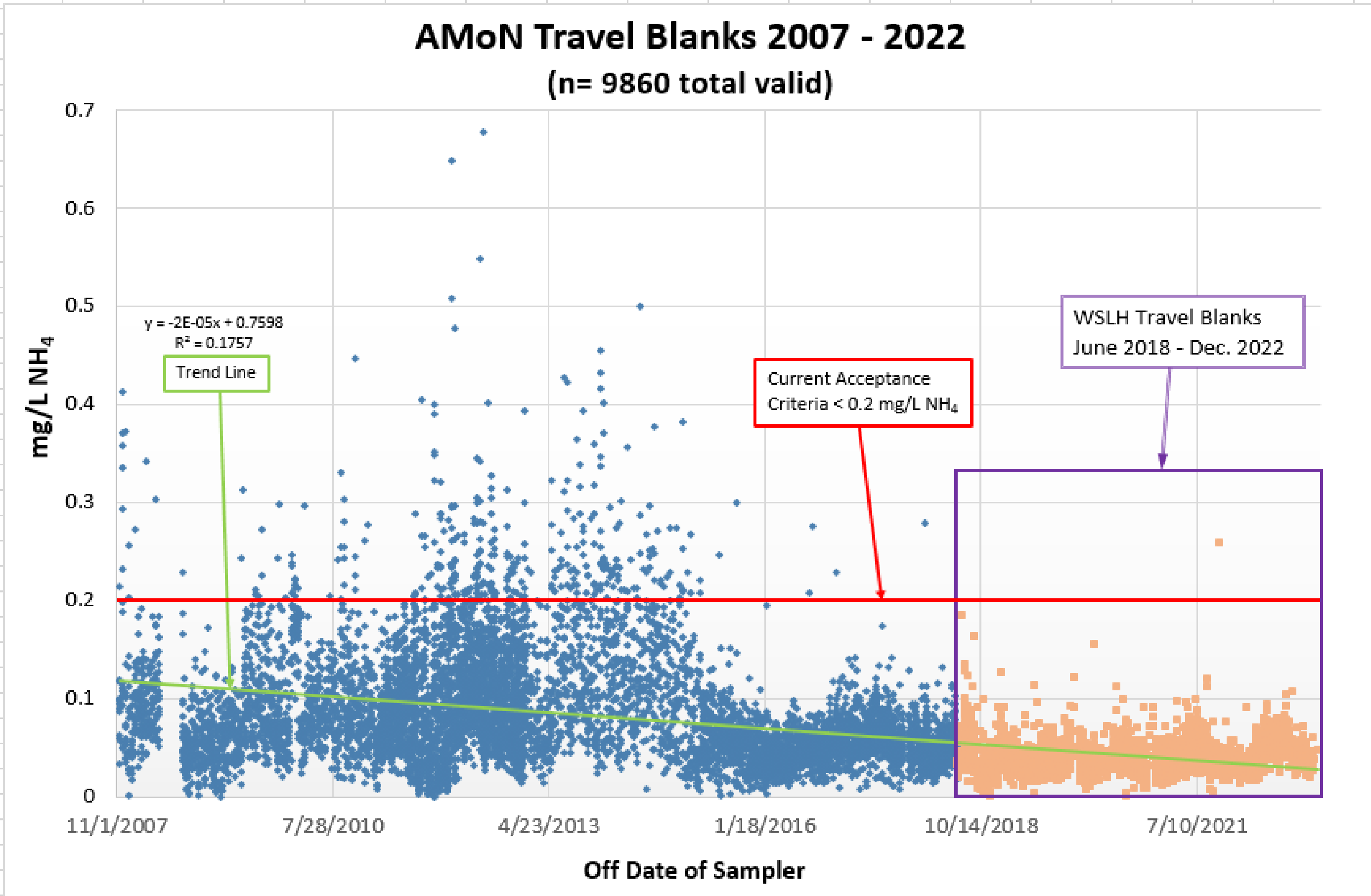

Figure 7. AMoN Travel Blank Historical Ammonia Levels 2007 – 2022. Samples from 2007 – June 2018 were prepared, received, and analyzed at the Illinois Central Analytical Laboratory (ICAL).

13.2 AMoN Field Duplicates

Triplicates (2018 & 2019)/Duplicates (2020-2021) that exceeded 15% Relative Standard Deviation (RSD = standard deviation divided by the mean, a.k.a Relative Percent Difference (RPD)) were retested to ensure that the difference was not an analytical issue, and noted in the qualifiers spreadsheet. However, since the disparate field results were confirmed every time, we have discontinued this retesting practice. In 2022, the NAL deployed and analyzed 297 valid duplicate sets.

In 2022, 85% of the replicate sets (across all ambient concentrations) had less than 12.5% RPD. All valid 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 10** and **11**, and **Figures 8** and **9**. It is more appropriate to assess the AD in concentration units. The 90th percentile of the 2022 AD was 0.25 µg/m^3 NH_3, and the 80th percentile was 0.12 µg/m^3 NH_3. This means that 90% of the duplicate pair ammonia results agreed within 0.25 µg/m^3 NH_3.

As can be seen in **Figure 8** and **9**, AMoN duplicate differences are generally very small. Field duplicates that are extreme outliers are generally due to field error and have very high RPDs.

Table 10. AMoN Relative Percent Difference (RPD) and Absolute Difference (AD) percentiles

AMoN Duplicate Sets 2022 (297 Sets)	2022	RPD	AD µg/m³ NH_3
	80th Percentile	9.14	0.12
	85th Percentile	12.39	0.15
	90th Percentile	21.32	0.25
	95th Percentile	36.98	0.79

Table 11. AMoN Average, Median, and Maximum Relative Percent Difference (RPD) and Absolute Difference (AD) of Field Duplicates

2022 Duplicates	RPD	AD (µg/m3 NH3)
Average	9.454	0.170
Median	4.633	0.030
Maximum	127.273	10.080

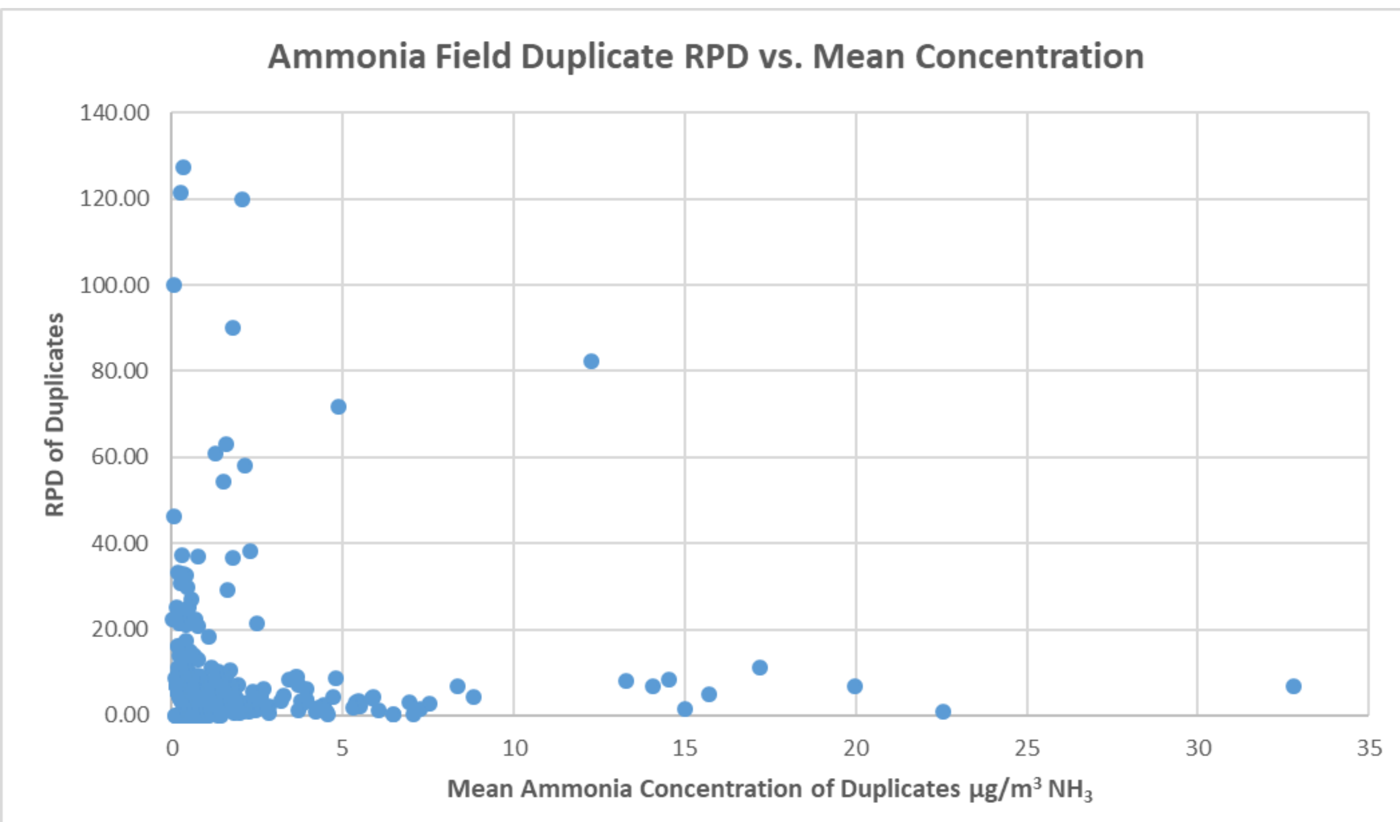

Figure 8. Relative percent difference of 2022 AMoN field duplicate versus mean ammonia concentration (n=297 sets)

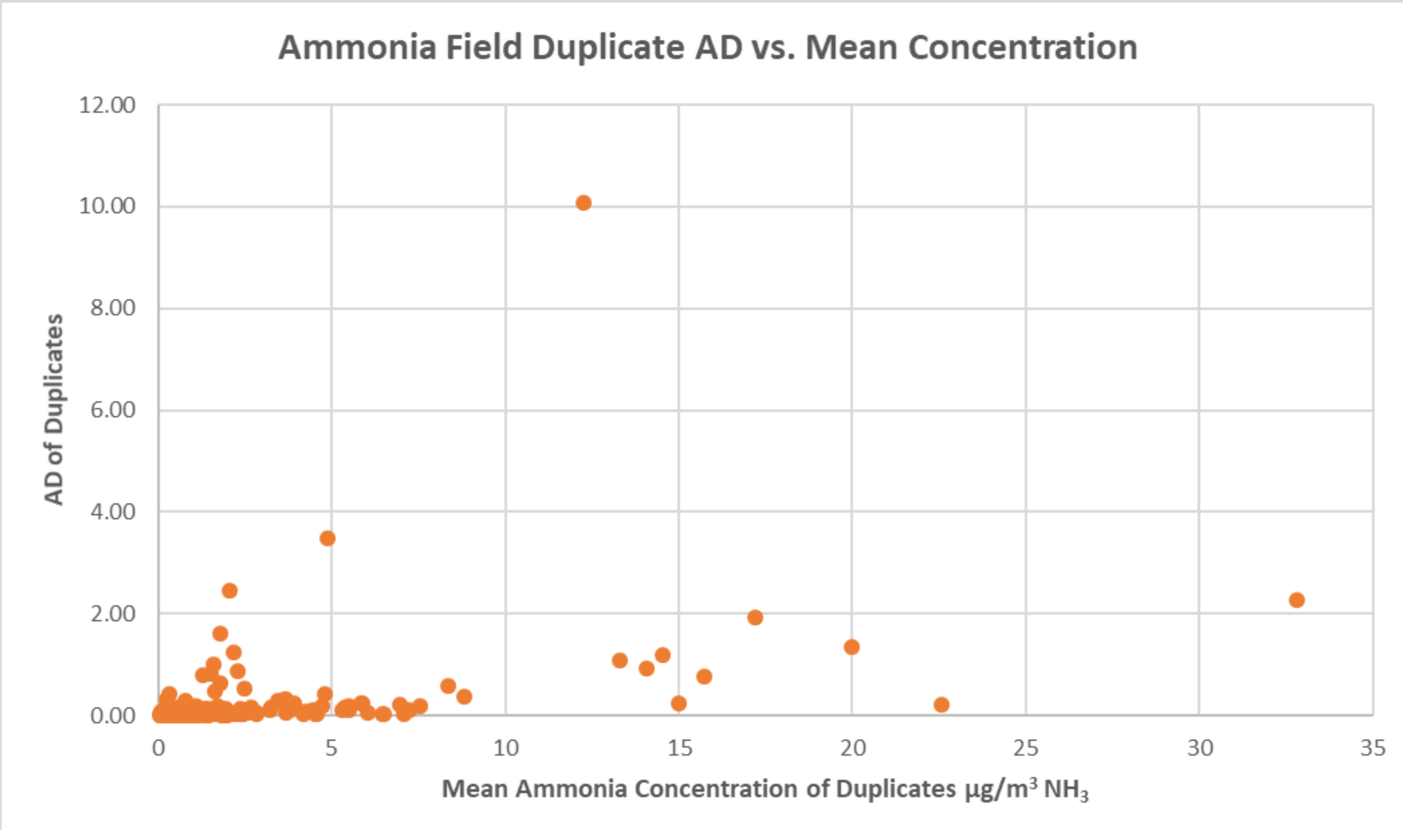

Figure 9. Absolute difference of 2022 AMoN field duplicates versus mean ammonia concentration (n=297 sets)

13. Proficiency Test results

In 2022, the NADP participated in and completed the following PT assessments:

- Two PT studies through the World Meteorological Organization (WMO)
- Two studies 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 the results are provided below.

Table 12. 2022 Proficiency Test Results Summary

PT Provider	PT Studies Completed	Results outside of Control Limits	Website Results
ECCC	ECCC 120 ECCC 121	ECCC 120 – Slight positive bias for conductivity, but they are very low concentrations. A few high results for NH_3-N, but values are close to the MDL. ECCC 121 –The cation analytes have a larger recovery range, see notes under table.	Not on website - Refer to summary provided below
WMO Global Atmosphere Watch (GAW)	WMO 65 WMO 66	WMO 65 – No analytes of concern WMO 66 – No analytes of concern	https://www.qasac-americas.org/study-results?lab=700175&study=65&type= https://www.qasac-americas.org/study-results?lab=700175&study=66&type=
USGS	2022 - Full Year of Samples	Notes below	https://bqs.usgs.gov/PCQA/Interlaboratory_Comparison/graphOutput.php?page=start
USGS SRS (Standard Reference Samples)	P-78, N-153, Hg-73 (Spring) P-79, N-155, Hg-75 (Fall)	Spring – A slight negative bias for the cations. Quite low recovery for the SO_4 value, but it was run three times with similar results. Looking across all labs, there was a large range of values (**Figure 15** below) for sulfate. Fall – No analytes of concern	Results are on the SRS website by blind laboratory number and available upon request

13.1. ECCC Results

Table 13. ECCC 120 PT Results Assessment – including Hg

	ECCC 120 RN-1	ECCC 120 RN-2	ECCC 120 RN-3	ECCC 120 RN-4	ECCC 120 RN-5	ECCC 120 RN-6	ECCC 120 RN-7	ECCC 120 RN-8	ECCC 120 RN-9	ECCC 120 RN-10	Mean % Recovery	RSD
pH	6.18	5.56	6.08	5.85	6.03	7.33	6.18	6.66	5.81	6.92		
pH Study Mean	6.2	5.57	6	5.8	5.98	7.18	6.03	6.41	5.72	6.81		
AD	0.02	0.01	0.08	0.05	0.05	0.15	0.15	0.25	0.09	0.11		
% Recovery	100	100	101	101	101	102	102	104	102	102	101	1.23
Cond	15.6	5.4	6.2	5.1	9.8	35.9	4.8	9.4	6	24.6		
Cond Study Mean	15.6	5.1	5.8	4.78	9.5	35	4.3	8.2	5.6	24		
AD	0.00	0.3	0.4	0.3	0.3	0.9	0.5	1.2	0.4	0.6		
% Recovery	100	106	107	107	103	103	112	115	107	103	107	4.18
Ca	1.426	0.1599	0.3164	0.1587	0.2779	4.051	0.1518	0.7564	0.1552	1.549		
Ca Study Mean	1.42	0.158	0.31	0.162	0.282	4.05	0.16	0.749	0.158	1.53		
% Recovery	100	101	102	98	99	100	95	101	98	101	99	2.17
Na	0.6903	0.2728	0.1521	0.1974	0.8092	2.058	0.0716	0.1212	0.1766	0.9458		
Na Study Mean	0.691	0.273	0.15	0.19	0.8	2	0.071	0.12	0.179	0.953		
% Recovery	100	100	101	104	101	103	101	101	99	99	101	1.58
K	0.2974	0.0201	0.0622	0.0193	0.0423	0.4948	0.0312	0.0487	0.0438	0.2248		
K Study Mean	0.308	0.02	0.065	0.02	0.045	0.499	0.03	0.05	0.047	0.23		
% Recovery	97	101	96	97	94	99	104	97	93	98	97	3.24
Mg	0.2288	0.0395	0.0925	0.0421	0.1731	0.6685	0.0266	0.1241	0.0361	0.2533		
Mg Study Mean	0.227	0.039	0.089	0.041	0.172	0.677	0.027	0.121	0.035	0.252		
% Recovery	101	101	104	103	101	99	99	103	103	101	101	1.78
Cl	0.3899	0.4727	0.2163	0.3318	1.4535	0.6831	0.0881	0.149	0.1808	0.3028		
Cl Study Mean	0.38	0.466	0.21	0.32	1.41	0.654	0.092	0.15	0.18	0.291		
% Recovery	103	101	103	104	103	104	96	99	100	104	102	2.62
SO_4	2.5379	0.307	0.6533	0.419	0.6083	1.8273	0.4236	1.0396	0.5033	2.6969		
SO_4 Study Mean	2.5	0.31	0.65	0.417	0.6	1.86	0.43	1.03	0.5	2.68		
% Recovery	102	99	101	100	101	98	99	101	101	101	100	1.17
NO_3-N	0.275	0.144	0.167	0.137	0.144	0.022	0.124	0.121	0.255	0.437		
NO_3-N Study Mean	0.265	0.14	0.162	0.134	0.141	0.023	0.122	0.118	0.247	0.429		
% Recovery	104	103	103	103	102	95	102	102	103	102	102	2.59
NH_3-N	0.057	0.096	0.197	0.174	0.118	0.020	0.247	0.158	0.239	0.859		
NH_3-N Study Mean	0.052	0.09	0.188	0.172	0.117	0.017	0.243	0.155	0.237	0.848		
% Recovery	110	107	105	101	101	117	102	102	101	101	105	5.08

Table 13. ECCC 120 PT Results Assessment – Continued

ECCC Sample ID	Description	Result ng/L	Converted to µg/L	Hg Study Mean µg/L	% Recovery
HG120-1	Hg PT rcv 6/7/22 comes brominated	109.623	**0.110**	0.103	106
HG120-2	Hg PT rcv 6/7/22 comes brominated	42.954	**0.043**	0.047	91
HG120-3	Hg PT rcv 6/7/22 comes brominated	66.281	**0.066**	0.068	97
HG120-4	Hg PT rcv 6/7/22 comes brominated	1.578	**0.002**	0.004	NA
HG120-5	Hg PT rcv 6/7/22 comes brominated	22.642	**0.023**	0.025	91

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. Results for Ca, Mg, Na, K, Cl, SO_4, NO_3-N, NH_3-N, and PO_4 have units of mg/L and conductivity has units of µS/cm. Slight positive bias for conductivity values, but the NAL uses the absolute difference (AD) calculation for values under 10 µS/cm and those are all acceptable. A few high values for NH_3-N, but these are also close to the MDL.

Table 14. ECCC 121 PT Results Assessment

	ECCC 121 RN-01	ECCC 121 RN-02	ECCC 121 RN-03	ECCC 121 RN-04	ECCC 121 RN-05	ECCC 121 RN-06	ECCC 121 RN-07	ECCC 121 RN-08	ECCC 121 RN-09	ECCC 121 RN-10	Mean % Recovery	RSD
pH	6.96	6.98	6.72	6.97	5.36	5.34	5.59	6.85	5.69	7.18		
pH Study Mean	6.9	6.83	6.53	6.8	5.44	5.34	5.6	6.75	5.62	7.13		
AD	0.06	0.15	0.19	0.17	0.08	0.00	0.01	0.10	0.07	0.05		
% Recovery	101	102	103	103	99	100	100	101	101	101	101	1.33
Cond	24.6	15.1	10.5	23.5	5.6	4.8	4.4	10.1	5.2	34.4		
Cond Study Mean	24.2	14.7	10.3	22.9	5.35	4.6	4.43	9.9	5.2	33.3		
AD	0.4	0.4	0.2	0.6	0.3	0.2	0.0	0.2	0.0	1.1		
% Recovery	102	103	102	103	105	104	99	102	100	103	102	1.66
Ca	2.21	1.79	0.651	2.26	0.117	0.117	0.106	1.5	0.11	3.58		
Ca Study Mean	2.18	1.78	0.663	2.25	0.119	0.118	0.107	1.51	0.11	3.73		
% Recovery	101	101	98	100	98	99	99	99	100	96	99	1.54
Na	1.56	0.665	0.452	0.397	0.206	0.0443	0.105	0.25	0.239	1.76		
Na Study Mean	1.56	0.66	0.45	0.39	0.21	0.05	0.11	0.25	0.234	1.78		
% Recovery	100	101	100	102	98	89	95	100	102	99	99	4.07
K	0.37	0.191	0.061	0.124	0.0207	0.0362	0.0259	0.028	0.023	0.408		
K Study Mean	0.363	0.19	0.065	0.127	0.02	0.03	0.023	0.03	0.023	0.42		
% Recovery	102	101	94	98	104	121	113	93	100	97	102	8.34
Mg	0.568	0.158	0.215	0.328	0.0344	0.0245	0.0261	0.0628	0.0341	0.601		
Mg Study Mean	0.568	0.156	0.216	0.325	0.031	0.022	0.025	0.062	0.033	0.627		
% Recovery	100	101	100	101	111	111	104	101	103	96	103	4.78
Cl	1.08	0.293	0.785	0.549	0.35	0.0577	0.158	0.341	0.295	1.51		
Cl Study Mean	1.03	0.3	0.76	0.54	0.35	0.06	0.17	0.34	0.31	1.43		
% Recovery	105	98	103	102	100	96	93	100	95	106	100	4.24
SO_4	2.09	1.34	0.68	2.76	0.384	0.344	0.418	0.321	0.565	2.48		
SO_4 Study Mean	2.01	1.29	0.68	2.74	0.4	0.35	0.42	0.34	0.57	2.42		
% Recovery	104	104	100	101	96	98	100	94	99	102	100	3.14
NO_3-N	0.071	0.071	0.195	0.293	0.154	0.175	0.134	0.094	0.121	0.173		
NO_3-N Study Mean	0.07	0.07	0.189	0.284	0.152	0.173	0.131	0.097	0.12	0.171		
% Recovery	102	101	103	103	101	101	102	97	101	101	101	1.56
NH_3-N	0.001	0.004	0.185	0.426	0.129	0.136	0.177	-0.002	0.151	0.003		
NH_3-N Mean	N/A	N/A	0.185	0.429	0.134	0.137	0.181	N/A	0.155	N/A		
% Recovery	N/A	N/A	100	99	96	99	98	N/A	97	N/A	98	1.35

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. Results for Ca, Mg, Na, K, Cl, SO_4, NO_3-N, NH_3-N, and PO_4 have units of mg/L and conductivity has units of µS/cm. A few samples (05, 06, 07) exhibited high recovery of either Na, K, or Mg. These 10 samples were run on the ICP in small batches over a few days to help account for potential daily bias. Samples RN-05 to RN-07 were run on the same day and an unidentified factor could have caused this high bias.

13.2. WMO Results

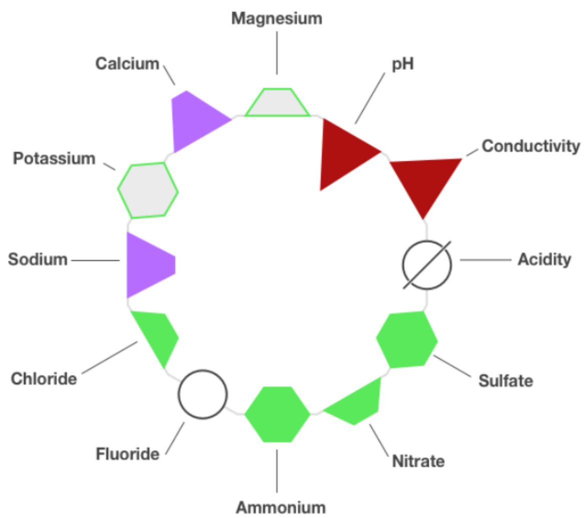

Figure 10. WMO PT Results Diagrams and Keys (not actual study results)

DQO – Data Quality Objective; "Qualitative and quantitative statements of the overall level of uncertainty that a decision-maker will accept in results or decisions based on environmental data. DQOs provide the statistical framework for planning and managing environmental data operations consistent with user's needs."

(U.S. EPA, 1997) https://qasac-americas.org/files/6-quality-assurance-quality-control.pdf

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 (e.g. see sulfate). For a measurement within the IQR that fails to meet the DQO, the green hexagon has a gray fill (e.g. 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 pseudo-standard deviation. A measurement that is outside of the median ±1 standard deviation 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.

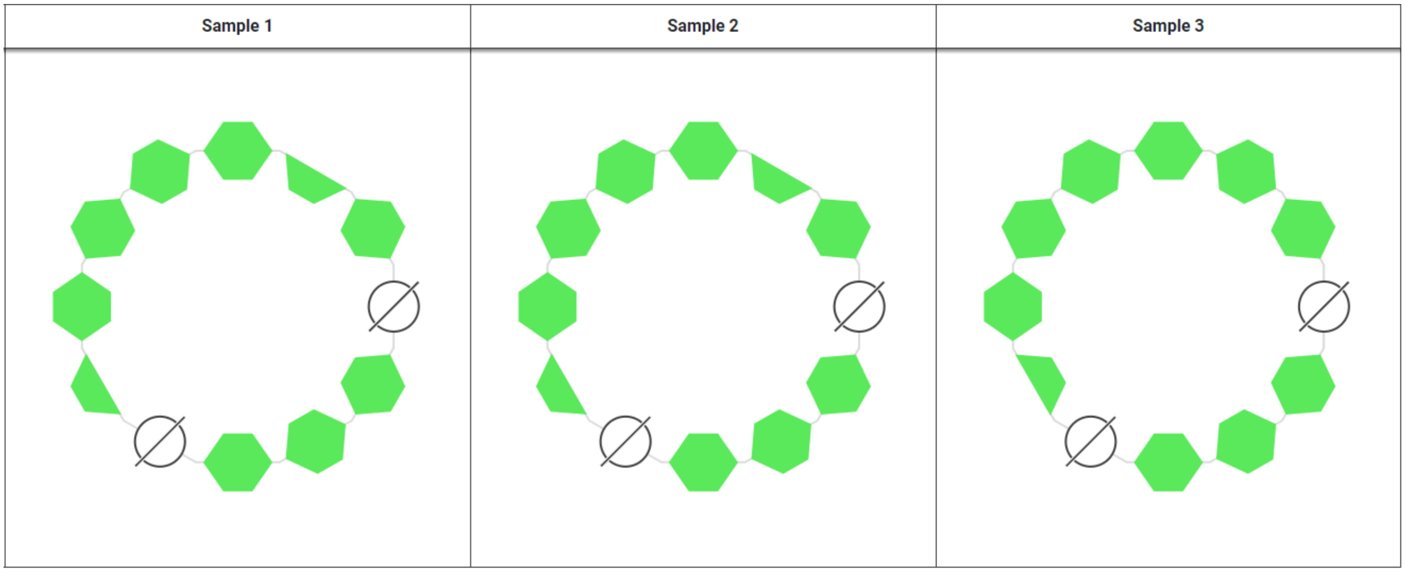

Figure 11. Results from WMO Study 65 –all values have results of satisfactory or higher and meet the DQOs.

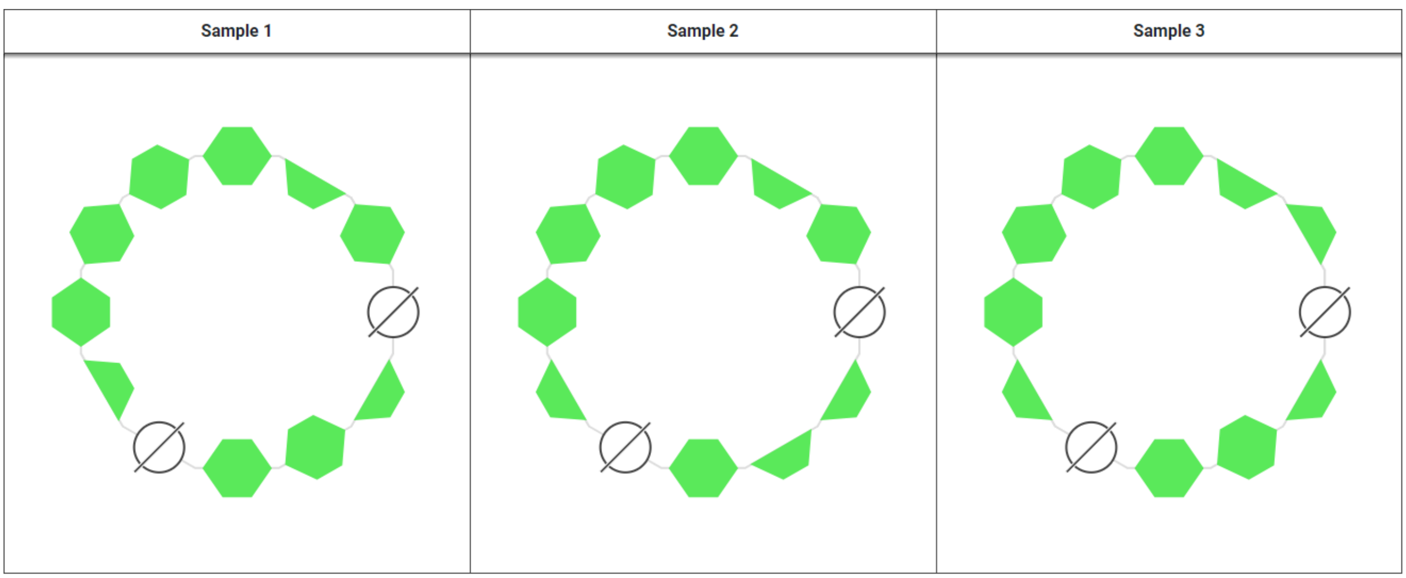

Figure 12. Results from WMO Study 66 –all values have results of satisfactory or higher and meet the DQOs.

Table 15. WMO 65 PT Results Assessment – May 2022

Date Received	Sample ID	LIMS ID	pH	Cond	Ca	Na	K	Mg	Cl	SO_4	NO_3	NH_4
5/23/2022	WMO65-1	22002510	4.73	20.8	0.269	1.111	0.214	0.117	2.074	1.936	0.972	0.384
TV Final			4.77	20.8	0.267	1.109	0.213	0.117	2.021	1.921	0.966	0.382
% of TV			99	100	101	100	100	100	103	101	101	101
		Difference WSLH - TV	-0.04	0.0	0.002	0.002	0.001	0.000	0.053	0.015	0.006	0.002
5/23/2022	WMO65-2	22002511	4.66	22.2	0.234	1.018	0.178	0.118	1.649	2.403	1.237	0.450
TV Final			4.71	21.8	0.233	1.020	0.178	0.118	1.594	2.389	1.219	0.449
% of TV			99	102	100	100	100	100	103	101	101	100
		Difference WSLH - TV	-0.05	0.4	0.001	-0.002	0.000	0.000	0.055	0.014	0.018	0.001
5/23/2022	WMO65-3	22002512	4.97	9.6	0.152	0.146	0.084	0.053	0.276	1.134	0.701	0.286
TV Final			5.02	9.4	0.151	0.143	0.082	0.053	0.294	1.123	0.711	0.286
% of TV			99	102	101	102	102	100	94	101	99	100
		Difference WSLH - TV	-0.05	0.20	0.001	0.003	0.002	0.000	-0.018	0.011	-0.010	0.000

TV = true value.

Table 16. WMO 66 PT Results Assessment – November 2022

Date Received	Sample ID	LIMS ID	pH	Cond	Ca	Na	K	Mg	Cl	SO_4	NO_3	NH_4
11/22/2022	WMO66-1	22005185	4.54	16.1	0.115	0.153	0.028	0.033	0.270	1.378	1.066	0.227
TV Final			4.59	15.6	0.114	0.153	0.031	0.033	0.283	1.346	1.053	0.220
% of TV			99	103	101	100	90	100	95	102	101	103
		Difference WSLH - TV	-0.050	0.500	0.001	0.000	-0.003	0.000	-0.013	0.032	0.013	0.007
11/22/2022	WMO66-2	22005186	4.40	43.2	0.778	1.294	0.289	0.247	2.137	5.427	4.146	1.354
TV Final			4.45	42.9	0.781	1.306	0.287	0.244	2.070	5.294	4.016	1.320
% of TV			99	101	100	99	101	101	103	103	103	103
		Difference WSLH - TV	-0.050	0.300	-0.003	-0.012	0.002	0.003	0.067	0.133	0.130	0.034
11/22/2022	WMO66-3	22005187	4.80	13.7	0.167	0.472	0.110	0.077	0.816	1.486	0.630	0.251
TV Final			4.85	13.2	0.163	0.472	0.106	0.076	0.791	1.443	0.632	0.247
% of TV			99	104	102	100	104	101	103	103	100	102
		Difference WSLH - TV	-0.050	0.500	0.004	0.000	0.004	0.001	0.025	0.043	-0.002	0.004

TV = true value.

Overall good results for both spring and fall data sets. No analytes of concern.

13.3. USGS Inter Comparison Results for 2022 data (per Noel Deyette – QAAG April 2023)

- Positive bias was observed for H^+, Ca and NH_4. Negative bias was observed for K, Cl, and SO_4.
- The NAL had the lowest variability for the NTN analytes amongst the participating labs.
- A negative bias of 0.38 ng/L was measured for Hg. Variability was 220% (i.e. 2.2 times) the overall variability displayed by all participating labs combined.
    - Much of the variability is explained by the now-rejected practice of aliquoting the PT for preparation.

13.4. USGS SRS Results

Table 17. USGS SRS Spring Results Assessment

USGS SRS Spring 2022				
Sample ID	**Analyte**	**Reported Value**	**True Value**	**% Recovery**
P-78	pH	3.83	3.9	98
	Conductivity	70.4	69.6	101
	Ca	0.575	0.576	100
	K	0.863	0.928	93
	Mg	0.066	0.07	94
	Na	0.073	0.077	95
	Cl	7.361	7.41	99
	SO_4	0.351	0.42	84
N-153	NO_3-N	0.41	0.396	104
	NH_3-N	0.066	0.066	100
	OPO_4	0.087	0.088	99
Hg-74	THg	0.036	0.035	102

Overall, excellent results. A slight negative bias for the cations. Quite low recovery for SO_4, but it was run three times with similar results. Looking across all labs, there was a large range of sulfate values (**Table 18** below).

Table 18. Table of results from all labs for SO_4 on USGS SRS sample P-78.
https://bqs.usgs.gov/srs_study/reports/analyte_report.php

Lab ID	Method	RV	Z-Value	% Error
1	07	0.381	-0.35	-9.29
2	07	0.495	0.66	17.86
8	07	1.21	6.99	188.10
23	07	<5.0	--	--
38	07	0.42	0.00	0.00
42	07	4.98	40.35	1085.71
64	07	0.384	-0.32	-8.57
110	07	0.421	0.01	0.24
138	07	0.405	-0.13	-3.57
151	07	0.528	0.96	25.71
180	07	0.346	-0.65	-17.62
193	07	0.36	-0.53	-14.29
224	07	0.491	0.63	16.90
321	07	0.61	1.68	45.24
323	07	0.63	1.86	50.00
536	07	0.64	1.95	52.38
552	07	0.37	-0.44	-11.90
590	07	0.534	1.01	27.14
601	06	0.401	-0.17	-4.52
604	07	0.391	-0.26	-6.90
615	07	0.351	-0.61	-16.43
619	07	0.29	-1.15	-30.95

Table 19. USGS SRS Fall Results Assessment

USGS SRS Fall 2022				
Sample ID	Analyte	Reported Value	True Value	% Recovery
P-79	pH	5.12	5.07	101
	Conductivity	23.4	23.5	100
	Ca	1.83	1.82	101
	K	0.734	0.72	102
	Mg	0.104	0.105	99
	Na	0.097	0.1	97
	Cl	4.71	4.65	101
	SO_4	0.481	0.487	99
N-155	NO_3-N	0.468	0.456	103
	NH_3-N	0.09	0.09	100
	OPO_4	0.12	0.123	98
Hg-745	THg	0.021	0.022	95

Overall, very good recoveries for all analytes. No values of concern.

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 (or fewer) samples and the precision of the duplicate results is evaluated. Duplicate samples are chosen at random and must be performed at a frequency of 10%. Refer to **Table 20** 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 2022 are provided in **Table 21** and show remarkably good precision for a large number of duplicates. Note – the exceedances listed below are failures based on the criteria in **Table 20**, 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 criteria are rerun if possible.

Table 20. Sample and Duplicate Scenarios and Criteria

Sample Result	Duplicate Result	Calculation	Acceptance 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 21. Analytical Duplicates and Percent Exceedances in 2022

Platform	# Replicates in 2022	# Failures in 2022	% Exceedance (prior to reanalysis)	# Reanalyzed successfully
FIA AMoN	348	0	0.000%	0
FIA NTN	1099	8	0.007%	8
ICP-OES	1172	5	0.004%	5
IC	1141	2	0.001%	2
pH/Conductivity	1035	25	0.024%	24

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 were successful, with the exception of 1 pH/conductivity sample due to failure not being noticed during the run.

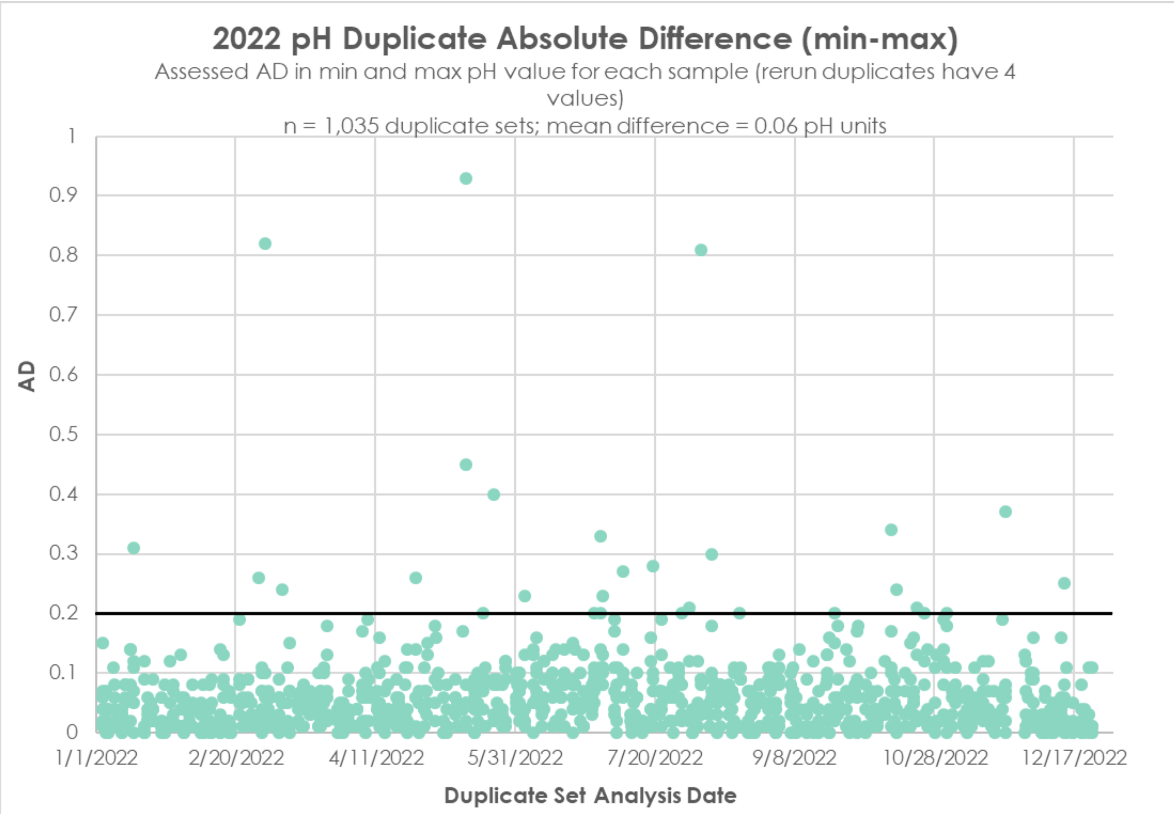

Figure 13. Absolute differences between minimum and maximum pH values from duplicate analyses for a particular sample. Line at 0.2 is the AD acceptance criteria for pH.

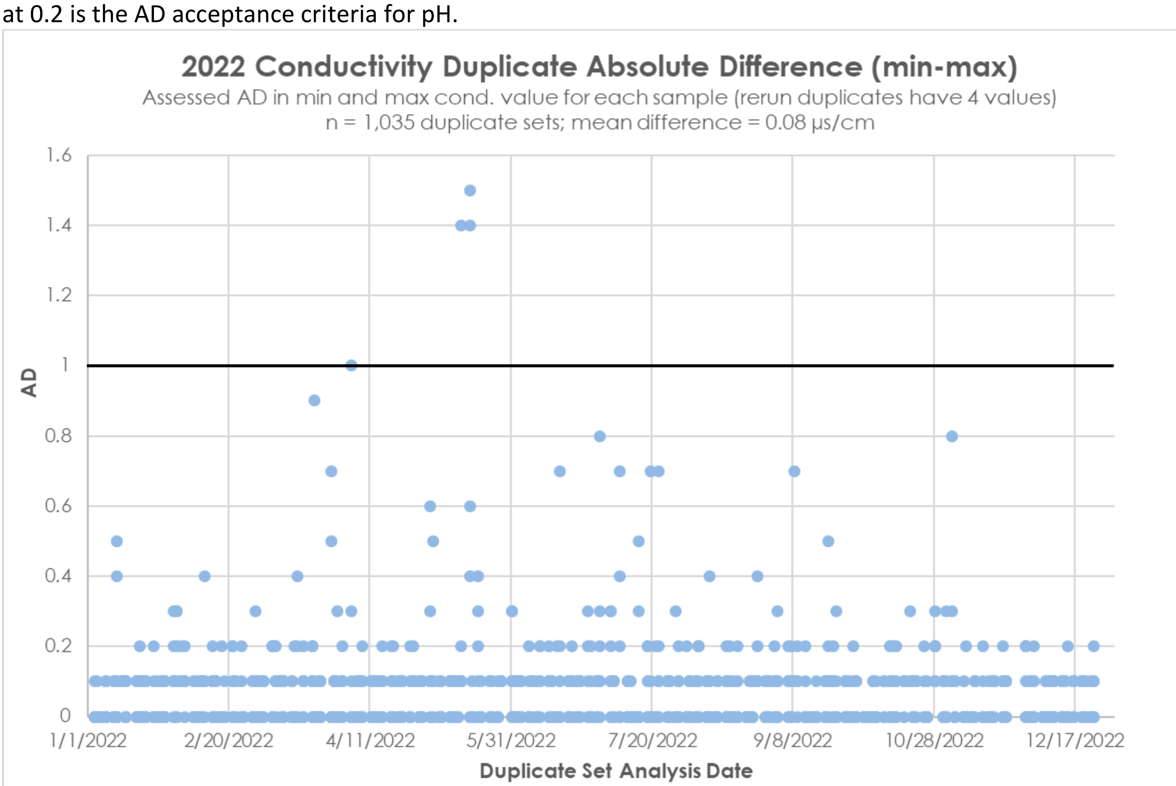

Figure 14. Absolute differences between minimum and maximum conductivity duplicate values for a particular sample. Line at 1.0 is the AD acceptance criteria for conductivity.

NOTE – The duplicate graphs below show duplicates above 10% RPD (black line) 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 20**.

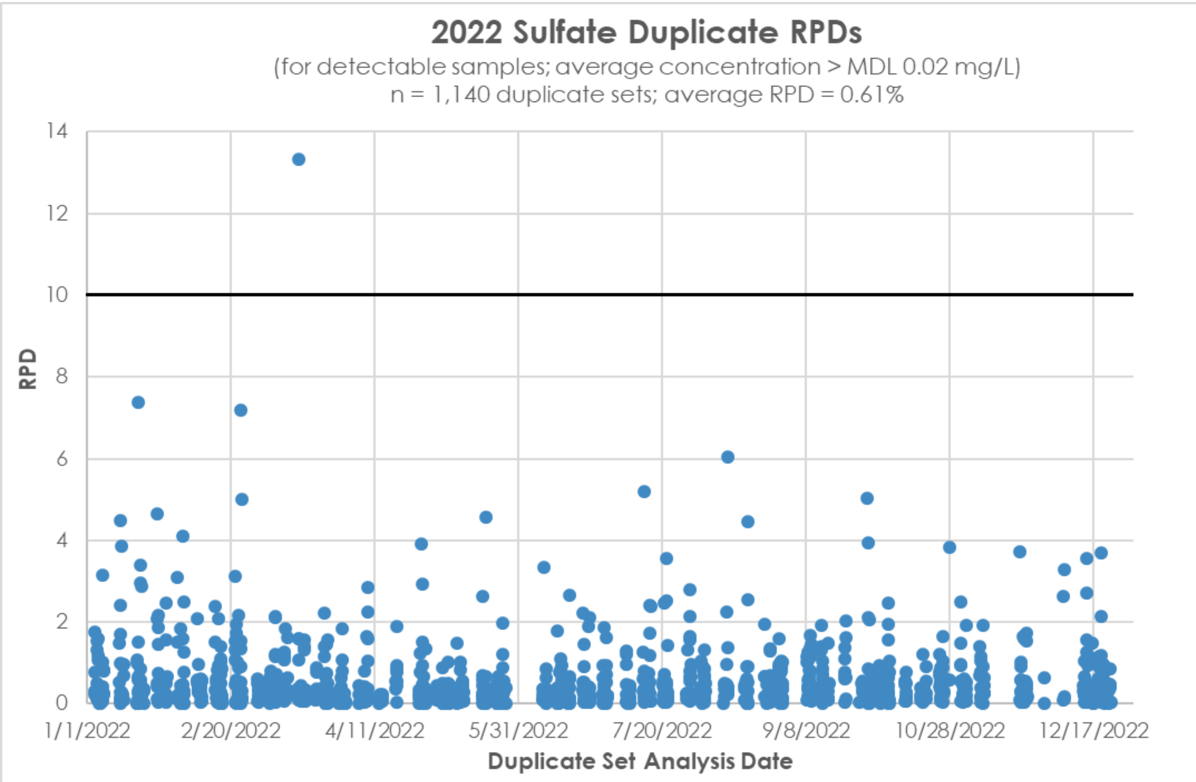

Figure 15. Sulfate (IC) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

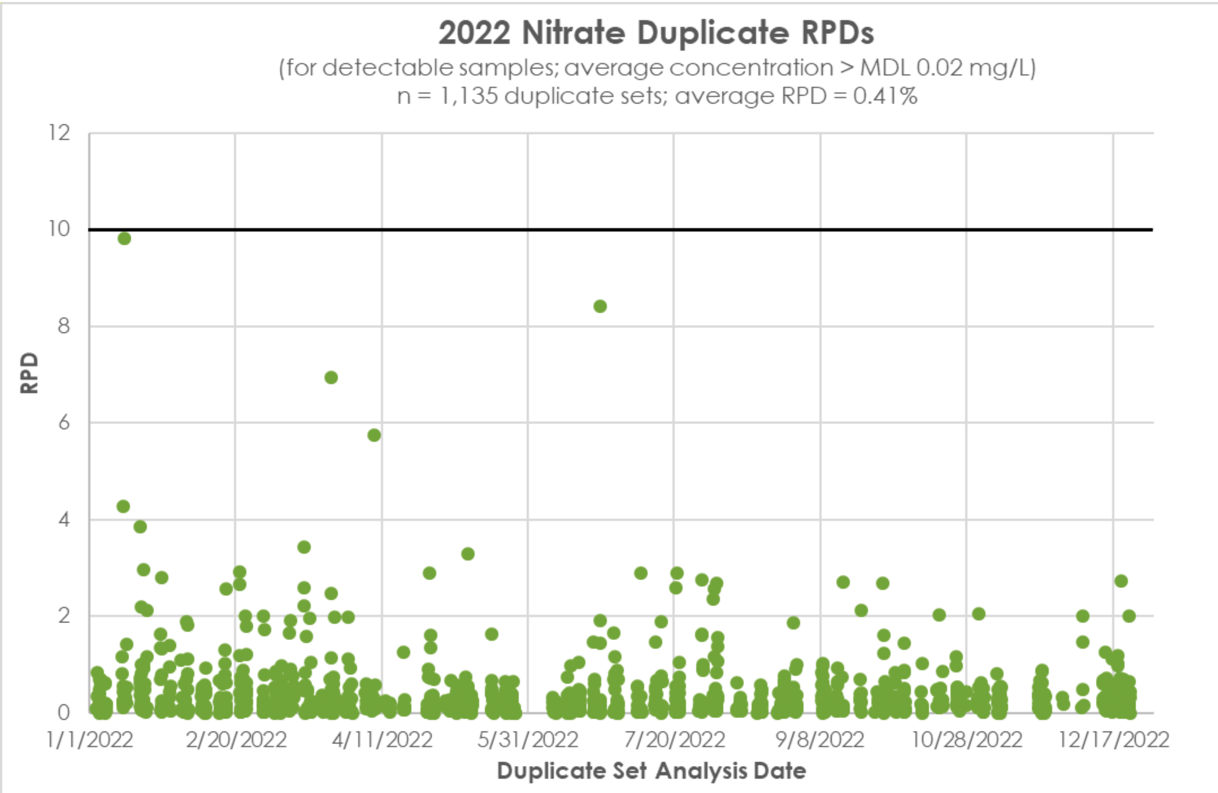

Figure 16. Nitrate (IC) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

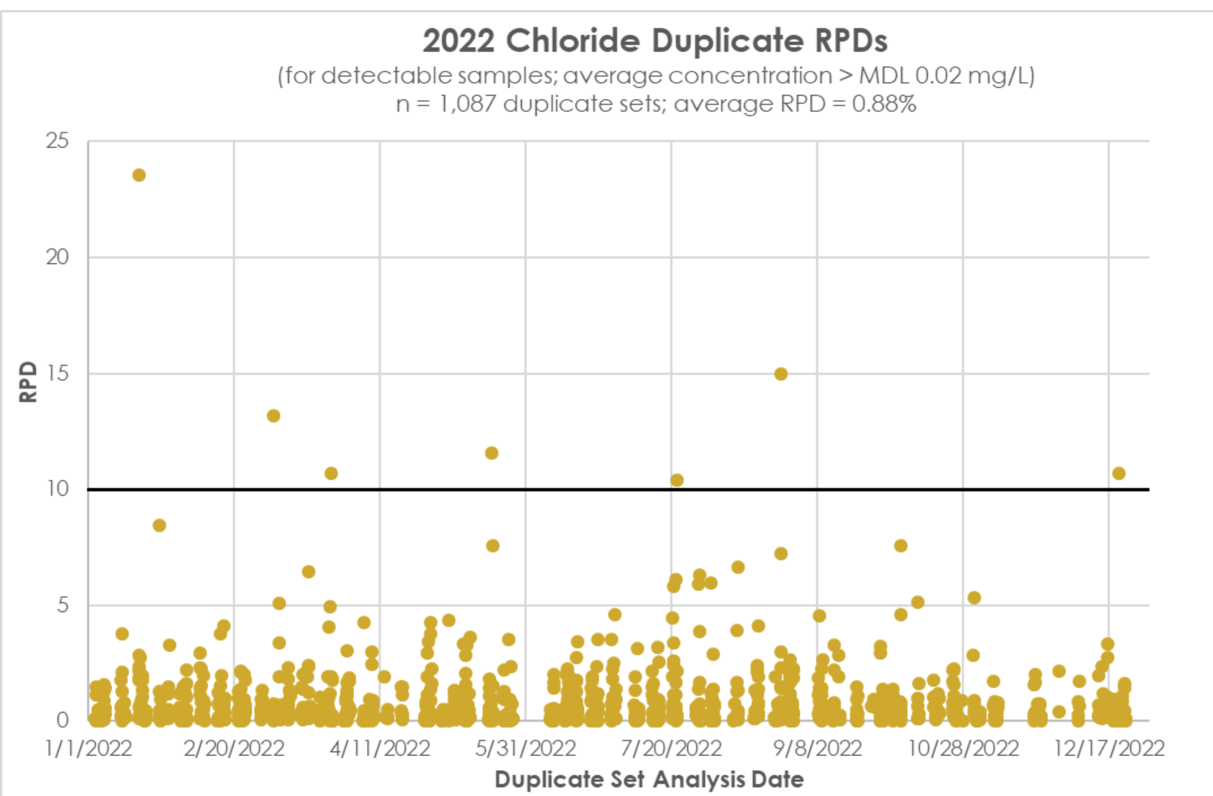

Figure 17. Chloride (IC) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

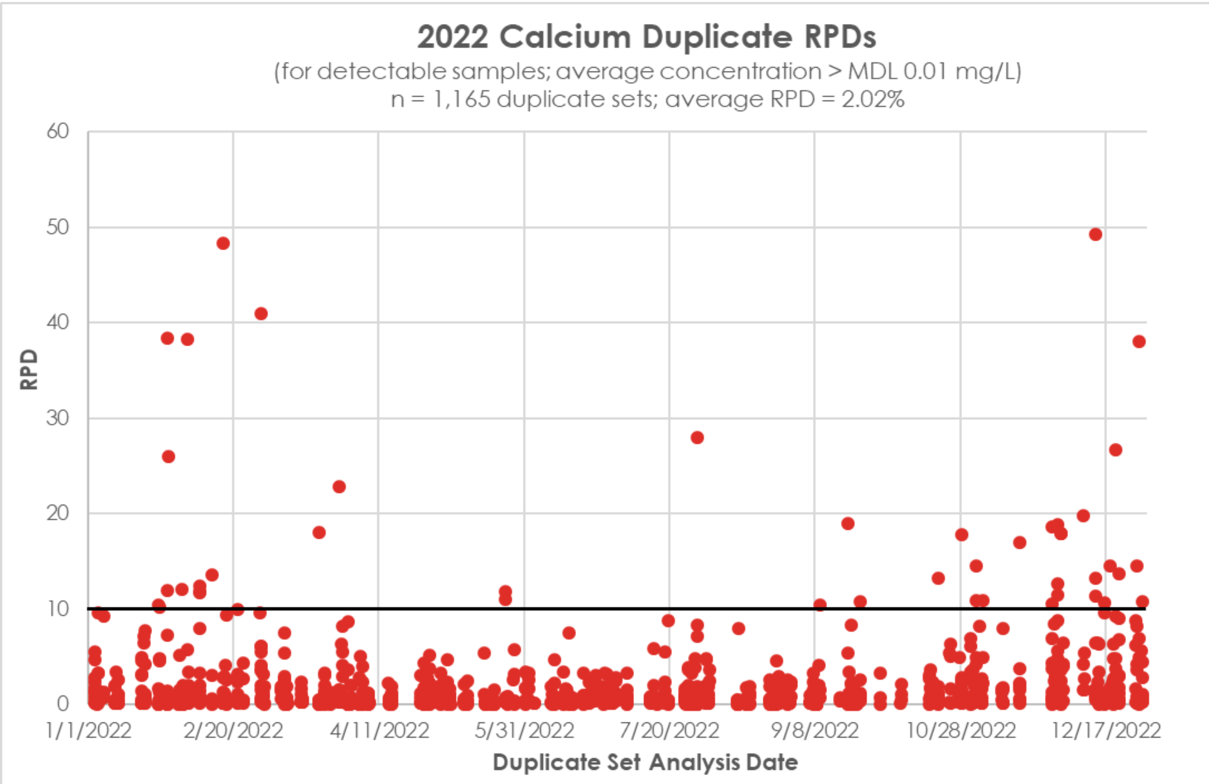

Figure 18. Calcium (ICP) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

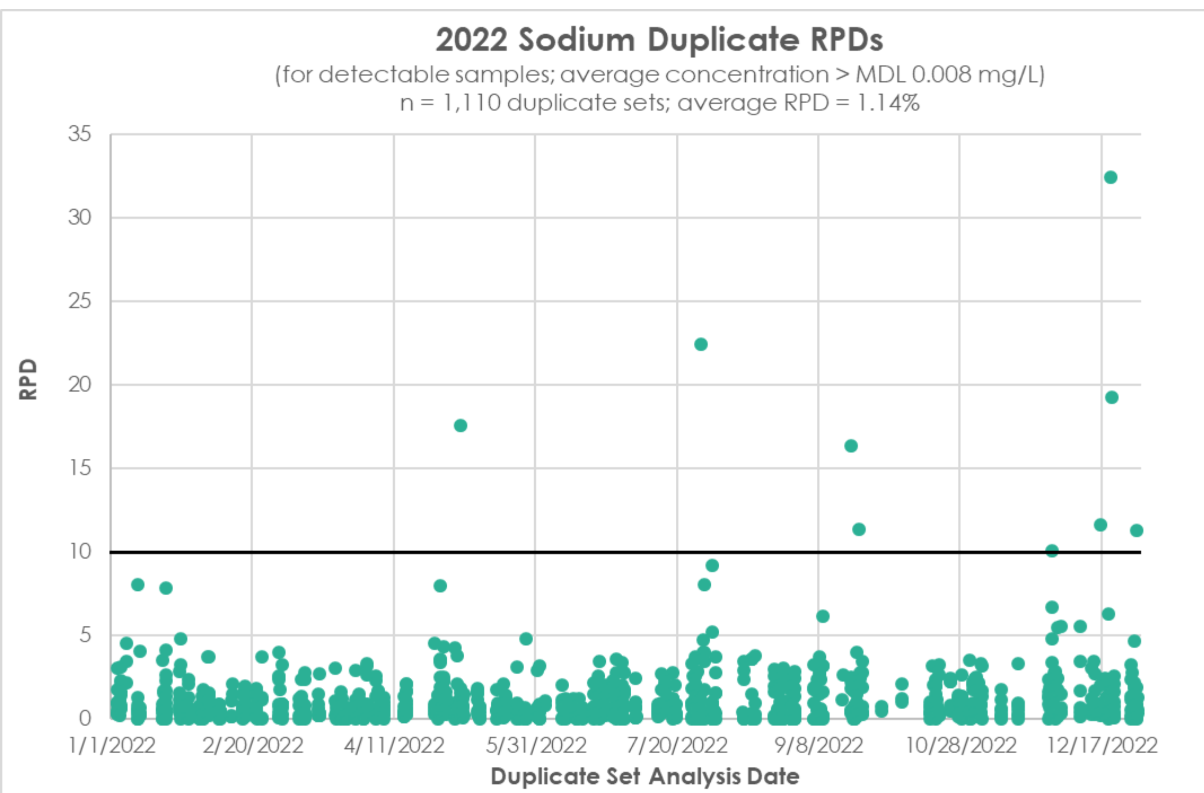

Figure 19. Sodium (ICP) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

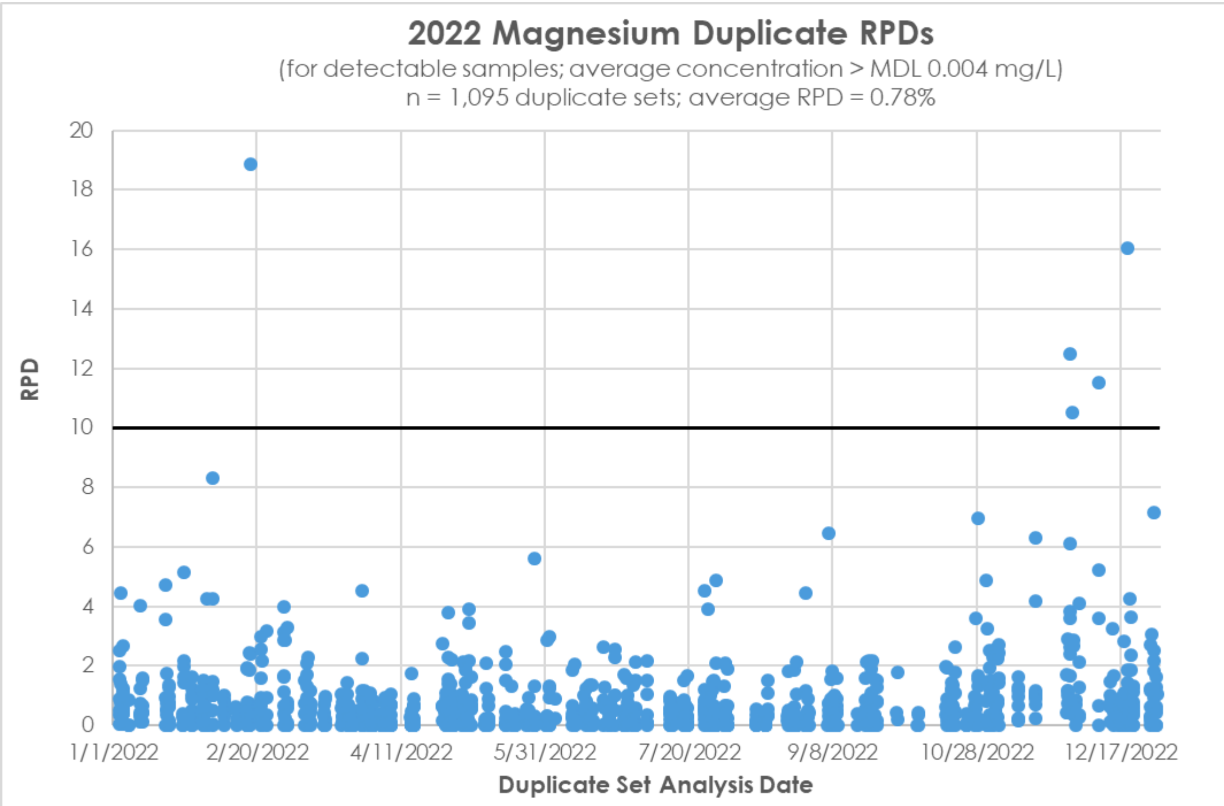

Figure 20. Magnesium (ICP) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

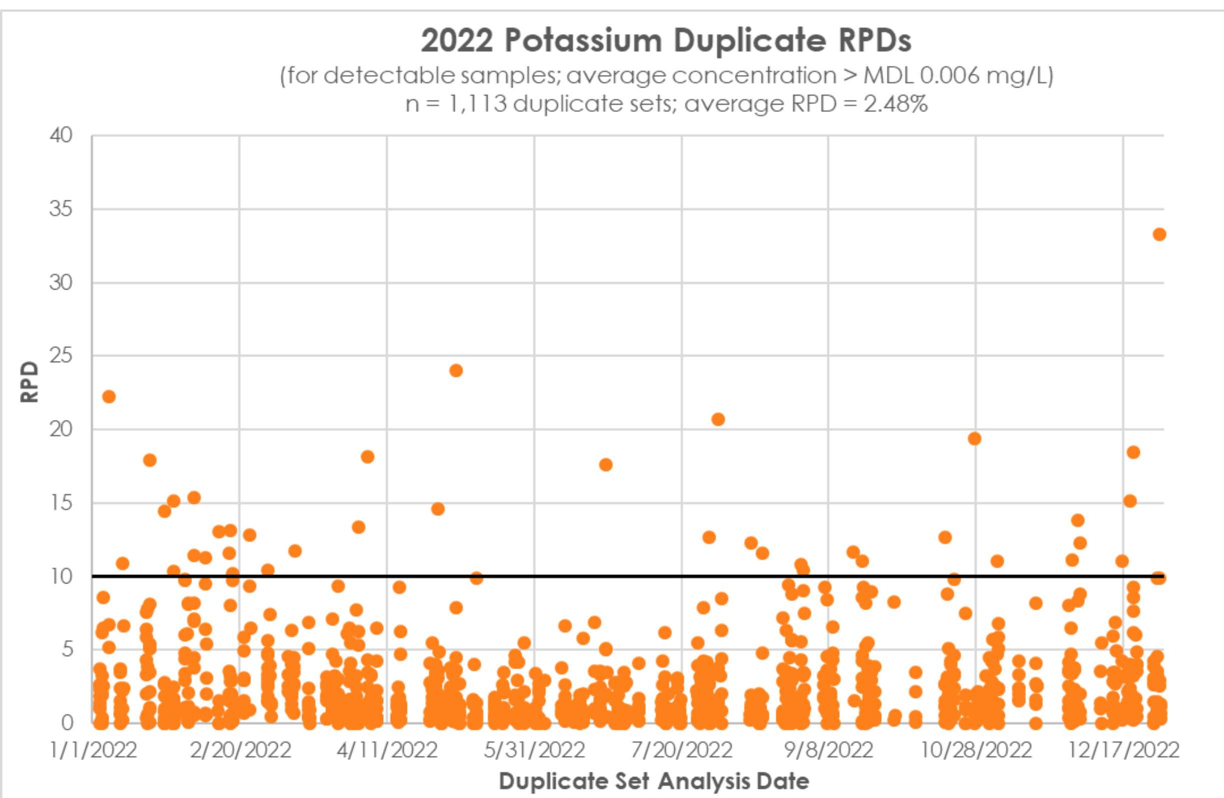

Figure 21. Potassium (ICP) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

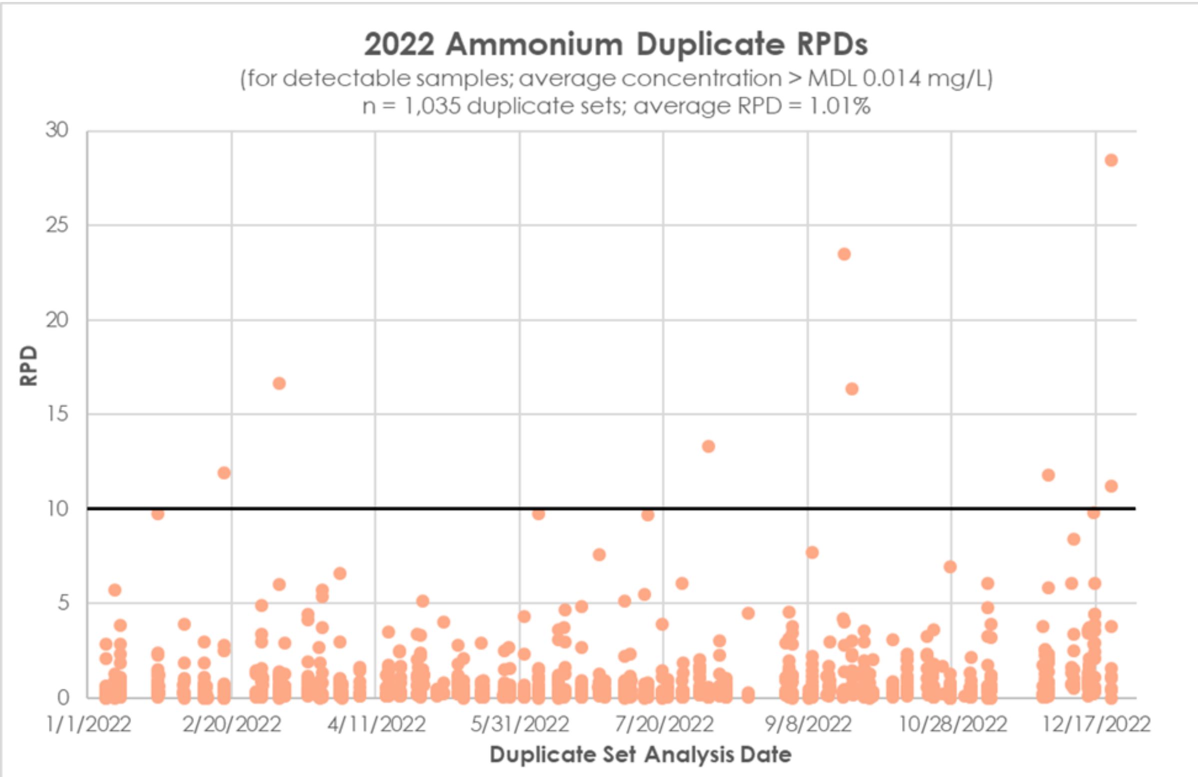

Figure 22. Ammonium (FIA) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

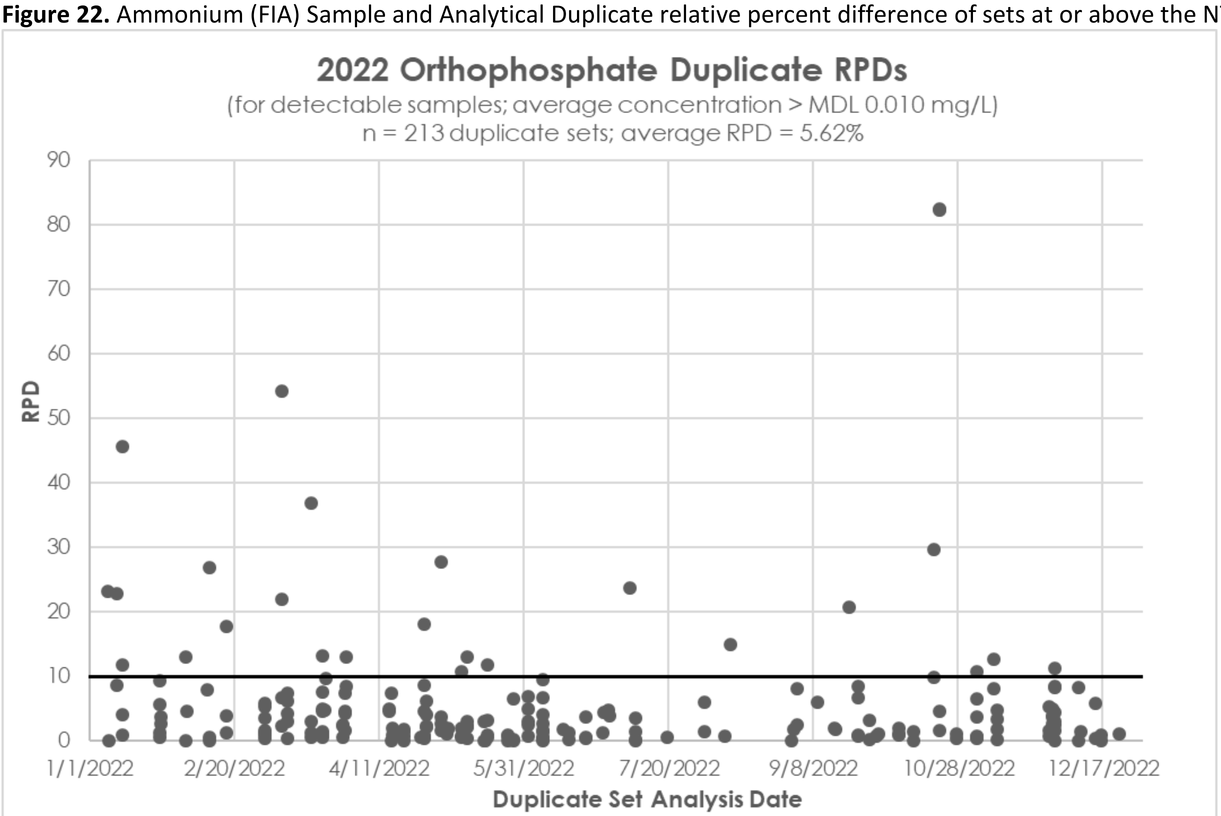

Figure 23. Orthophosphate (FIA) Sample and Analytical Duplicate relative percent difference of sets at or above the network detection limit. Note very few duplicates are displayed here because although over 1000 sets were analyzed only 213 were at or above the MDL.

14.2. MDN and MLN Analytical Sample Matrix Spikes and Duplicates

A second and third aliquot from a randomly chosen MDN total mercury sample (>400 mL) are analyzed with a spike level of 15 ng Hg/L and the precision between the two results is evaluated. A matrix spike (MS) and matrix spike duplicate (MSD) pair are prepared for every batch of 10 (or fewer) samples. Matrix spikes must recover between 75%-125% and the two spike results must have an RPD <24% (per EPA Method 1631). Refer to **Table 22** for all MDN QA/QC samples and associated criteria.

Table 22. MDN Analytical Limits and Batch Run Sample Sequence

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

For Litterfall total mercury, a duplicate and matrix spike are analyzed every batch of 10 (or fewer) samples. Samples are chosen at random. Duplicates must have an RPD <20%. Litterfall samples are analyzed with a spike of 5 ng Hg. 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 recover between 80-120% and a blank must measure below the MDL. Please refer to **Table 23** for all Litterfall QA/QC samples and associated criteria.

Table 23. Litterfall Analytical Limits and Batch Run Sample Sequence

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

14.2.1. 2022 MDN and MLN MS/MSD Results

In 2022, there were no MS recovery failures and no MS/MSD failures associated with reported samples for MDN or MLN (Litterfall). Infrequent failures may occur due to instrument instability, matrix interference, or analyst errors. In such a case, all samples in the affected batch are promptly reanalyzed and documented. The mean recovery for accepted matrix spikes was 102.9% for MDN; the mean RPD was 1.25%. All matrix spikes met criteria for MLN (Litterfall) in the 2021-2022 season.

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. Mercury levels in the 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 2022, results for 285 DLRBs were reported. No LRBs measured above the method detection limit (MDL) of 0.2 ng/L in 2022. The average LRB result was 0.0097 ng/L.

14.4. Digested Quality Control Standards (DQCS)

Each batch of MDN samples includes a spiked control sample (8 ng/L), using a 2nd source standard (i.e. different than the standard used for the calibration). 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. DQCS recoveries must be between 80%-120% for the run to be considered within control limits.

Each MLN-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 passing (TV = 43.2 ng/g).

14.4.1. DQCS Results

In 2022, 96 DQCS samples were reported for MDN. One of the QCS samples exceeded the control limit but was reanalyzed and passed. The average recovery was 96.8%. All NIST 1515 samples for MLN-Litterfall met criteria in the 2021-2022 season.

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 NAL QAP. Also, **Tables 25-28** show the run sequences for both the NTN and AMoN instruments and include all applicable criteria.

Table 24. Analytical NTN and AMoN Limits for Internal QC Solutions.

NADP Combined NTN/AMoN Control Limits						
Version 39		6/12/2024	Round to 3 decimal places per rounding rules below			
ICP	ID	Criteria	Ca	K	Mg	Na
TV (Acceptance Range)	FBFB2101	±MDL	0.000 (-0.008 to 0.008)	0.000 (-0.006 to 0.006)	0.000 (-0.004 to 0.004)	0.000 (-0.008 to 0.008)
	FR50240#	±MDL	0.130 (0.122 to 0.138)	0.022 (0.016 to 0.028)	0.023 (0.019 to 0.027)	0.060 (0.052 to 0.068)
	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)
	FMDL240#	70-130%	0.028 (0.020 to 0.036)	0.010 (0.007 to 0.013)	0.012 (0.008 to 0.016)	0.020 (0.014 to 0.026)
FIA	ID	Criteria	NH_4	OPO_4		
TV (Acceptance Range)	FBFB2101	±MDL	0.000 (-0.014 to 0.014)	0.000 (-0.010 to 0.010)		
	FR50240#	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)		
	FMDL240#	70-130%	0.029 (0.020 to 0.038)	0.024 (0.017 to 0.031)		
IC	ID	Criteria	Cl	SO_4	NO_3	
TV (Acceptance Range)	FBFB2101	±MDL	0.000 (-0.020 to 0.020)	0.000 (-0.020 to 0.020)	0.000 (-0.020 to 0.020)	
	FR50240#	90-110%	0.100 (0.090 to 0.110)	0.958 (0.862 to 1.054)	0.898 (0.808 to 0.988)	
	FLFL2301	80-120%	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)	
	FMDL240#	70-130%	0.050 (0.035 to 0.065)	0.078 (0.055 to 0.101)	0.031 (0.022 to 0.040)	
AMoN	ID	Criteria	NH_4			
TV (Acceptance Range)	FBFB2101	±MDL	0.000 (-0.014 to 0.014)			
	FR50240#	90-110%	0.250 (0.225 to 0.275)			
	FLFL2101	80-120%	0.050 (0.040 to 0.060)			
	FMAM2101	90-110%	0.750 (0.675 to 0.825)			
	FMDL240#	70-130%	0.029 (0.020 to 0.038)			

Any analytical sample that has a result above the carryover limit for the platform will require the subsequent sample to be rerun to confirm that it was not affected. The LDR (linear dynamic range) is the concentration at which the analyte recovery is ≥ 90% and is utilized when an over range sample cannot be diluted. That result is only accepted (but qualified) if it is under the LDR.

Table 25. ICP Analytical Limits and Batch Run Sample Sequence

Sequence #	Sample/Control Type	Criteria
1	Calibration Blank (0.00 mg/L)	< MDL
2	Calibration Standard 1 (0.25 mg/L)	r value ≥ 0.995
3	Calibration Standard 2 (0.50 mg/L)	r value ≥ 0.995
4	Calibration Standard 3 (0.75 mg/L)	r value ≥ 0.995
5	Calibration Standard 4 (1.00 mg/L)	r value ≥ 0.995
6	Calibration Standard 5 (2.00 mg/L)	r value ≥ 0.995
7	Calibration Standard 6 (5.00 mg/L)	r value ≥ 0.995
8	FB (blank)	< MDL
9	FR50 (historical 50th percentile)	± MDL
10	FCRM (certified reference material)	85-115%/± MDL
11	FL (quality control standard low - second source)	80-120%
12	FMDL (method detection limit)	70-130%
13	FM (mid-level calibration standard)	90-110%
14	sample A	< highest standard
15	sample	< highest standard

16	sample	< highest standard
17	sample	< highest standard
18	sample	< highest standard
19	sample	< highest standard
20	sample	< highest standard
21	sample	< highest standard
22	sample	< highest standard
23	sample	< highest standard
24	sample A-Q (duplicate can be any of the first 10 samples)	use AD or RPD
25	FM (mid-level calibration standard)	90-110%
26	FB (continuing calibration blank)	< MDL

Table 26. NTN FIA Analytical Limits and Batch Run Sample Sequence

Sequence #	Sample/Control Type	Criteria
1	Calibration Standard 1 (3.177 mg/L NH_4; 1.600 mg/L PO_4)	r value ≥ 0.995
2	Calibration Standard 2 (1.059 mg/L NH4; 0.800 mg/L PO4)	r value ≥ 0.995
3	Calibration Standard 3 (0.530 mg/L NH4; 0.400 mg/L PO4)	r value ≥ 0.995
4	Calibration Standard 4 (0.106 mg/L NH4; 0.100 mg/L PO4)	r value ≥ 0.995
5	Calibration Standard 5 (0.053 mg/L NH4; 0.050 mg/L PO4)	r value ≥ 0.995
6	Calibration Standard 6 (0.026 mg/L NH4; 0.025 mg/L PO4)	r value ≥ 0.995
7	Calibration Blank (0.000 mg/L)	r value ≥ 0.995
8	FB (blank)	< MDL
9	FR50 (historical 50^{th} percentile)	90-110%
10	FM (mid-level calibration standard)	90-110%
11	FL (quality control standard low -second source)	80-120%
12	FMDL (method detection limit)	70-130%
13	FCRM (certified reference material)	85-115%
14	sample A	< highest standard
15	sample	< highest standard
16	sample	< highest standard
17	sample	< highest standard
18	sample	< highest standard
19	sample	< highest standard
20	sample	< highest standard
21	sample	< highest standard
22	sample	< highest standard
23	sample	< highest standard
24	sample A-Q (duplicate can be any of the first 10 samples)	use AD or RPD
25	FM (mid-level calibration standard)	90-110%
26	FB (continuing calibration blank)	< MDL

Table 27. IC Analytical Limits and Batch Run Sample Sequence

Sequence #	Analytical Protocol Run	Criteria
1	RINSE	N/A
2	RINSE	N/A
3	Calibration Standard 1 (0.015 mg/L)	r value ≥ 0.995
4	Calibration Standard 2 (0.025 mg/L)	r value ≥ 0.995
5	Calibration Standard 3 (0.050 mg/L)	r value ≥ 0.995
6	Calibration Standard 4 (0.100 mg/L)	r value ≥ 0.995
7	Calibration Standard 5 (0.250 mg/L)	r value ≥ 0.995
8	Calibration Standard 6 (0.750 mg/L)	r value ≥ 0.995
9	Calibration Standard 7 (2.00 mg/L)	r value ≥ 0.995
10	Calibration Standard 8 (3.00 mg/L)	r value ≥ 0.995
11	FB (blank)	< MDL
12	FR50 (historical 50th percentile)	90-110%
13	FL (quality control standard low -second source)	80-120%
14	FMDL (method detection limit)	70-130%
15	FCRM (certified reference material)	85-115%
16	sample A	< highest standard
17	sample	< highest standard
18	sample	< highest standard
19	sample	< highest standard
20	sample	< highest standard
21	sample	< highest standard
22	sample	< highest standard
23	sample	< highest standard
24	sample	< highest standard
25	sample	< highest standard
26	sample A-Q (duplicate can be any of the first 10 samples)	use AD or RPD
27	FM (mid-level calibration standard)	90-110%
28	FB (continuing calibration blank)	< MDL

Table 28. AMoN FIA Analytical Limits and Batch Run Sample Sequence

Sequence #	Sample/Control Type	Criteria
1	Calibration Standard 1 (6.354 mg/L)	r value ≥ 0.995
2	Calibration Standard 2 (3.177 mg/L)	r value ≥ 0.995
3	Calibration Standard 3 (1.059 mg/L)	r value ≥ 0.995
4	Calibration Standard 4 (0.530 mg/L)	r value ≥ 0.995
5	Calibration Standard 5 (0.265 mg/L)	r value ≥ 0.995
6	Calibration Standard 6 (0.106 mg/L)	r value ≥ 0.995
7	Calibration Standard 7 (0.053 mg/L)	r value ≥ 0.995
8	Calibration Standard 8 (0.026 mg/L)	r value ≥ 0.995
9	Calibration Standard 9 (0.000 mg/L)	r value ≥ 0.995
10	FB (blank)	<MDL

11	FR50 (historical 50th percentile)	90-110%
12	FL (quality control standard low -second source)	80-120%
13	FMAM (mid-level calibration standard)	90-110%
14	FCRM (certified reference material)	85-115%
15	FMDL (method detection limit)	70-130%
16	sample A	< highest standard
17	sample	< highest standard
18	sample	< highest standard
19	sample	< highest standard
20	sample	< highest standard
21	sample	< highest standard
22	sample	< highest standard
23	sample	< highest standard
24	sample	< highest standard
25	sample	< highest standard
26	sample A-Q (duplicate can be any of the first 10 samples)	use AD or RPD
27	FMAM (mid-level calibration standard)	90-110%
28	FB (continuing calibration blank)	<MDL

15. Supply QC

15.1. Overview of Supply QC

Each network within the NADP long-term monitoring program (NTN, MDN, MLN, AMoN) requires very specific sampling and processing supplies, which are all cleaned and prepared in the HAL laboratories 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. In order to verify that supplies are adequately clean, supply blanks are measured as outlined below. Lot testing protocols are listed in **Table 29**, and results for the numbers of samples in 2022 are shown in **Table 30** and **Table 31**.

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. In addition, one filter is blanked at the start or end of each day that filtration is performed and monthly for syringe filters (used to filter low-volume samples).

15.4. New Bottle, Bag, and Test Tube Testing

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

Table 29. New Lot Supply QC Sampling Protocols for NTN and MDN

NADP NTN and MDN Supply Lot Approval QC Frequency and Log In (Version 6 (2024) 6/12/2024)						
Item	**Solution**	**Amount & Frequency**	**Project**	**Client Number***	**LIMS Description**	**Rinse** Collection Bottle?**
BAG LOTS						
NTN Sample Bags	~150 mL MQ/~250 Spike	15/new lot (unless <2000 then 10)	New Sampling Bag Lot Check	Date Collected & Collector Initials	Bag Type, Lot #, Bag# (i.e. NTN Sample Bag Lot X 1of20)	Yes
NTN Bucket or Lid Bags	~150 mL MQ	5/new lot	Bag Blank Study	Date Collected & Collector Initials	Bag Type, Lot #, Bag# (i.e. NTN Bucket Bag Lot X 1of5)	Yes
BOTTLE LOTS						
NTN 60mL HDPE Bottles	~60mL MQ	10/new lot (unless <100 then 5)	NADP New Bottle Blanks	Date Collected & Collector Initials	Bottle Type, Lot #, Bottle# (i.e. 60mL NTN LotX 1of10)	No
NTN 1 Liter HDPE (New)	~150 mL MQ	10/new lot (unless <100 then 5)	NADP New Bottle Blanks	Date Collected & Collector Initials	Bottle Type, Lot #, Bottle# (i.e. 1L NTN LotX 1of10)	No
MDN PETG or PET 125 mL, 250 mL, 1L or 2L	20 mL 1% HCl + 100mL MQ	20/new lot from 10 boxes (unless <200 then 2%)	MDN Bottle Blanks	Date Collected & Collector Initials	Bottle Type, Lot #, BottleID, Bottle# (i.e. 250mL MDN LotX; 1of10)	No
FILTER LOTS						
NTN 47mm Disc Filters	60 mL MQ	20/New Lot min 2 boxes from lot	Filter Blank Lot Testing	Date Collected & Collector Initials	Lot, Box#, Filter #, Brand, filter type	Yes
NTN Syringe Filters	20 mL MQ	5 per lot of 150	Filter Blank Lot Testing	Date Collected & Collector Initials	Lot, Box#, Filter #, Brand, filter type	Yes
NTN Syringes	20 mL MQ	5 per lot of 150	Filter Blank Lot Testing	Date Collected & Collector Initials	Lot of Syringes, Syringe number	Yes
TUBE LOTS						
NTN Test Tubes	2-10 mL MQ	10/New Lot ICP/FIA	Test Tube QC Blank	Date Collected & Collector Initials	Brand, Test tube type, lot # & tube # (i.e. Fisher, ICP, Lot 3434, 2 of 10)	No
OTHER LOTS						
MDN Acid Preservative	30 mL (15 mL analyzed)	2/Batch of Acid Preservative with 1 lot	Acid Checks	Date Collected & Collector Initials	"Acid Preservative Blank", Acid Lot # and Batch ID	Yes
Must Meet LOT Approval Before Use of these Supplies						
* Date collected 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.						

Note that the "Client Number" is not the same as the LIMS ID that is generated upon creation of the sample. It is a field on the log in screen that is used internally for more description of the sample.

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 MDN supplies NAL only assess total mercury). If the criteria are met, the new lot can be used. If the QC criteria are not met then another set of 10 must be tested or the entire lot is rejected and returned to manufacturer.

If the second test fails, the lot must be rejected. For lots of filter or bag supplies greater than 1000, a minimum sample set of 20 QC checks are analyzed.

Table 30. NTN Lot Approval QC Samples and Failures

Item tested	# of 2022 QC Samples	Number Individual Samples Failed	Lots Tested	Lots Rejected	Lots Approved
Bottles	38	1	5	0	5
Large NTN Disk Filters	40	10*	1	0	1
Syringe Filter	34	3	5	0	5
Syringes Only	35	0	5	0	5
Test Tubes - ICP and FIA	105	3	10	0	10
Total	252	17	26	0	26

*The one lot of disc filters was retested due to 10 samples having some analyte values over the MDL. Both the filter apparatus and water blank associated with the first test had acceptable values. The retest was done with the QA specialist present. This retest contained samples of pre- and post- rinsed filters with Type I water and the FMDL solution. All data was acceptable on this retest and the lot was approved.

Table 31. MDN Lot Approval QC Samples and Failures

Bottle Size Tested	# of 2022 QC Samples	# of Individual Exceedances	Lots Tested	Lots Rejected	Lots Approved
PETG 1L	23	15	3	1	2
PET 1L	31	0	5	0/1*	5/4*
PETG 2L	3	0	1	0	1
PETG 250 mL	13	0	2	0	2
PETG 500 mL	10	0	3	0	3
Total	80	15	14	1	13

*There was a sporadic contamination issue with a lot of previously approved PET bottles that was discovered during a later comparison study. Unfortunately, some bottles from this lot were active in the field for sample collection before this issue was identified. Shipment of this lot was stopped immediately, and further QC testing preformed. A series of discussions among NADP management, QAAG members and the NADP Executive Committee were convened to decide how to process the data from the MDN samples associated with this bottle lot. A procedure was approved, and a memo of the issue was posted to the NADP website https://nadp.slh.wisc.edu/news/mdn-bottle-contamination-and-affected-samples/.

15.6. New Acid Preservative Testing

Total mercury sample 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. Acid preservative must be <0.4 ng/L in order to be approved for official use. One batch of acid preservative failed this criteria with results of 0.511 ng/L and 0.447 ng/L. Two new aliquots of this batch were retested and passed with results of 0.290 ng/L and 0.264 ng/L.

15.7. Litterfall Collector QC

The collector materials that are used for capturing, storing, and transporting MLN-Litterfall samples are extracted in a solution of 1% hydrochloric acid. This extract is then brominated and analyzed for mercury to ensure that the materials do not contaminate samples. Current lots of sample bags and collector netting were previously tested for the 2020-2021 season, and the test was not repeated for 2021-2022. All material blanks were below the detection limit in 2020.

15.8. Litterfall Process Blanks

MLN-Litterfall laboratory processing blanks were prepared at a rate of one blank per five sites for the 2021-2022 Litterfall season samples. Processing blanks consisted of running ~50 g of dry milk powder through the grinder used for all Litterfall samples. All process blanks measured below the MDL in 2022.

15.9. Ongoing Supply Assessment

Ongoing supply testing protocols for NTN and MDN are listed in **Table 32**.Data from the ongoing supply QC program is assessed, on a quarterly basis at a minimum. Trends in potential contamination or supply issues are investigated and corrective action taken as needed. Analysts must notify the QA staff if they notice high supply blanks in analytical runs so that they can be followed up on as quickly as possible. Results for 2022 ongoing supply QC testing are shown in **Table 33** and **Figure 24**. Overall, these data demonstrate that the cleaning and supply/lot screening protocols are clearly in control, with remarkably few exceedances. There were no ongoing supply QC exceedances for MDN.

Table 32. Ongoing Supply QC Types and Frequency

NADP NTN and MDN Ongoing Supply QC Frequency/Log In (Version 5 (2024) 6/12/2024)						
Item	**Project**	**Amount/Frequency**	**Solution**	**Rinse Collection Bottle?****	**Client Number***	**LIMS Description**
NTN SUPPLIES						
NTN 60 mL bottes	**Bottle Blanks**	2 bottles per month	60 mL MQ	**No**	Date Collected & Collector Initials	"Ongoing 60 mL from bin LOT#"
NTN 47mm Disc Filters	**Filter Blanks DI**	1/ Filter day	60 mL MQ	**Yes**	Date Collected & Collector Initials	"Start OR End Filter" & Sample Range
NTN Syringe Filters	**Weekly Syringe Filter Blank**	1 per month	20 mL MQ	**Yes**	Date Collected & Collector Initials	"Syringe Filter Blank", Syringe and Filter Lot#
NTN Sample Bags	**Bag Blank Study**	2/month	~150 mL MQ	**Yes**	Date Collected & Collector Initials	Bag Type, Lot#
NTN 1 Liter HDPE	**Bottle Blanks**	1/wash day	~150 mL MQ	**Yes**	Date Collected & Collector Initials	"1L NTN Washed"
NTN Buckets	**Bucket Blanks**	1/wash day	~150 mL MQ	**Yes**	Date Collected & Collector Initials	"New" or "Used" "Bucket"
NTN Lids	**Lid Blanks**	1/wash day /per type	~100 mL MQ	**Yes**	Date Collected & Collector Initials	Lid Type
MDN SUPPLIES						
MDN Sample Train	**Sample Train Blanks**	1/week in bag ≥2 days	~ 100 mL MQ	**No**	Date Collected & Collector Initials	"Sample Train Week of XXXXX"
MDN Travel Blanks	**MDN Travel Blanks**	Up to 4 a month	acid preservation in bottle	**No**	Date Collected & Collector Initials	Site ID shipped from, approximate time in the field (i.e. 4 weeks)
QC STANDARDS						
NTN MDL Sample	**NTN MDL Sample**	2 times per month	150 mL MDL sol. or Type I	**No**	Date Collected & Collector Initials	NADP MDL Solution ID (or Type I Water), Bag Lot if new
Special Checks	**Special QA Checks**	As needed	Varies	**Varies**	Date Collected & Collector Initials	Test Info

*Date collected 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. NTN Ongoing Supply QC Exceedances

Item Tested	Ca	Na	K	Mg	Cl	SO_4	NO3	NH4	PO4
Used 1L Bottles (n=212)	0	0	0	0	0	0	0	0	2
60 mL Bottles (n=74)	0	0	0	0	0	0	0	0	0
Used Buckets (n=22)	0	0	0	0	0	0	0	0	1
Bags(n=22)	0	0	0	0	0	0	0	0	0
Used Lids (n=210)	0	3	7	0	2	0	0	0	1
Disc Filters (n=203)	5	5	4	0	5	2	0	1	3
Syringe Filters (n=12)	3	0	0	0	0	0	0	0	0

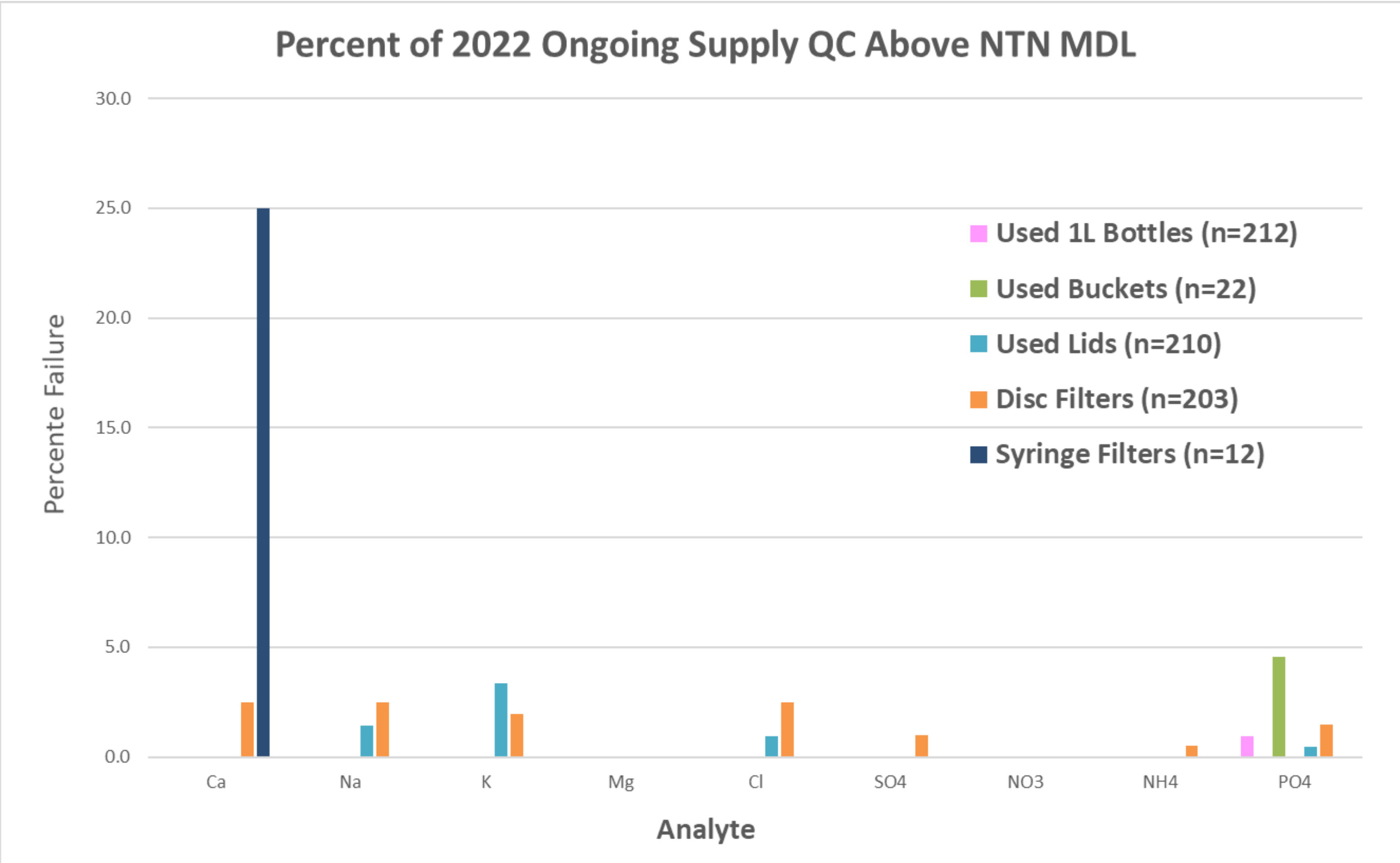

Figure 24. Percent of 2022 Ongoing Supply QC Tests that Exceeded NTN Network MDLs

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 2022

NADP AMoN Supply QC Frequency and QC Log In to LIMS (Version 5 (2024) 6/12/2024)					
Item	**Solution**	**Amount & Frequency**	**Project**	**Client Number**	**LIMS Description**
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", Sampler batch ID, and Core lot**
Glass Jar Blanks (body+core+jar)	10 mL MQ	1/sampler per glass jar wash batch	**AMoN QA Samples**	Date Extracted and Initials	**"Glass Jar Blank", Sample batch ID, Core lot, and Glass Jar wash batch**
Water Only Blanks					
Sonicator Blank	10 mL Sonicator H_2O	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**. AMoN Supply QC Summary 2021-2022 and results in mg/L NH_4.

QC Type	2021 Mean	2022 Mean	2021 # Tested	2022 # Tested	Number of exceedances in 2021	Number of exceedances in 2022	2021 % Exceedance	2022 % Exceedance	Criteria for 2022
Preparation Blanks	0.009	0.008	59	53	0	0	0%	0%	0.036 mg/L NH_4
Core Blanks	0.004	0.005	64	28	0	0	0%	0%	0.036 mg/L NH_4
2 Week Hood Blanks	0.096	0.159	54	52	0	0	0%	0%	0.400 mg/L NH_4
Room Blanks	0.792	N/A	16	N/A*	0	N/A*	0%	N/A*	1.200 mg/L NH_4
Hood Extraction Blanks	0.012	N/A	30	N/A*	0	N/A*	0%	N/A*	0.200 mg/L NH_4
Water Blanks	0.000	0.000	131	97*	1	0	0.76%	0%	0.010 mg/L NH_4
Jar Blanks	0.005	0.006	130	75	22	11**	16.92%	14.67%	0.010 mg/L NH_4
Total			**484**	**305**	**23**	**11**	**4.75%**	**3.61%**	

*The room blank, hood extraction blank, and type I water blank (part of the water blanks) were discontinued in late July 2021 due to continued low results.

**Glass jars were historically tested by filling a clean jar with 10 mL of Type I water and placed upside down in the hood overnight and then poured off. This process did not really depict the use of the glass jars within the network and the procedure was changed in June of 2022. This QC sample type is now processed like preparation blanks. One clean jar per batch has a passive sampler places inside, capped, and kept at least overnight in the freezer. Since this switch, there have been no QC exceedances.

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. These records are available upon request. A summary of NADP-associated occurrence metrics is provided in **Table 36**.

Table 36. Summary of Occurrences 2022

Number of Occurrences	Category of Issue
3	Recording Protocol Deviation/Change
3	Sample Handling
4	Analytical QC
7	Supply QC
4	Data/Reporting
5	Instrumentation/Equipment
26	**Total**

18. Method Improvement Projects

The NADP Laboratories continue to test and assess new techniques and supplies that might improve outcomes and efficiencies of the networks. Some of the initiatives pursued in 2022 include:

- 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. Is archiving even viable? Critical information for the precipitation (and water quality in general) community.
- Method modification of Litterfall MeHg analysis by distillation and CVAFS
- MDN field spiking experiments to determine if Hg loss is occurring
- Exploring the possibility of MDN passive samplers and collocated studies
- Method verification of Total Nitrogen/Total Phosphorus on the FIA instrument
- PET vs. PETG MDN bottle study to assess the possible use of a secondary bottle material
- Discussion of replacing AMoN Radiello samplers with ALPHA samplers to reduce network cost

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 NAL and PO. This begins with the completion of an official request form and review by PO and NAL. If approved, the requested NADP samples can be used for the research project. It is the goal of the NAL/PO review to provide constructive feedback to the researcher to improve the study outcomes. Special Studies that were in-place or implemented in 2022 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 January 2022 through December 2022.

Cooperator and Affiliation	Network	# of Samples Provided	Notes
Ty Coplen (USGS)	NTN	97 filtered water samples	Measure stable hydrogen and oxygen isotopic abundances to generate a historic timeline of these data in the subject area.
Monica Ramirez-Andreotta, Project Harvest (Univ. of Arizona)	NTN	78 unfiltered water samples	Samples will be analyzed to compare results from sample collected from rooftop systems for home agriculture purposes.
Carl Bern (USGS)	NTN	20 filtered water samples	To use the isotopic composition of water (18O and 2H) 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	111 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).
Ross Edwards (WI State Lab of Hygiene)	NTN	240 unfiltered water samples	Black Carbon Analysis.
Deni Murray/Adam Wymore (University of New Hampshire)	NTN	297 archived samples from 2017/2018	Determine the role of atmospheric DOC and DON in ecosystem biogeochemistry. Wet deposition samples will be analyzed for DOC/N concentration and basic optical properties.
Janice Brahney (Utah State University)	NTN	Filters plus excess sample	Investigate the chemical and elemental fingerprints of large wildfires in rainwater and quantify associated wet deposition fluxes.

20. Data Review

20.1. Analytical Data Review

NAL 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 table – 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 Comparison – quarterly data packet review per instrument platform, where data packets are 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 monthly.

20.2. Network Data review

Prior to releasing reports to sites or publishing data to the PO, the NAL 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 (4 weeks from receipt for NTN, 4 weeks from date off for AMoN, and 60 days 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. NAL 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 program office (PO). Publishing on the website is the responsibility of the PO. In 2022, our turnaround times (TAT) have seen a steady increase up to around 200 days by December due to delays related to staffing changes and crossover training. There is work being done to streamline this process to return to our target TAT. Refer to **Figure 25** for Data Review TATs.

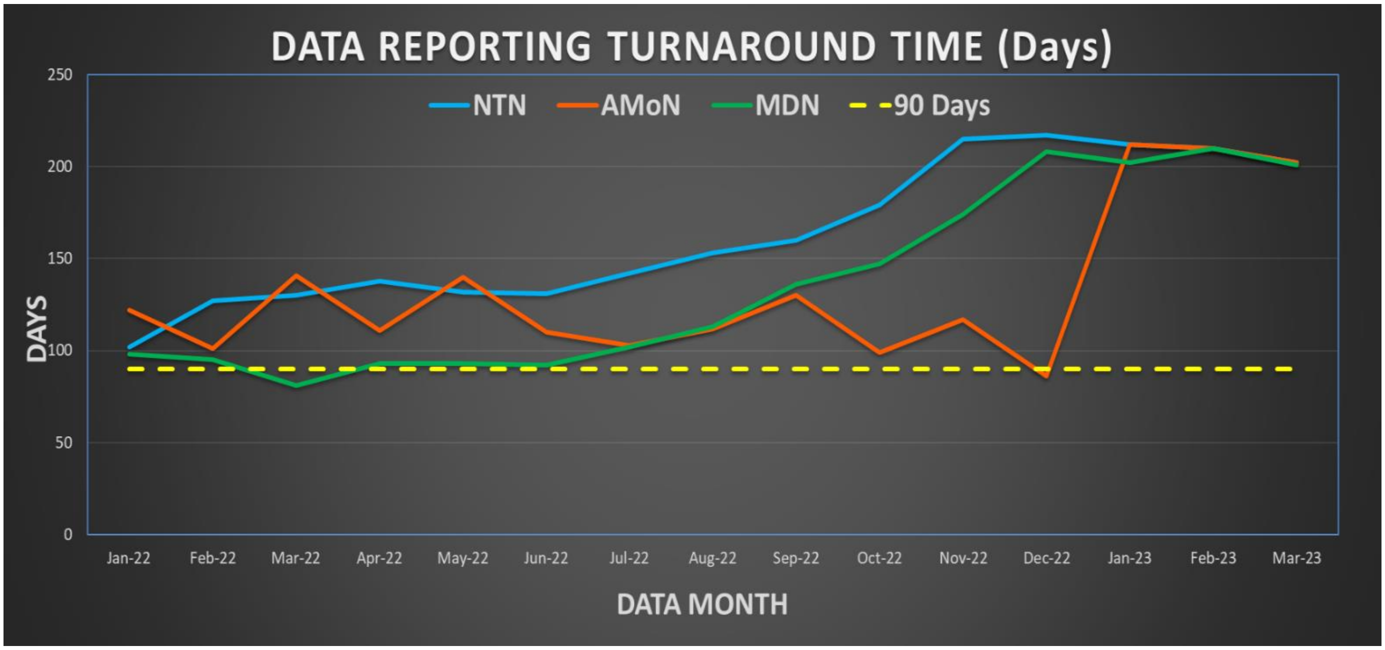

Figure 25. WSLH NAL Data Deliverables: Preliminary Reports to Sites and Data Delivered to the NADP Program Office by Network as of Month Year. Note: 90 days is our target TAT.

22. References

- Applicable NADP SOPs for instrumentation and laboratory procedures and requirements (managed in the WSLH document storage platform (OnBase) and available on request)
- National Atmospheric Deposition Program Laboratory Quality Assurance Plan, Mercury and Central Analytical Laboratories: refer to NADP website nadp.slh.wisc.edu/quality-assurance/
- USGS Precipitation Chemistry Quality Assurance Project (PCQA) https://bqs.usgs.gov/pcqa/

23. Approvals

- 2022 NAL 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: Summer of 2023
- Shared with NADP Management for review as draft on: 10/10/2023
- Reviewed and revised by Systems QA and Special Projects Manager Martin Shafer on: 04/03/2024
- Approved by the NADP Laboratory Director Amy Mager on: 4/4/2024
- Shared with the QAAG for review on: 4/8/2024