2024 Quality Assurance Report

January 01 – December 31, 2024

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, 2024

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 10,000 (209E) (ISO 7) 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.

2024 NADP NAL Staff

- Environmental Health Division (EHD) Environmental Survey Programs Director – Amy Mager
- Systems QA and Special Projects Manager - Martin Shafer
- Chemist Supervisor – Katie Blaydes, Christa Dahman
- Field Operations Supervisor – Dana Grabowski (until October 2024)
- Data and Sample Processing Supervisor – Zac Najacht
- Research Operations Analyst – Dana Grabowski (as of October 2024)
- Laboratory QA Specialist – Nichole Miller
- NTN/AMoN Chemists – Katie Blaydes, Chris Bauknecht, Abby Carr, Kat McKinnon, Walter Ballesteros (as of November 2024 – split 50/50 with MDN)
- Mercury Chemist – Chris Lepley, Walter Ballesteros (as of November 2024 – split 50/50 with NTN/AMoN)
- Environmental Health Technologists – Colin Kelly, Anita Peterson, Cami Ritonia, Maya Giordano

See section 4.2.1. for detailed explanation of staffing changes.

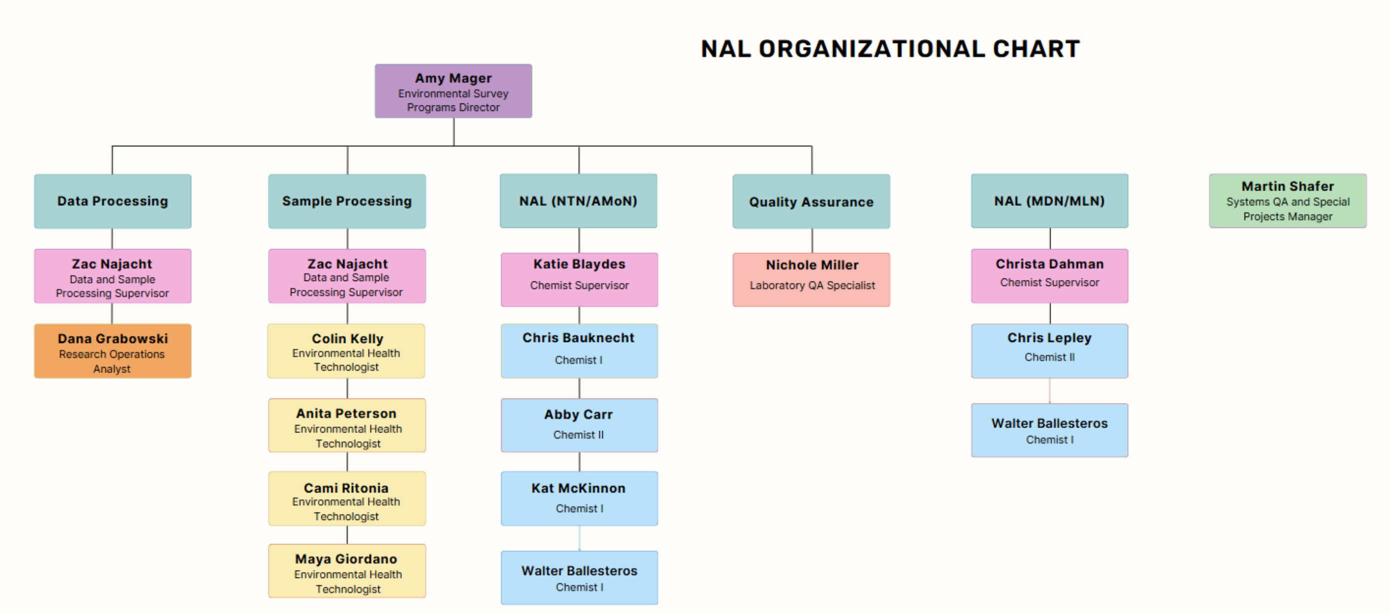

Figure 1. Organizational chart of laboratory staff as of December 2024. The following employees are involved with other departments at the State Lab and are part time NADP staff: Amy Mager, Christa Dahman, Chris Lepley, and Martin Shafer.

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 2020-2024

Year	Total Samples	Wet Samples		Trace Samples		Dry Samples		Valid Samples	
		Number	Percent	Number	Percent	Number	Percent	Number	Percent
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
2023	12828	10178	79.3	270	2.1	1829	14.3	10373	80.9
2024	12447	10113	81.2	300	2.4	2034	16.3	9761	78.4

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 2020-2024

Year	Active Sites	Total Samples	Wet Samples		Dry Samples		Valid Samples	
			Number	Percent	Number	Percent	Number	Percent
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
2023	82	4138	3620	87.5	509	12.3	3818	92.3
2024	76	4152	3557	85.7	595	14.3	3724	89.7

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 2020-2024

Year	AMoN Sites	# of Sample Sets	Valid Samples	
			Number	Percent
2020	111	2760	2735	99.1
2021	115	3100	3072	99.1
2022	90	2545	2512	98.7
2023	89	2346	2308	98.4
2024	93	2378	2359	99.2

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.

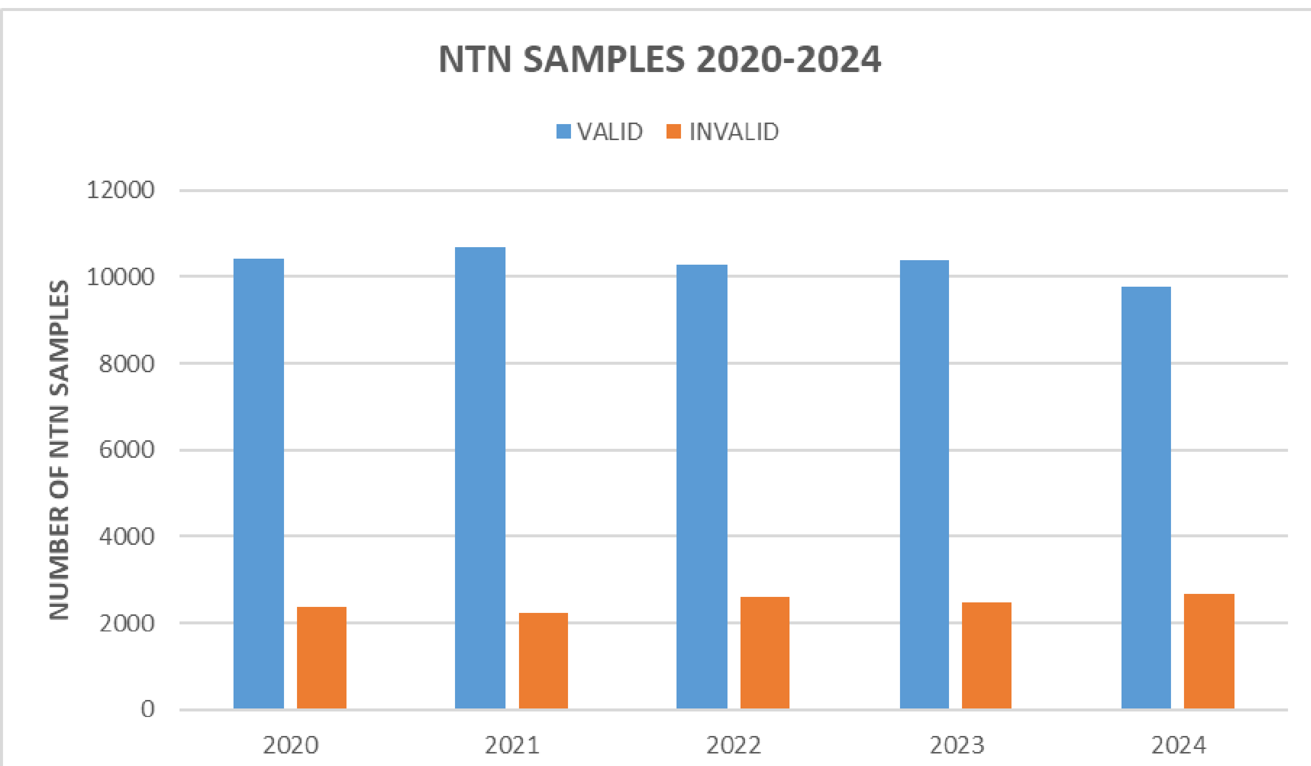

Figure 2. Total Valid and Invalid NTN Samples from January 2020 - December 2024.

The number of NTN valid samples has remained constant with a bit of a decrease in 2024.

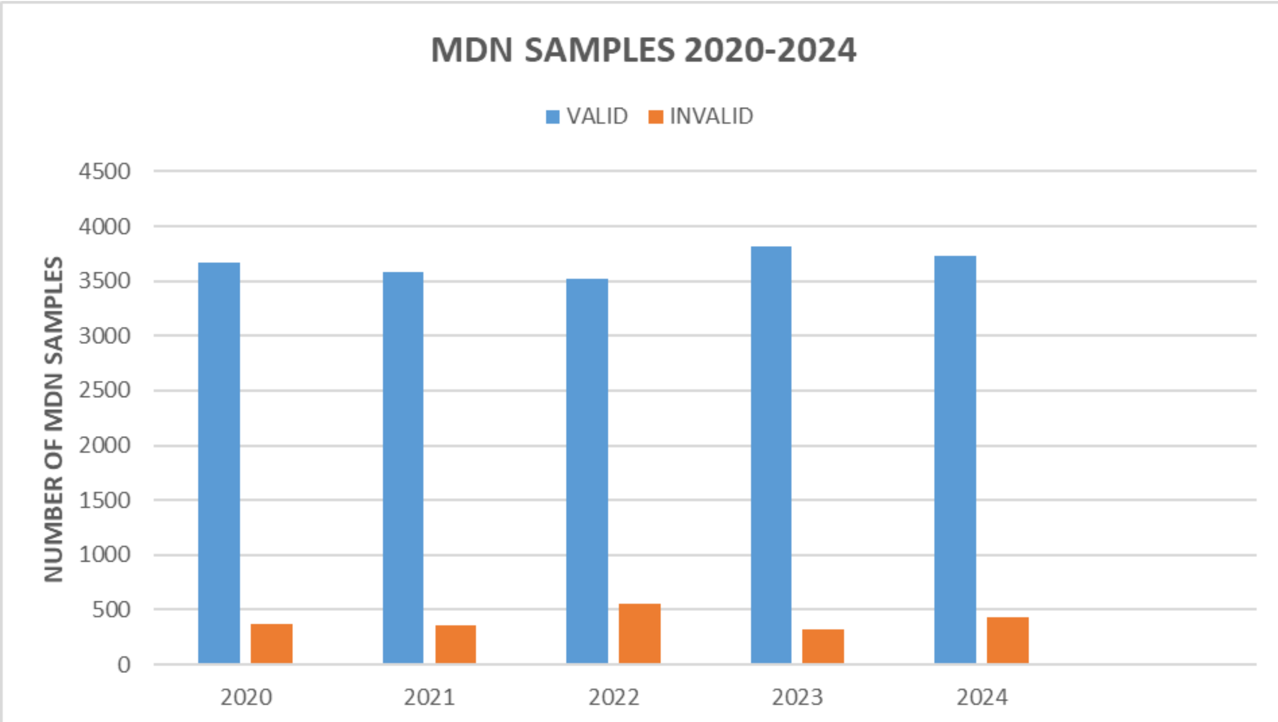

Figure 3. Total Valid and Invalid MDN Samples from January 2020 - December 2024.

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. This is associated with a bottle contamination issue that is detailed in the 2022 QAR (https://nadp.slh.wisc.edu/wp-content/uploads/2024/06/NAL_2022_QAR.pdf) and within a memo one the data webpage (https://nadp.slh.wisc.edu/news/mdn-bottle-contamination-and-affected-samples/).

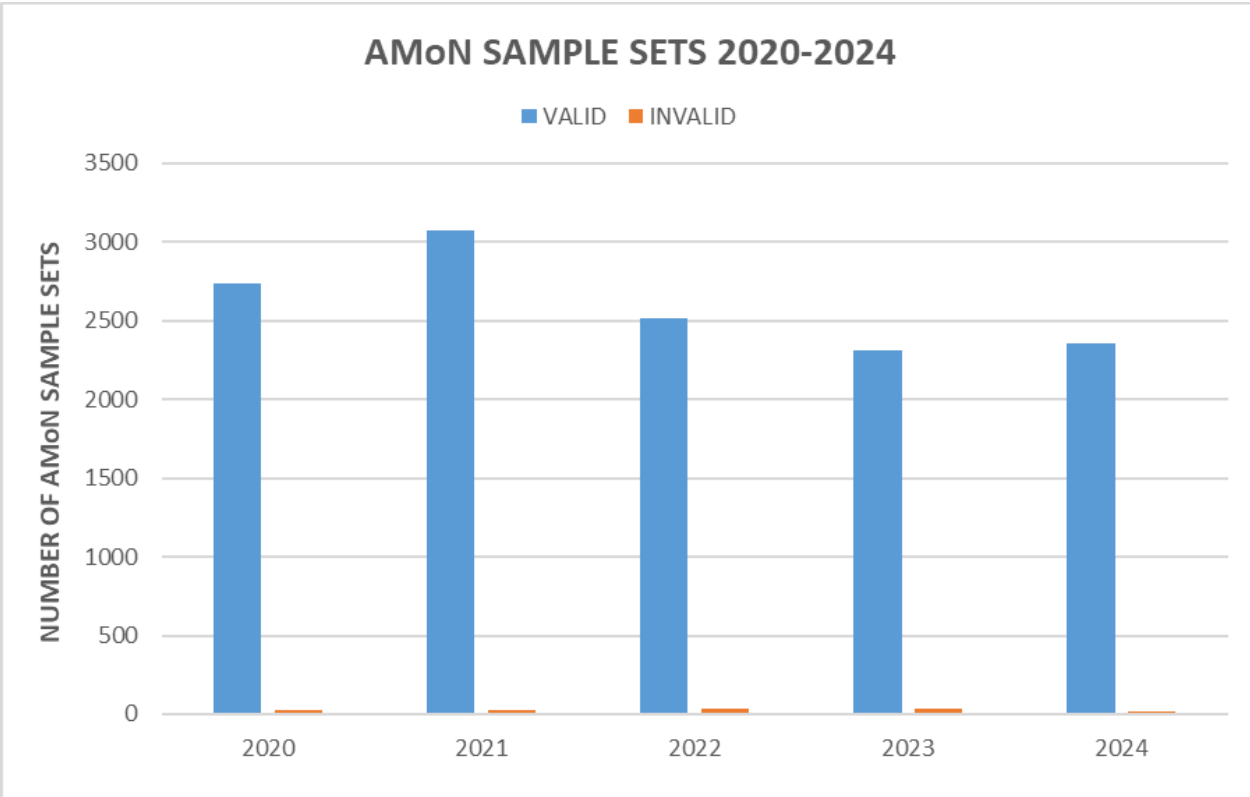

Figure 4. Total Valid and Invalid AMoN Samples from January 2020 - December 2024.

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

The Litterfall Initiative transitioned to the Mercury Litterfall Network in the 2021-2022 litterfall season. There were 25 sites contributing samples for the 2023-2024 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 332 individual samples submitted for the 2023-2024 sample season. After grinding and compositing (all retrievals from a given collector are composited), there were a total of 100 samples (25 sites x 4 collectors) measured for THg (four per site) and 25 composite samples measured for MeHg (one per site – the four collectors are composited). Measured MeHg concentrations contributed between 0.24% - 1.0% of the total mercury measured.

3. Network Operations

The NTN has been in operation for 46 years, MDN for 28 years, AMoN for 17 years, and MLN has been operating for 3 years. The AIRMoN ended operation in September of 2019. **Table 4** shows the total number of samples (including dry and trace) received through December 2024 since inception of the networks. **Figure 5** depicts the numbers of active sites per network per calendar year.

Table 4. Total Number of Samples in the History of NADP by Network (Samples Received prior to 1/2025)

Network	Date Network Began	Date Network Ended (if applicable)	Number of Years in Operation	Total Samples
NTN	7/5/1978	Continuing	46	528,544
AMoN	10/29/2007	Continuing	17	51,071
AIRMoN	9/23/1992	9/1/2019	27	7,709
MDN - THg	2/27/1996	Continuing	28	125,681
MDN – MeHg	5/28/2019	4/26/2022	3	165
MLN – THg	8/1/2021	Continuing	3	280
MLN – MeHg	8/1/2021	Continuing	3	70
TOTAL				**713,355**

3.1. Active Sites

The number of active field sites in each network has varied from year to year. Over the last 8 years, the number of NTN sites has seen a slight decline. AMoN had steady growth, but due to significant budget cuts within the funding agencies, many sites were put on long term hold in 2022. A portion of those sites have restarted sampling since then. 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.

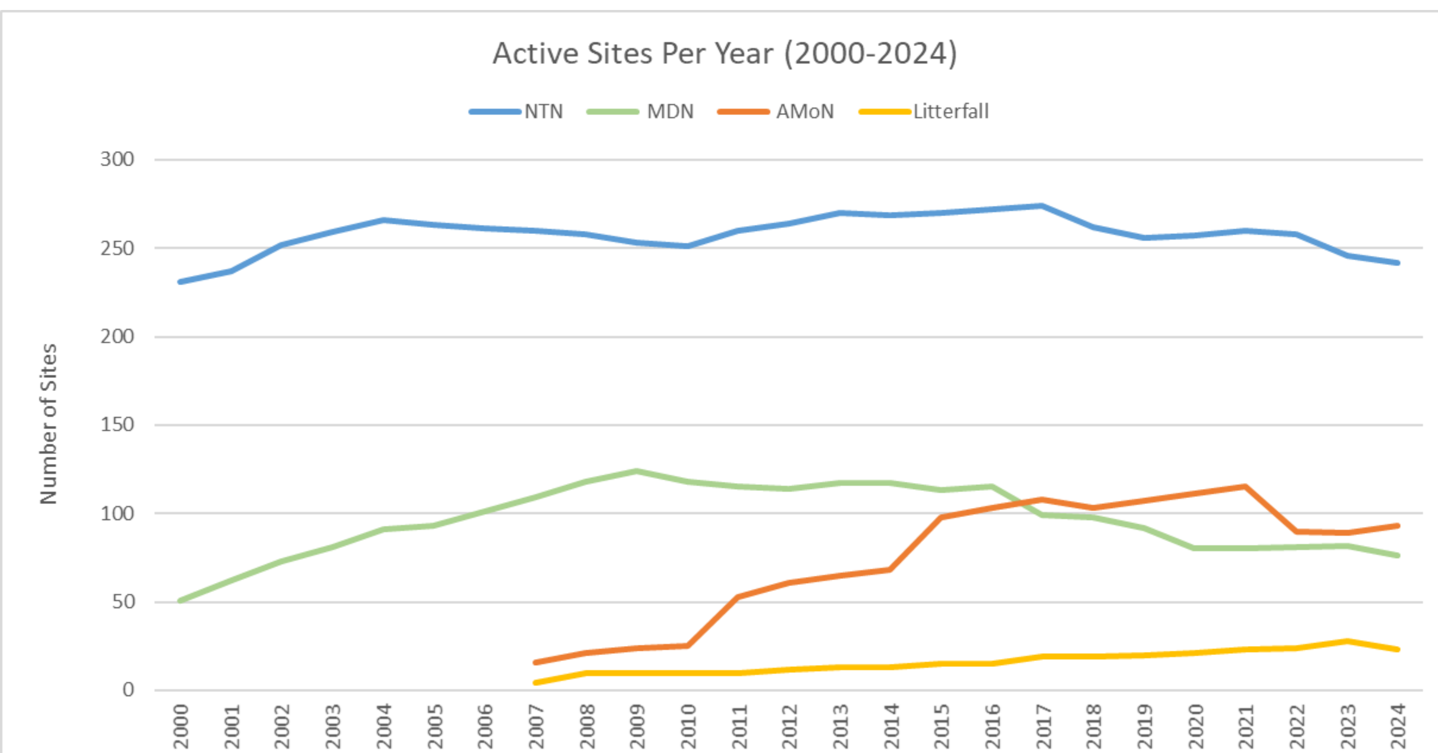

Figure 5. Active sites per network from 2000-2024.

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, 2024 to December 31, 2024
Department: NADP
Person responsible for department's review: Nichole Miller, Amy Mager, Christa Dahman Zaborske, Katie Blaydes, Dana Grabowski, and Zac Najacht
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, Nonconforming Event Reporting Procedure, Nonconforming Event System Management Policy, and Lab Wide Accident Reporting (**this all has been completed for 2024**).

4.1.2. NADP 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 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 (and document that this has been completed). In 2023, this requirement was incorporated into a UW Canvas Course to more efficiently track completion of this requirement for each employee.

4.1.3. SOPs in development into 2024 included: NADP Data Management/Backup, Precipitation Review, Internal Systems and Method Audits, MDN System Blanks, MLN Supply Prep and Shipment.

4.1.4. The NTN Supply Preparation and NTN Supply Shipping and Receiving SOPs need substantial updates due to many changes related to the switch to bag sampling and the evolution of those new processes and procedures. There is a goal to complete these revisions by August 2024. As of September 2024, these have been completed.

4.2. Reports from managerial and supervisory personnel:

4.2.1. **Staffing.** Four APHL Interns (Jaden Anderson, Rachel Mallum, Mia Peck, and Natasha Francis) and 2 fellows (Jean Steele and Walter Ballesteros) were brought on in 2024. Walter Ballesteros began as an APHL Fellow for the NAL (both NTN and MDN) in January 2024. He was then hired on as a full time Chemist I in November 2024 and will continue to share time between NTN and MDN analytical responsibilities. Jason Worden left his position as an Instrumentation Technologist/Site Operations Support Specialist and Nathaniel Boerner was hired as a Research Support Analyst I to fill Jason's position. See **Figure 1** on page 4.

4.2.2. **Audits.** An external audit for the NAL and PO was completed on October 1st-2nd, 2024. This was preformed in a hybrid manner by the following team: Ryan McCammon (USGS), Noel

Deyette (USGS), Sarah Janssen (USGS), Tracy Dombek (RTI), Michael Butler (EEMS), Kevin Mishoe (WSP), Brian Izbicki (USFS), and Yongqiang Liu (USFS). All findings and responses have approved and finalized. This report is available upon request.

4.2.3. Major Network Changes.

4.2.3.1. Implemented a rinse of the pH probe with Type I water after any sample reading 6.8 or higher.

4.2.3.2. Changed the naming system for NTN from AA####SW to T2400000 (where 24 is the year associated with the sample date and the remaining number increases incrementally.

4.3. Changes in the scope/scale and type of work during 2023:

4.3.1. Development of total nitrogen and total phosphorus measurements in precipitation is ongoing.

4.3.2. Pilot study of a different type of passive sampler, the ALPHA, for AMoN began in 2024.

4.3.3. Pilot study of the Passive Mercury Network (MerPAS) began in 2024.

4.3.4. The number of NTN sites participating in PFAS testing as part of EPA and other agency funded projects was 25 at the end of 2024. A year-long pilot PFAS sub network was approved with a start date of 1/1/2024.

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

4.4.1. A proposed overhaul of the MDN sample collection materials could provide major savings for the network, allowing for expansion of sites. David Gay has proposed a single-use bag that would eliminate the need for costly PETG bottles and glassware cleaning and shipment.

4.4.2. A proposed change in the sampler type, Radiello to ALPHA, for AMoN could reduce staff time in preparing the samplers and provide major savings for the network. Radiello supplies are expensive and tedious to clean.

4.4.3. A revamped precipitation management program was started in 2023 but work ceased due to higher priority items needing completion and lack of help with LIMS programming and management. It is still being considered.

4.4.4. FedEx federal government rates have been put in place and initial results are showing some savings with a majority of our shipping costs. In 2024, FedEx and FedEx Express are currently being used for a majority of NADP shipping, except for a few exceptions due to remote locations or better service in a specific area via UPS or USPS. Implementing FedEx and federal rates have shown substantial reductions in NADP monthly overall shipping costs.

4.4.5. Savings gained from reduced shipping rates, MDN overhaul, and more cost-efficient AMoN supplies should be put towards additional staffing.

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 5110
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. It will be due for review in 2025. The NADP QAP contains detailed QA information on all aspects of the NADP laboratories. An Annual Management Review (summarized above) was completed in 2024 and the full document is available upon request.

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 (https://nadp.slh.wisc.edu/wp-content/uploads/2025/09/NADP-SOP-list-2025.pdf). 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 screen and filter 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 1987-2024

NTN Historical Network Method Detection Limits (mg/L) Revision 3/2025											
Sample Start ID	Sample End ID	Approximate Year Received	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
TY9104	UA1999	2023	0.008	0.006	0.004	0.008	0.020	0.020	0.020	0.014	0.010
UA2000	T2410258	2024	0.008	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 2024, 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 26 valid core blank values from February 2023 – December 2023 and these were used to determine a mean of 0.014 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 2024 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 6/25/2025			
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
N23000001 - N23002490	2023	0.084	0.014
N24000001 - N24002468	2024	0.084	0.014
N25000001 - present	2025	0.084	0.014

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 limit of detection (LOD) and limit of quantification (LOQ) for MDN have not changed from 2020. The LOD and LOQ for MeTHg has decreased by approximately a factor of 3 since 2020.

Table 8. Network MDLs for Mercury

Year/Limit type	MDN (THg) ng/L	MDN (MeHg) ng/L	MLN (THg) ng	MLN (MeHg) ng/L
2021 LOD	0.20	0.10	0.1*	0.1
2022 LOD	0.20	0.029	0.096	0.10
2023 LOD	0.20	NA**	0.096	0.10
2024 LOD	0.20	NA**	0.054	0.10
2021 LOQ	0.67	0.30	0.33	0.3
2022 LOQ	0.67	0.096	0.32	0.34
2023 LOQ	0.67	NA**	0.32	0.34
2024 LOQ	0.67	NA**	0.18	0.34

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

***MeHg analysis for MDN samples ended in 2022*

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) with every analytical run. Annually, these spiked samples and all of the batch method blanks are assessed. The lab MDL is calculated and compared to the previous MDL. The lab MDL may remain unchanged if all of the following criteria are met (per 40 CFR 136, Appendix B, Vol. 82, No. 165, Aug. 28, 2017, U.S. Environmental Protection Agency):

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

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

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

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

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 2024 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 2024. 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 interlaboratory 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

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://pubs.usgs.gov/publication/sir20245054/full.

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. This has continued into the following seasons. Operators who received system blank samples from the NAL waited to process their samples after a week without wet deposition at their site. 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 the 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://pubs.usgs.gov/publication/sir20245054/full.

12. Internal Field QA Programs

12.1. AMoN Travel Blanks and Field Duplicates

In 2024, 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 365 travel blanks sent to sites and analyzed between January and December of 2024. 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 were no valid travel blanks above 0.2 mg/L NH_4 criteria 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 2024 AMoN travel blanks and **Figure 7** for the AMoN travel blanks since the beginning of the network.

Table 9. AMoN Travel Blank Results 2023-2024

	2023	2024	2024
	mg/L NH_4	mg/L NH_4	µg/m^3 NH_3
Mean	0.050	0.044	0.089
Median	0.046	0.041	0.080
Max	0.116	0.149	0.300
Number of Valid Travel Blanks	326	362	362
Number of Invalid (QR=C) Travel Blanks (not used)	4	3	3

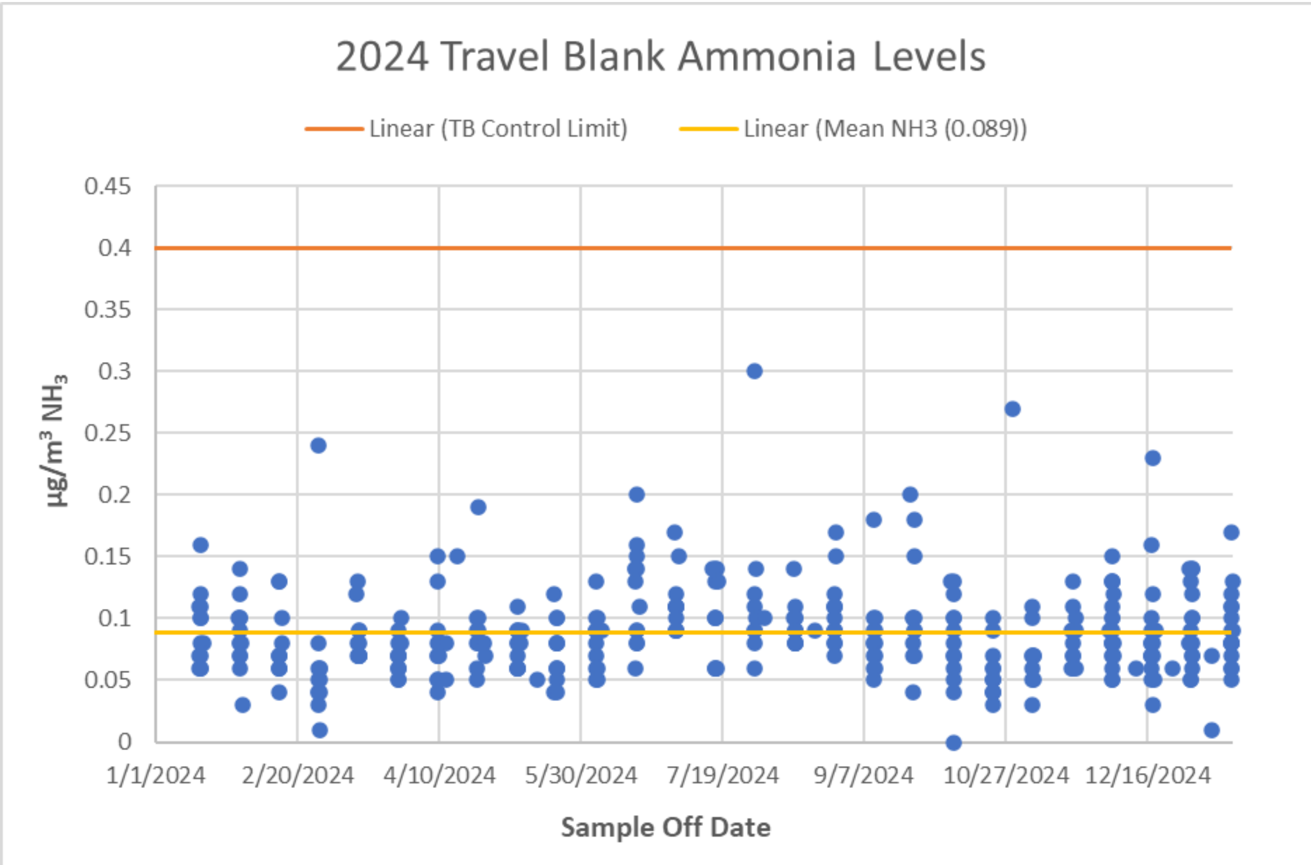

Figure 6. AMoN Travel Blank Ammonia Levels 2024

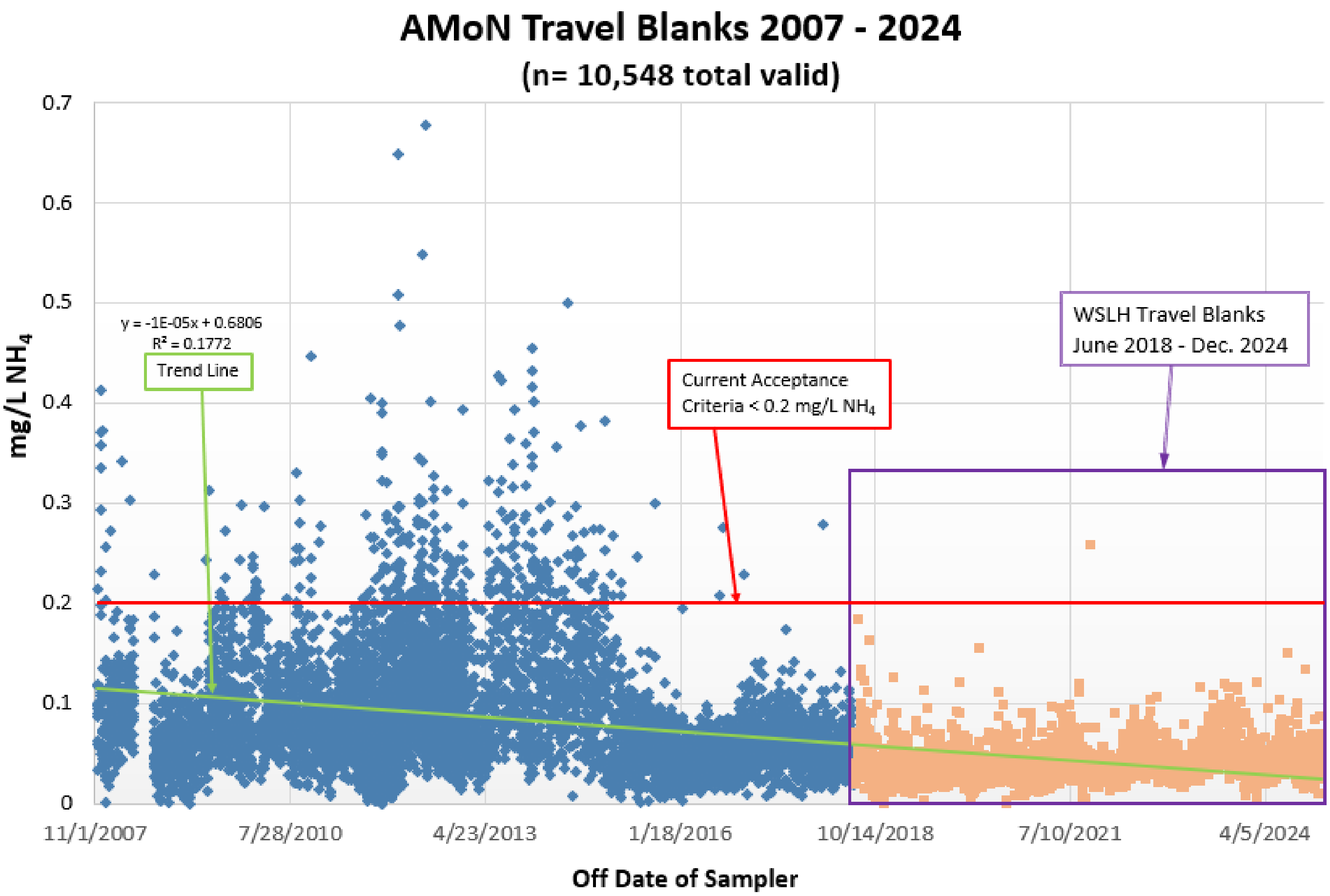

Figure 7. AMoN Travel Blank Historical Ammonia Levels 2007 – 2024. Samples from 2007 – June 2018 were prepared, received, and analyzed at the Illinois Central Analytical Laboratory (ICAL).

13.2 AMoN Field Duplicates

Triplicates (utilized in 2018-2019) or duplicates (utilized in 2020-2021) that exceeded 15% relative standard deviation were retested to ensure that the difference was not an analytical issue and were noted in the qualifiers spreadsheet. Relative standard deviation (RSD) divided by the mean is the relative percent difference (RPD). However, since the disparate field results were confirmed every time, we have discontinued this retesting practice. In 2024, the NAL deployed and analyzed 309 valid duplicate sets.

In 2024, 80% of the replicate sets (across all ambient concentrations) had less than 17.27% 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 2024 AD was 0.43 µg/m^3 NH_3, and the 80th percentile was 0.18 µg/m^3 NH_3. This means that 80% of the duplicate pair ammonia results agreed within 0.18 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 2024 (309 Sets)	2024	RPD	AD µg/m³ NH_3
	80th Percentile	**17.27**	**0.18**
	85th Percentile	**19.86**	**0.29**
	90th Percentile	**25.45**	**0.43**
	95th Percentile	**43.67**	**0.72**

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

2024 Duplicates (309 sets)	RPD	AD (µg/m³ NH_3)
Average	12.49	0.22
Median	6.90	0.06
Maximum	179.02	7.65

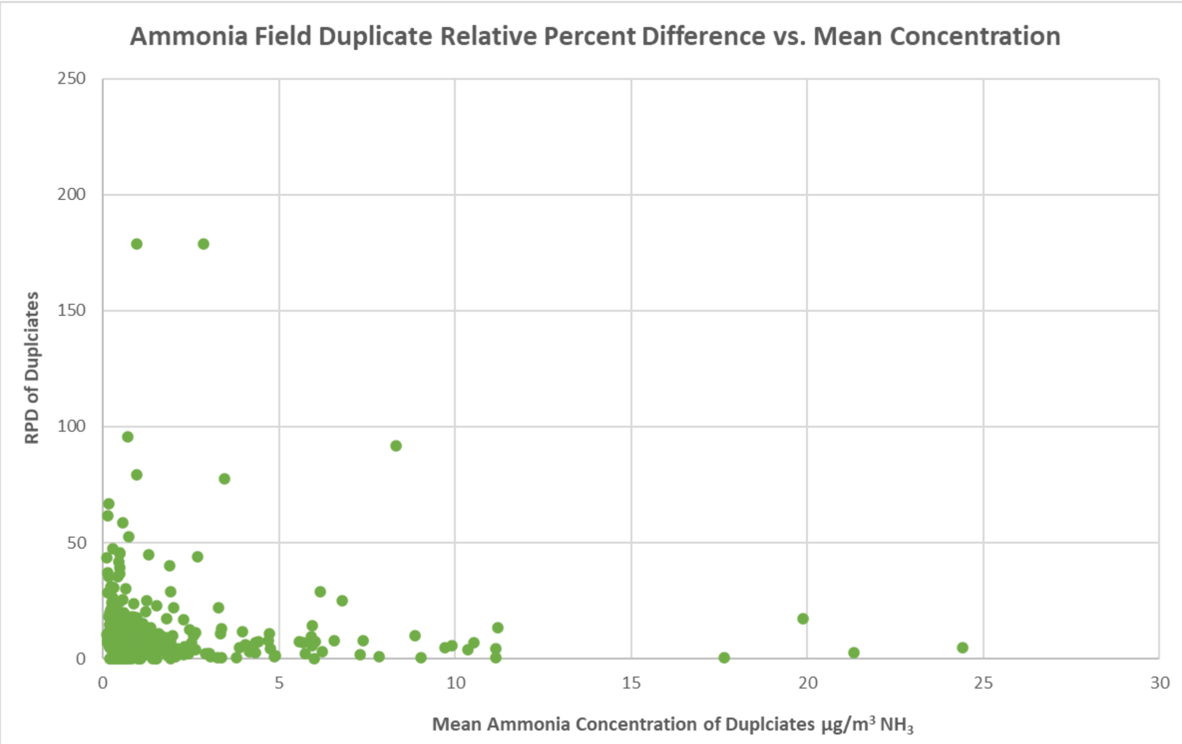

Figure 8. Relative percent difference of 2024 AMoN field duplicate versus mean ammonia concentration (n=309 sets)

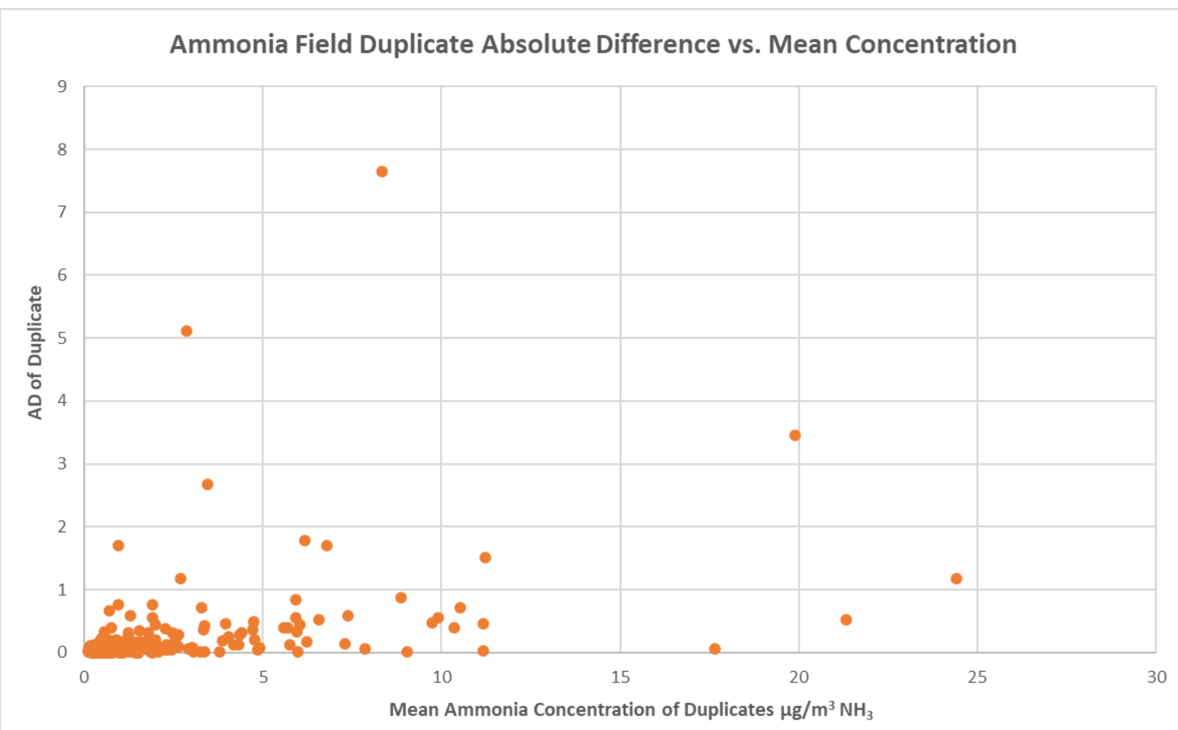

Figure 9. Absolute difference of 2024 AMoN field duplicates versus mean ammonia concentration (n=309 sets)

13. Proficiency Test results

In 2024, 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

Summaries of the results are provided below.

Table 12. 2024 Proficiency Test Results Summary

PT Provider	PT Studies Completed	Results outside of Control Limits	Website Results
ECCC	ECCC 124 ECCC 125	ECCC 124 – See notes under table ECCC 125 – See notes under table	Not on website - Refer to summary provided below
WMO Global Atmosphere Watch (GAW)	WMO 69 WMO 70	WMO 69 – No issues WMO 70 – Some high bias on the cations	Results are on the WMO website by blind laboratory number and available upon request. All laboratory data is linked below. https://qasac-americas.org/study-results?lab=&study=67&type= https://qasac-americas.org/study-results?lab=&study=68&type=
USGS Interlaboratory Comparison	2024 - Full Year of Samples	Notes below	https://www.sciencebase.gov/catalog/item/6476195dd34e4e58932d9d0e
USGS SRS (Standard Reference Samples)	P-82, N-161, Hg-81 (Spring) P-83, N-163, Hg-83 (Fall)	Spring – No issues Fall – High recovery for Hg	Results are on the SRS website by blind laboratory number and available upon request. All laboratory data is linked below. https://qsb.usgs.gov/srs_study/reports/index.php

13.1. ECCC Results

Table 13. ECCC 124 PT Results Assessment – including Hg

	ECCC 124 RN-01	ECCC 124 RN-02	ECCC 124 RN-03	ECCC 124 RN-04	ECCC 124 RN-05	ECCC 124 RN-06	ECCC 124 RN-07	ECCC 124 RN-08	ECCC 124 RN-09	ECCC 124 RN-10	Mean % Recovery	RSD
pH	5.68	6.57	7.24	6.26	6.85	6.26	6.54	5.93	5.88	5.6		
pH Study Mean	5.59	6.41	7.02	5.97	6.83	6.02	6.32	5.73	5.85	5.56		
AD	0.09	0.16	0.22	0.29	0.02	0.24	0.22	0.20	0.03	0.04		
% Recovery	102	102	103	105	100	104	103	103	101	101	102	1.56
Cond	6.1	7.5	34.5	9.9	24.7	3.6	8.7	5.2	4.7	5.4		
Cond Study Mean	6	7.2	33.6	9.8	24.3	3.5	8.6	5.1	4.6	5.3		
AD	0.1	0.3	0.9	0.1	0.4	0.1	0.1	0.1	0.1	0.1		
% Recovery	102	104	103	101	102	103	101	102	102	102	102	0.90
Ca	0.1576	0.6331	3.825	0.2781	2.164	0.2837	0.7486	0.1637	0.1572	0.1069		
Ca Study Mean	0.156	0.642	3.74	0.278	2.21	0.281	0.74	0.163	0.154	0.109		
% Recovery	101	99	102	100	98	101	101	100	102	98	100	1.57
Na	0.1803	0.3191	1.865	0.7693	1.524	0.1079	0.116	0.1869	0.0721	0.2333		
Na Study Mean	0.18	0.327	1.8	0.785	1.56	0.113	0.118	0.192	0.075	0.239		
% Recovery	100	98	104	98	98	95	98	97	96	98	98	2.32
K	0.0444	0.037	0.4287	0.0438	0.3603	0.04	0.0458	0.02	0.0306	0.0232		
K Study Mean	0.045	0.045	0.413	0.049	0.359	0.05	0.051	0.03	0.036	0.03		
% Recovery	99	82	104	89	100	80	90	67	85	77	87	13.18
Mg	0.0377	0.1631	0.6564	0.1731	0.5657	0.0262	0.1242	0.0435	0.0273	0.0352		
Mg Study Mean	0.038	0.164	0.632	0.172	0.571	0.027	0.122	0.043	0.028	0.035		
% Recovery	99	99	104	101	99	97	102	101	98	101	100	2.03
Cl	0.1852	0.5761	1.4855	1.4587	1.0755	0.2003	0.1456	0.32	0.0945	0.293		
Cl Study Mean	0.182	0.557	1.44	1.42	1.02	0.21	0.15	0.322	0.099	0.3		
% Recovery	102	103	103	103	105	95	97	99	95	98	100	3.62
SO_4	0.4973	0.4598	2.357	0.5959	2.0932	0.1526	1.0395	0.4245	0.431	0.5674		
SO_4 Study Mean	0.5	0.476	2.47	0.605	2.06	0.163	1.03	0.433	0.441	0.572		
% Recovery	99	97	95	98	102	94	101	98	98	99	98	2.48
NO_3-N	0.2600	0.0277	0.1717	0.1447	0.0745	0.0550	0.1220	0.1380	0.1270	0.1218		
NO_3-N Study Mean	0.258	0.029	0.17	0.144	0.075	0.056	0.123	0.138	0.128	0.123		
% Recovery	101	96	101	100	99	98	99	100	99	99	99	1.60
NH_3-N	0.2289	0.0270	< MDL	0.1154	0.0014	0.0360	0.1582	0.1733	0.2406	0.1568		
NH_3-N Mean	0.234	0.030	0.007	0.117	NA	0.040	0.162	0.175	0.246	0.161		
% Recovery	98	90		99		90	98	99	98	97	96	3.89

Table 13. ECCC 124 PT Results Assessment – Continued

ECCC Sample ID	ECCC 124 HGLL-01	ECCC 124 HGLL-03	ECCC 124 HGLL-06	ECCC 124 HGLL-07	ECCC 124 HGLL-09	Mean % Recovery	RSD
Hg (ng/L)	1.0112	106.5511	56.55444	77.32828	32.55201		
Converted to ug/L	**0.00101**	**0.107**	**0.0566**	**0.0773**	**0.0326**		
Hg Study Mean (ug/L)	0.001	0.099	0.0525	0.0729	0.024		
% Recovery	101	108	108	106	136	112	12.26

The analyte row 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. Hg units reported in the NAL are ng/L, but converted to ug/L when reported to ECCC.

There is a consistent negative bias for K on this set, but the concentrations are relatively low. All in run QC looked okay when investigated. Table 24. shows in run QC criteria on the ICP, for reference. Also, one high recovery for Hg which was confirmed with reanalysis.

Table 14. ECCC 125 PT Results Assessment

	ECCC 125 RN-01	ECCC 125 RN-02	ECCC 125 RN-03	ECCC 125 RN-04	ECCC 125 RN-05	ECCC 125 RN-06	ECCC 125 RN-07	ECCC 125 RN-08	ECCC 125 RN-09	ECCC 125 RN-10	Mean % Recovery	RSD
pH	6.81	6.27	5.79	6.11	5.74	7.29	5.5	5.8	6.4	4.74		
pH Study Mean	6.73	6.18	5.66	5.97	5.74	7.15	5.4	5.76	6.39	4.73		
AD	0.08	0.09	0.13	0.14	0.00	0.14	0.10	0.04	0.01	0.01		
% Recovery	101	101	102	102	100	102	102	101	100	100	101	0.89
Cond	15.1	16.1	4.5	21.5	3.7	36.7	30.5	27.2	10.5	18		
Cond Study Mean	14.7	15.8	4.6	21	3.8	35.6	30.1	26.7	10.4	17.5		
AD	0.4	0.3	0.1	0.5	0.1	1.1	0.4	0.5	0.1	0.5		
% Recovery	103	102	98	102	97	103	101	102	101	103	101	2.01
Ca	1.818	1.441	0.1222	1.626	0.1062	4.125	2.149	0.7361	0.6764	0.6954		
Ca Study Mean	1.75	1.39	0.12	1.51	0.11	4.02	2.15	0.73	0.66	0.668		
% Recovery	104	104	102	108	97	103	100	101	102	104	102	2.87
Na	0.6489	0.6618	0.0463	0.9542	0.1059	2.058	0.5764	3.24	0.4716	0.0738		
Na Study Mean	0.666	0.68	0.05	0.941	0.11	2.02	0.58	3.17	0.46	0.08		
% Recovery	97	97	93	101	96	102	99	102	103	92	98	3.89
K	0.189	0.3027	0.0335	0.2324	0.0233	0.5021	0.3282	0.2282	0.063	0.0401		
K Study Mean	0.19	0.302	0.03	0.226	0.03	0.502	0.334	0.233	0.064	0.04		
% Recovery	99	100	112	103	78	100	98	98	98	100	99	8.52
Mg	0.161	0.2308	0.0247	0.2669	0.0198	0.6879	0.2192	0.4275	0.2287	0.2704		
Mg Study Mean	0.159	0.229	0.024	0.255	0.02	0.673	0.222	0.41	0.218	0.262		
% Recovery	101	101	103	105	99	102	99	104	105	103	102	2.17
Cl	0.3029	0.3945	0.0626	0.3049	0.0575	0.7219	0.772	5.387	0.8032	0.1849		
Cl Study Mean	0.3	0.39	0.06	0.3	0.06	0.68	0.742	5.18	0.774	0.19		
% Recovery	101	101	104	102	96	106	104	104	104	97	102	3.20
SO_4	1.3879	2.7028	0.362	2.9383	0.4028	1.9715	3.3651	1.5293	0.7007	2.975		
SO_4 Study Mean	1.31	2.51	0.364	2.72	0.4	1.87	3.2	1.43	0.68	2.9		
% Recovery	106	108	99	108	101	105	105	107	103	103	104	2.81
NO_3-N	0.0725	0.2908	0.1856	1.1338	0.1030	0.0229	0.5447	0.0030	0.2047	0.3374		
NO_3-N Study Mean	0.071	0.267	0.172	1.1	0.098	0.023	0.515	NA	0.191	0.314		
% Recovery	102	109	108	103	105	100	106	NA	107	107	105	2.92
NH_3-N	0.0082	0.0516	0.2029	0.2215	0.1200	0.0269	0.6690	0.0111	0.1839	0.0940		
NH_3-N Mean	0.008	0.053	0.207	0.226	0.128	0.025	0.684	0.013	0.190	0.099		
% Recovery	102	97	98	98	94	107	98	85	97	95	97	5.79

The analyte row 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. All mean recoveries looked good for all analytes.

13.2. WMO Results

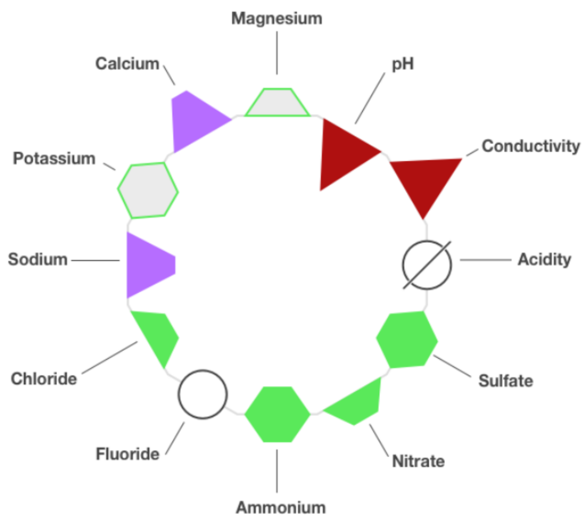

Figure 10. WMO PT Results Diagrams and Keys (not actual study results)

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.

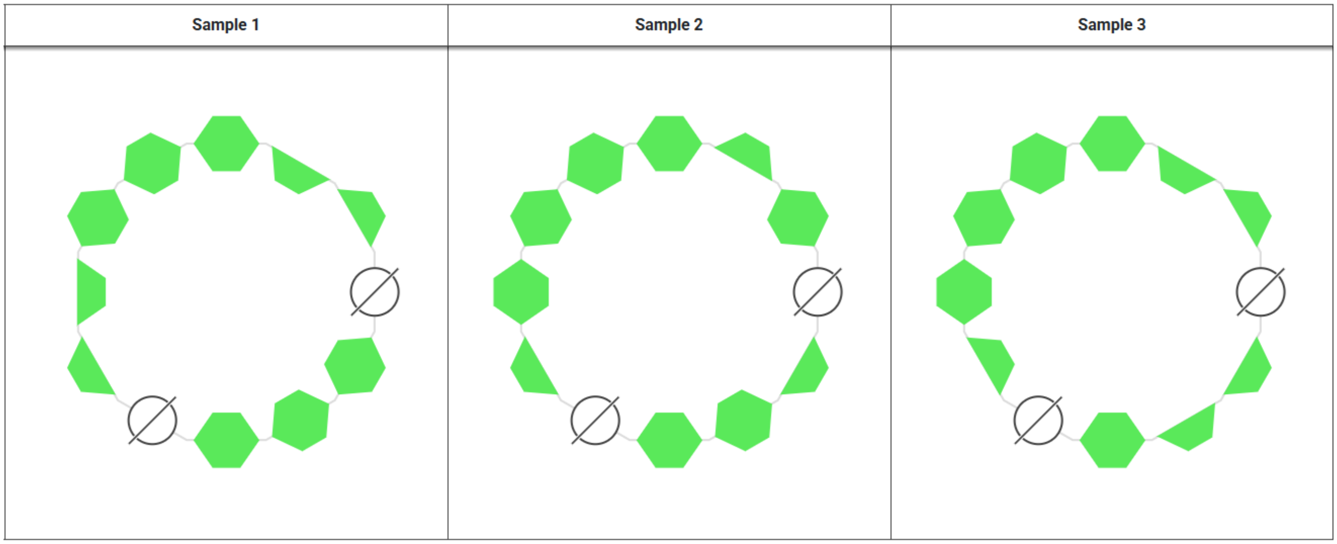

Figure 11. Results from WMO Study 69 – all values have results of satisfactory or higher and meet the DQOs.

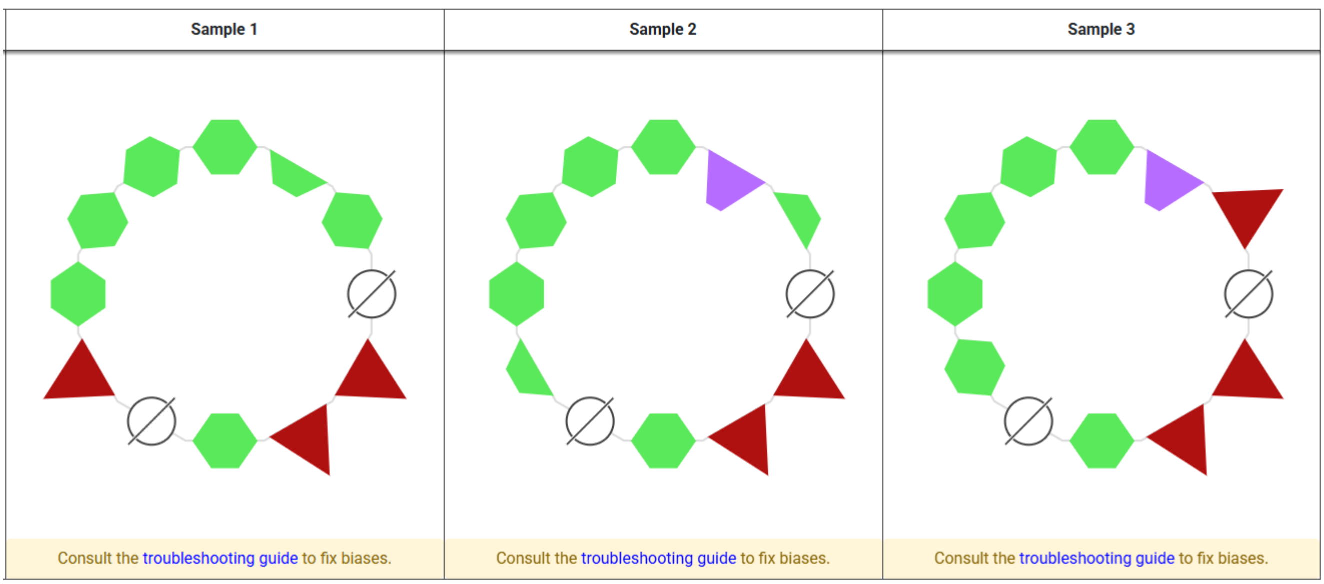

Figure 12. Results from WMO Study 70 – two marginally low values for pH, one biased high value for conductivity (sample 3), one biased high value for Cl (sample 1), and all three sample had biased high values for NO_3 and SO_4. All samples were rerun to confirm values. Issues related to analysis of the anions on the ICs is being investigated. The anion analysis in the Spring 2025 set were okay.

Table 15. WMO 69 PT Results Assessment – May 2024

Date Received	Sample ID	LIMS ID	pH	Cond	Ca	Na	K	Mg	Cl	SO4	NO3	NH4
5/23/2024	WMO69-1	24001917	4.37	45.4	0.769	1.276	0.286	0.247	2.156	5.394	4.126	1.360
TV Final			4.44	43.3	0.799	1.329	0.290	0.251	2.136	5.418	4.137	1.360
% of TV			98	105	96	96	99	98	101	100	100	100
		Difference WSLH - TV	-0.070	2.100	-0.030	-0.053	-0.004	-0.005	0.020	-0.024	-0.011	0.000
5/23/2024	WMO69-2	24001918	5.9	16.7	0.581	0.426	0.123	0.130	0.900	1.977	2.382	0.961
TV Final			5.80	16.5	0.604	0.438	0.121	0.128	0.884	1.938	2.357	0.966
% of TV			102	101	96	97	102	102	102	102	101	99
		Difference WSLH - TV	0.100	0.200	-0.023	-0.012	0.002	0.002	0.016	0.039	0.025	-0.005
5/23/2024	WMO69-3	24001919	4.67	12.8	0.105	0.079	0.034	0.042	0.111	1.067	1.096	0.202
TV Final			4.72	12.1	0.113	0.079	0.032	0.043	0.118	1.022	1.051	0.209
% of TV			99	106	93	99	106	98	94	104	104	97
		Difference WSLH - TV	-0.050	0.700	-0.008	0.000	0.002	-0.001	-0.007	0.045	0.045	-0.007

TV = true value.

Table 16. WMO 70 PT Results Assessment – November 2024

Date Received	Sample ID	LIMS ID	pH	Cond	Ca	Na	K	Mg	Cl	SO4	NO3	NH4
11/15/2024	WMO70-1	24004199	4.67	21.6	0.269	1.088	0.212	0.118	2.223	2.106	1.051	0.385
TV Final			4.73	21.6	0.269	1.111	0.214	0.116	2.018	1.919	0.968	0.381
% of TV			99	100	100	98	99	102	110	110	109	101
		Difference WSLH - TV	-0.060	0.000	0.000	-0.023	-0.002	0.002	0.205	0.187	0.083	0.004
11/15/2024	WMO70-2	24004200	5.01	23.8	0.450	1.384	0.282	0.201	2.463	2.910	1.864	0.709
TV Final			5.18	22.4	0.436	1.401	0.282	0.198	2.240	2.680	1.680	0.695
% of TV			97	106	103	99	100	102	110	109	111	102
		Difference WSLH - TV	-0.170	1.400	0.014	-0.017	0.000	0.003	0.223	0.230	0.184	0.014
11/15/2024	WMO70-3	24004201	5.05	12.3	0.318	0.212	0.061	0.072	0.358	1.438	1.633	0.483
TV Final			5.17	11.3	0.308	0.215	0.061	0.071	0.353	1.327	1.480	0.484
% of TV			98	109	103	99	100	101	101	108	110	100
		Difference WSLH - TV	-0.120	1.000	0.010	-0.003	0.000	0.001	0.005	0.111	0.153	-0.001

TV = true value.

Overall good results for the spring set. Some bias issues with the fall set. A high bias is noticed on the anions (Cl, SO_4, and NO_3), which are all analyzed on the ICs. The anion analysis in the Spring 2025 set were okay.

13.3. USGS Interlaboratory Comparison Results for 2024 data (per Noel Deyette – Spring Meeting: May 2025)

- NTN Intercomparison
  - Weak positive bias for Na and NO_3 and strong bias for H^+
  - Strong increase in NO_3 loss, but reduced NH_4 and H^+ loss
  - Low variability for all analytes except NO_3, SO_4, and H^+
  - Large increases in sample contamination for Na, Cl, and SO_4
- MDN Intercomparison
  - Weak positive analytical bias of 5%
  - Low variability ~63% overall among labs
  - Max contamination increased to ~0.310 ng/L

13.4. USGS SRS Results

Table 17. USGS SRS Spring Results Assessment

USGS SRS Spring 2024				
Sample ID	**Analyte**	**Reported Value**	**True Value**	**% Recovery**
P-82	pH	4.40	4.44	99
	Conductivity	23.5	23.4	100
	Ca	0.201	0.200	100
	K	0.101	0.100	101
	Mg	0.128	0.128	100
	Na	0.783	0.76	102
	Cl	2.69	2.66	101
	SO_4	0.687	0.696	99
	PO_4 as P	0.037	0.039	95
N-161	NO_3-N	0.374	0.360	104
	NH_3-N	0.124	0.122	102
	PO_4 as P	0.125	0.124	101
Hg-78	THg	0.0213	0.021	101

Good results overall for the spring set.

Table 18. USGS SRS Fall Results Assessment

USGS SRS Fall 2024				
Sample ID	**Analyte**	**Reported Value**	**True Value**	**% Recovery**
P-83	pH	4.75	4.80	99
	Conductivity	13.2	12.7	104
	Ca	0.292	0.287	102
	K	0.099	0.099	100
	Mg	0.050	0.051	99
	Na	0.165	0.168	98
	Cl	1.62	1.55	105
	SO_4	0.151	0.164	92
	PO_4 as P	0.012	0.013	95
N-163	NO_3-N	0.183	0.180	102
	NH_3-N	0.067	0.067	100
	PO_4 as P	0.066	0.068	98
Hg-79	THg	0.019	0.016	119

High recovery for THg, although it was a low concentration sample.

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 19** 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 2024 are provided in **Table 20** and show remarkably good precision for a large number of duplicates. Note – the exceedances listed below are failures based on the criteria in **Table 19**, 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 19. 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 20. Analytical Duplicates and Percent Exceedances in 2024

Platform	# Replicates in 2024	# Failures in 2024	% Exceedance (prior to reanalysis)	# Reanalyzed successfully
FIA AMoN	377	1	0.27%	1
FIA NTN	1067	0	0%	N/A
ICP-OES	1062	0	0%	N/A
IC	1156	4	0.35%	4
pH/Conductivity	999	16	1.60%	16

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.

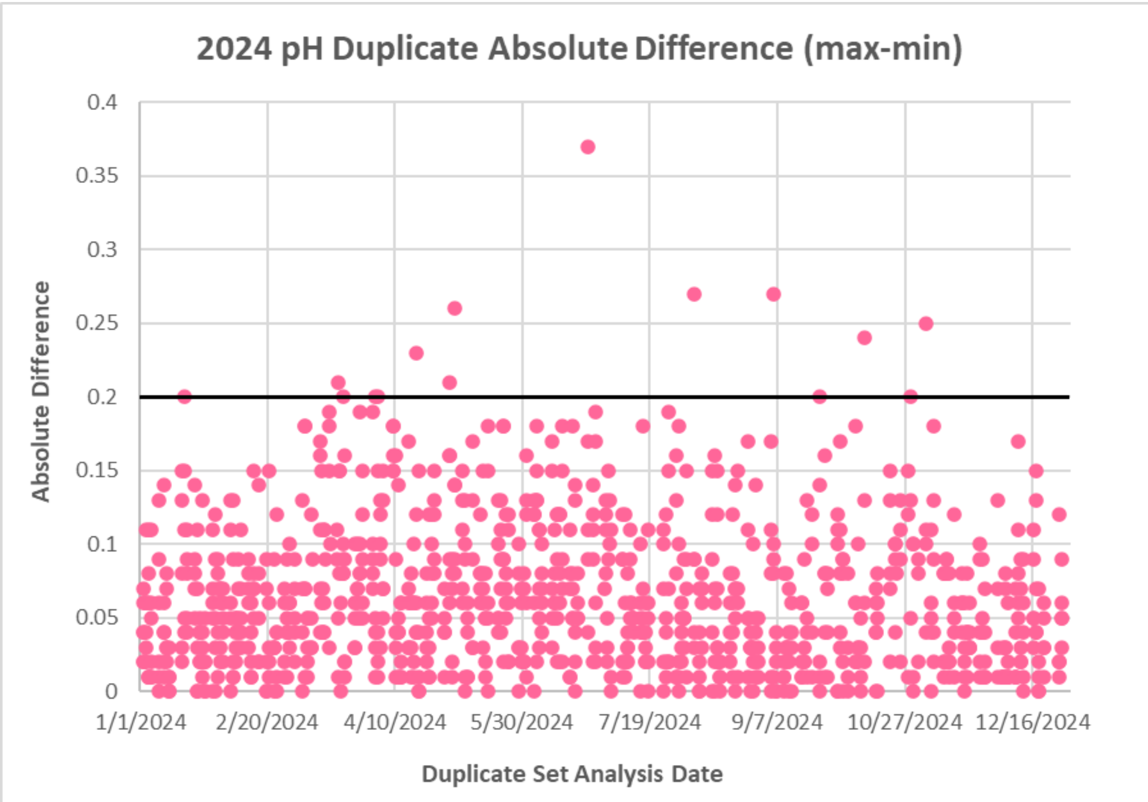

Figure 13. Absolute differences between minimum and maximum pH values from duplicate analyses for a sample. Line at 0.2 is the AD acceptance criteria for pH. This sample set has 999 data points with an average AD value of 0.064.

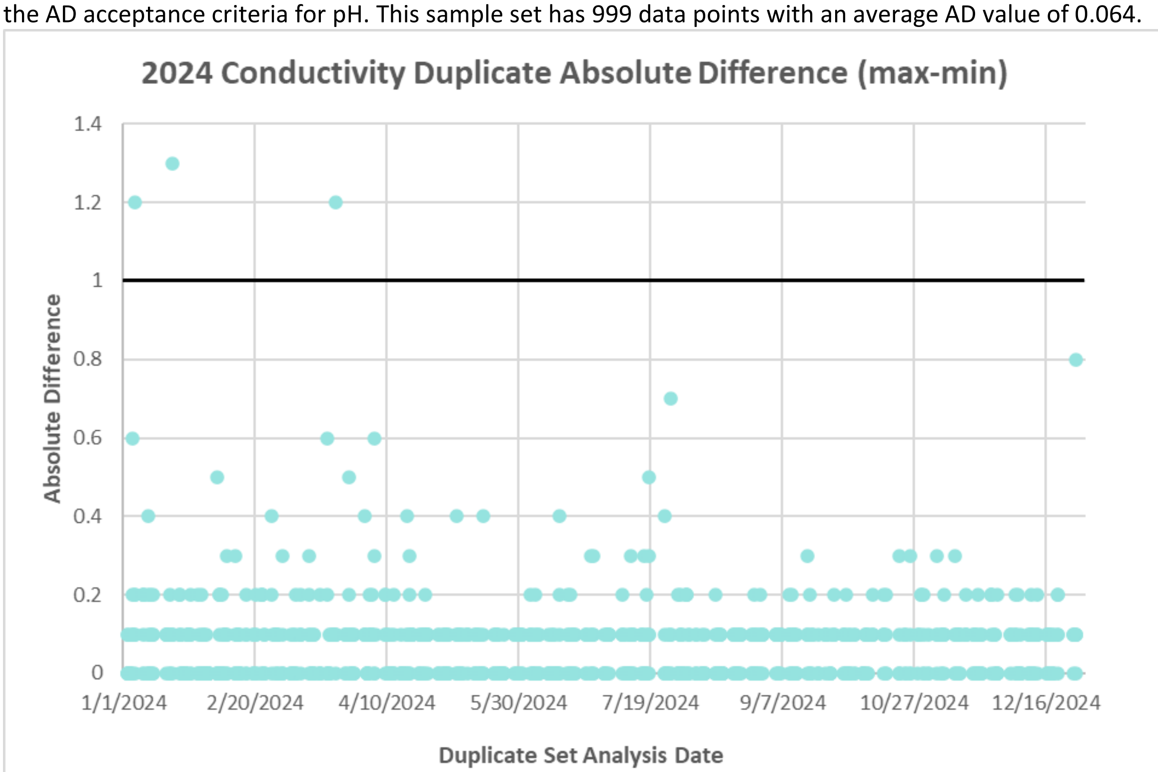

Figure 14. Absolute differences between minimum and maximum conductivity duplicate values for a sample. Line at 1.0 is the AD acceptance criteria for conductivity. This sample set has 999 data points with an average AD value of 0.073.

NOTE – The graphs below depicting the duplicate data show some duplicates that are above the 10% RPD criteria (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 19**.

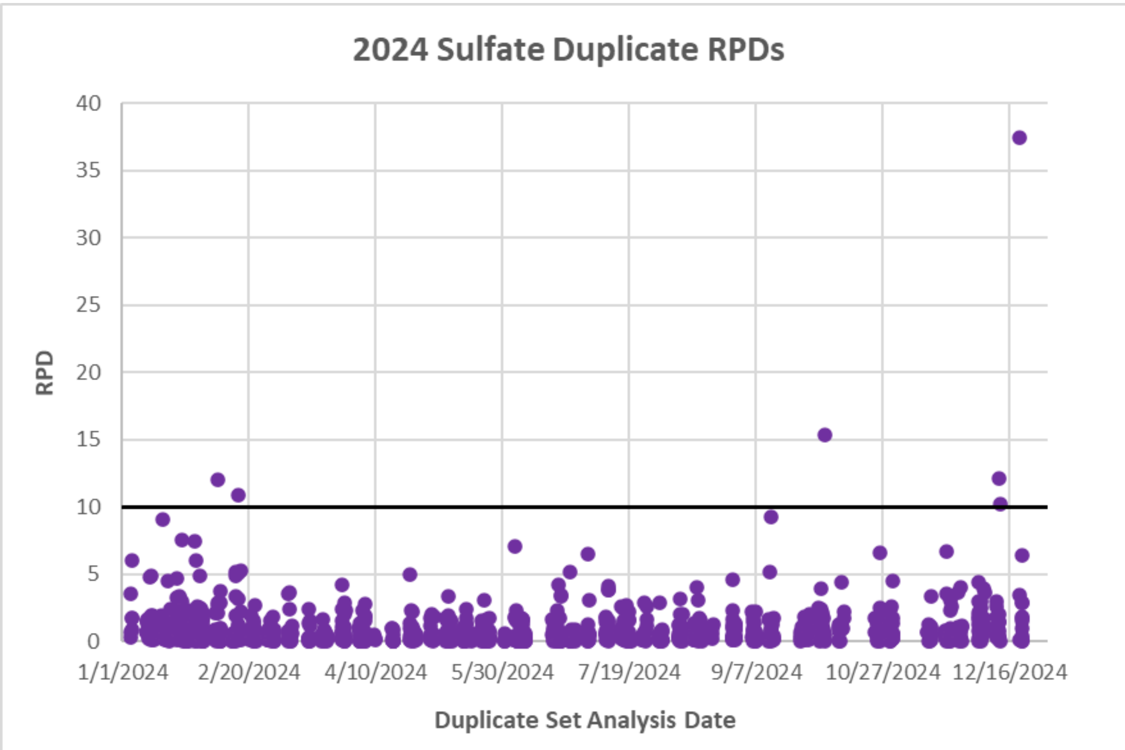

Figure 15. Sulfate (IC) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.02 mg/L. This sample set has 1,154 data points with an average RPD of 0.97%.

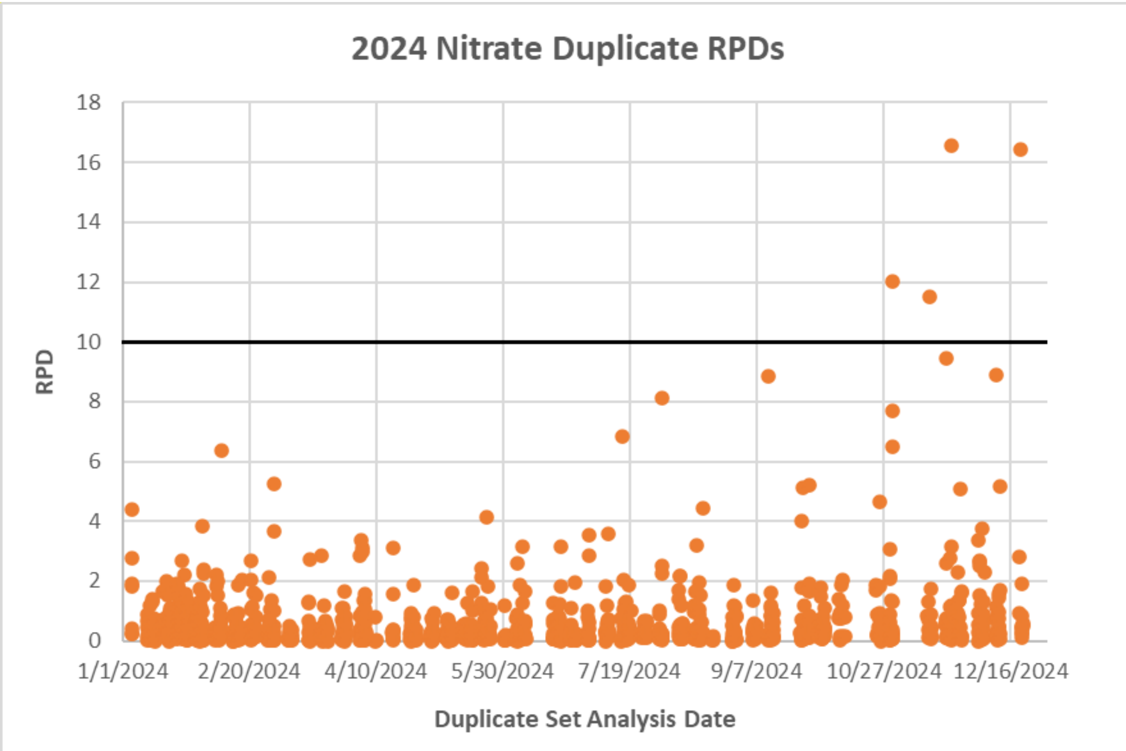

Figure 16. Nitrate (IC) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.02 mg/L. This sample set has 1,151 data points with an average RPD value of 0.66%.

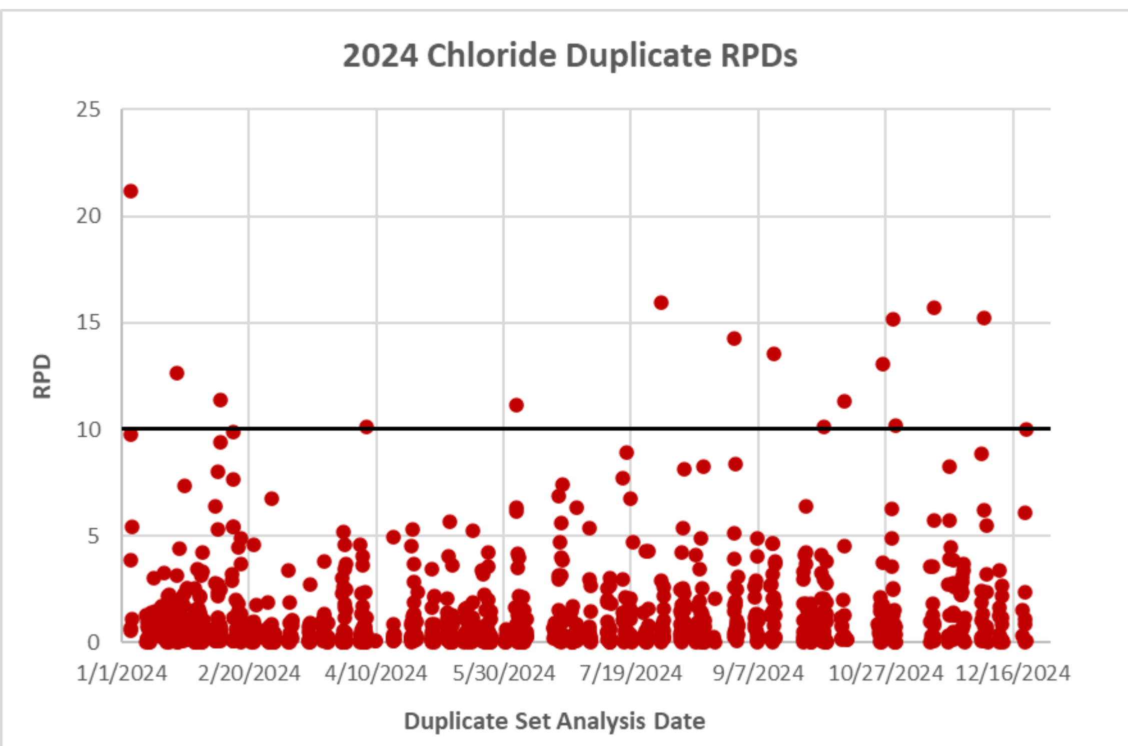

Figure 17. Chloride (IC) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.02 mg/L. This sample set has 1,077 data points with an average RPD value of 1.35%.

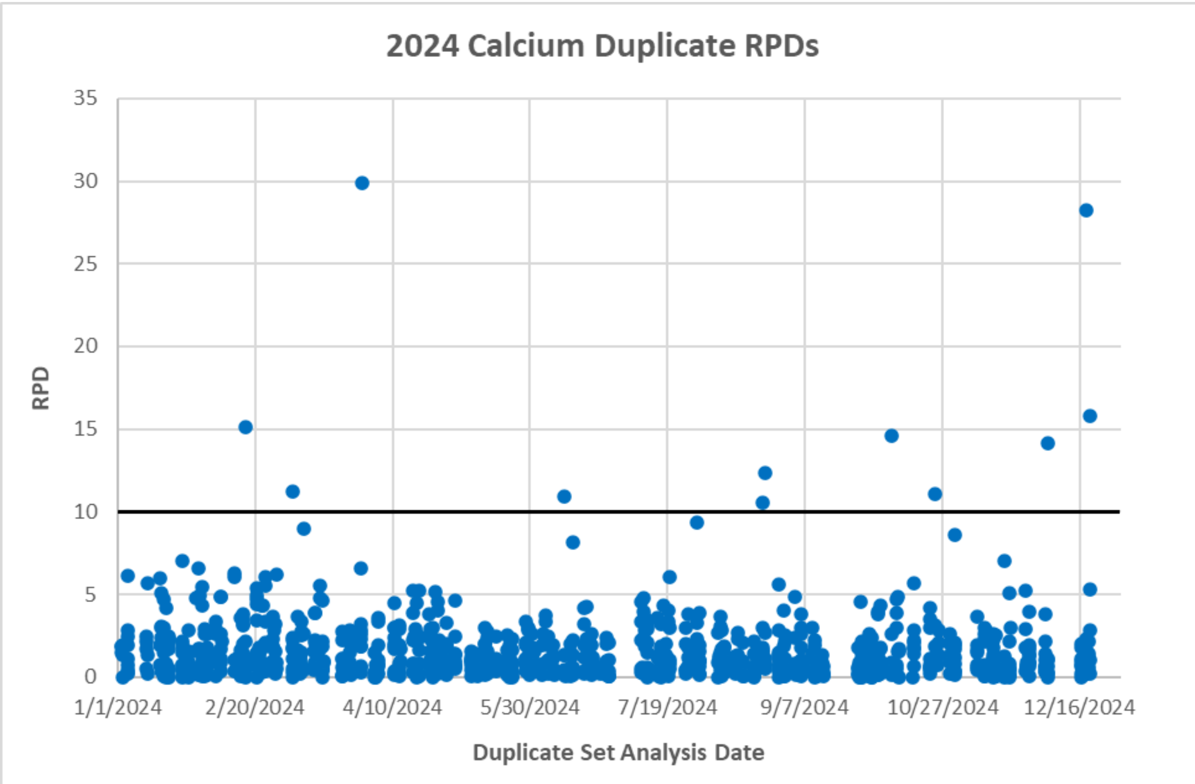

Figure 18. Calcium (ICP) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.008 mg/L. This sample set has 1,050 data points with an average RPD value of 1.55%.

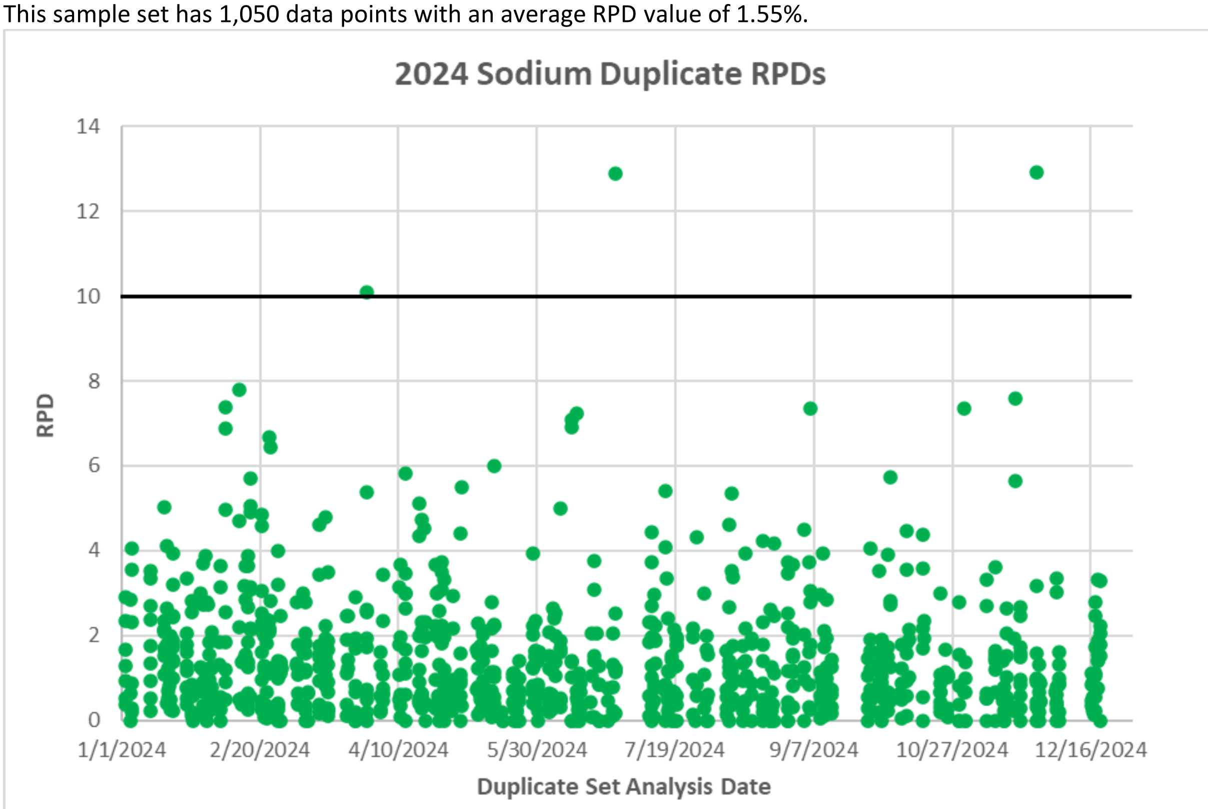

Figure 19. Sodium (ICP) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.008 mg/L. This sample set has 974 data points with an average RPD value of 1.42%.

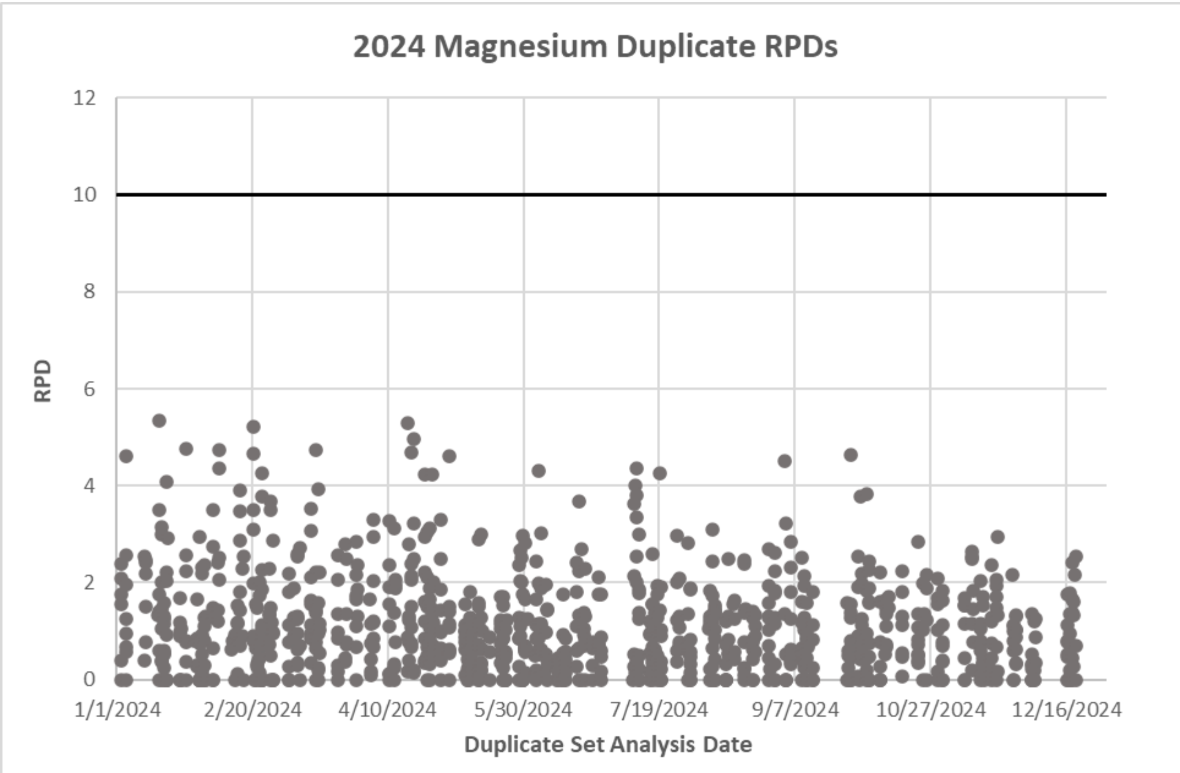

Figure 20. Magnesium (ICP) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.004 mg/L. This sample set has 968 data points with an average RPD value of 1.10%.

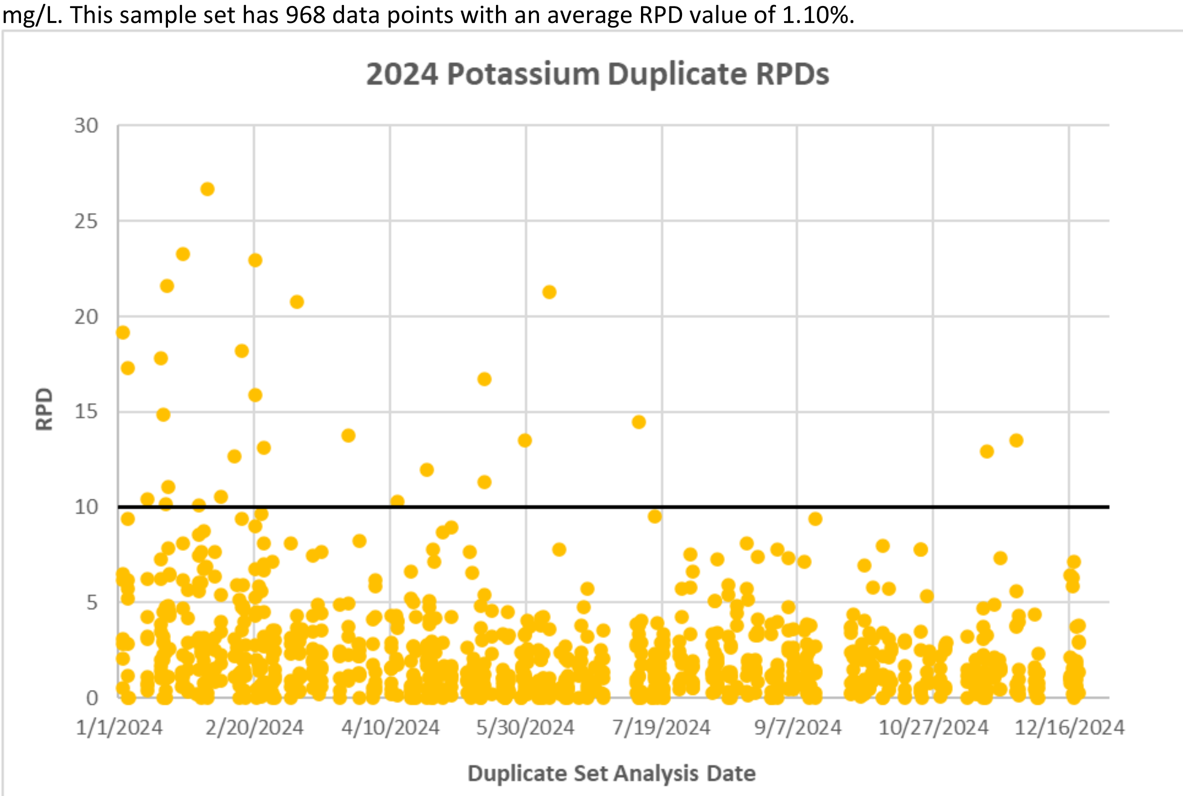

Figure 21. Potassium (ICP) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.006 mg/L. This sample set has 985 data points with an average RPD value of 2.48%.

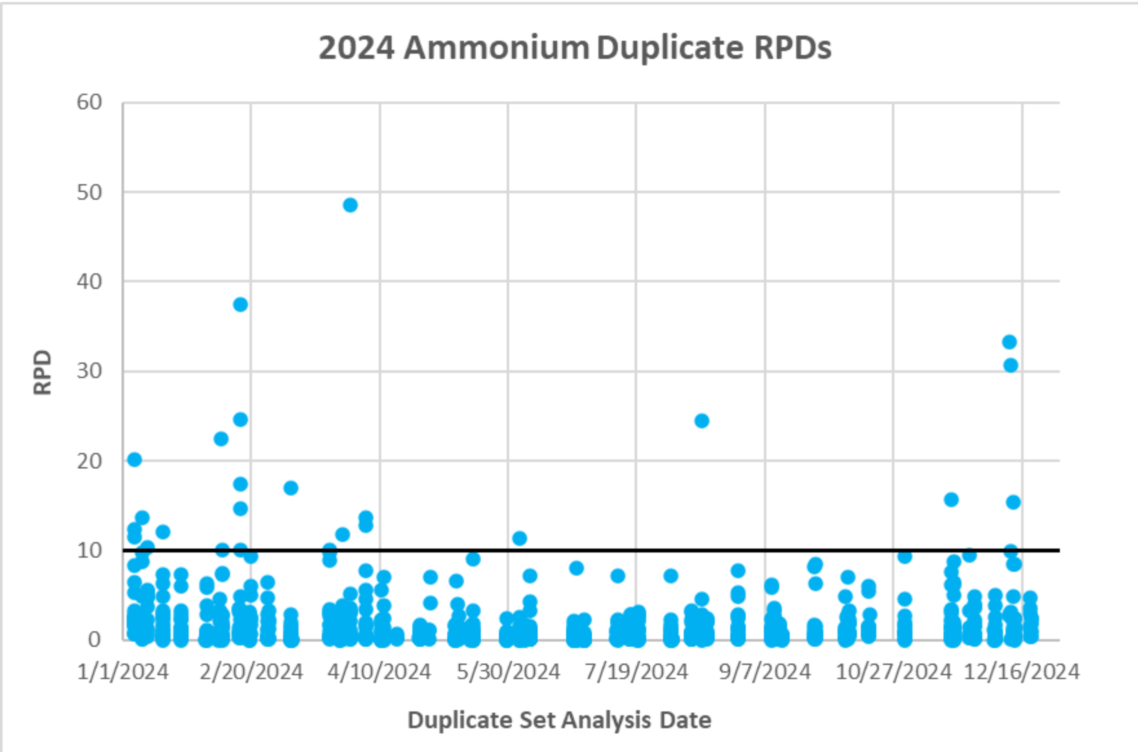

Figure 22. Ammonium (FIA) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.014 mg/L. This sample set has 999 data points with an average RPD value of 1.79%.

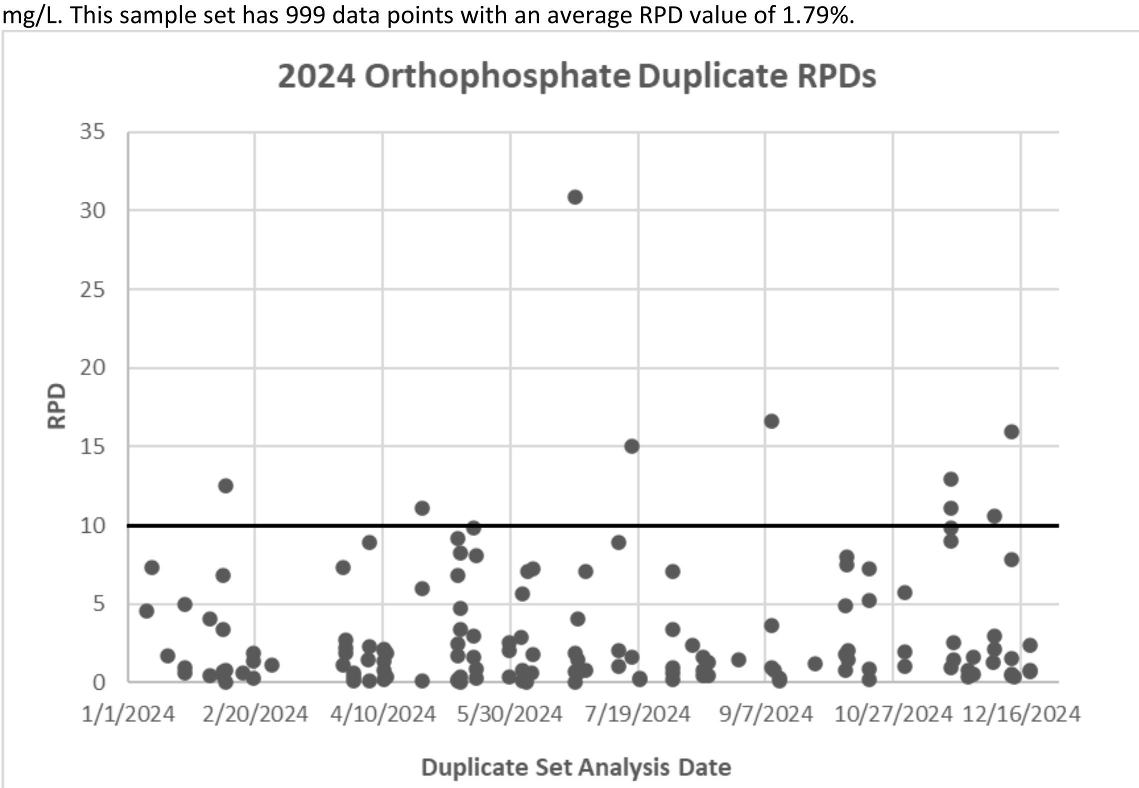

Figure 23. Orthophosphate (FIA) sample and analytical duplicate relative percent difference of sets at or above the MDL_N of 0.01 mg/L. Note very few duplicates are displayed here because although over 1000 sets were analyzed only 145 were at or above the MDL. The average RPD value is 3.25%.

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 21** for all MDN QA/QC samples and associated criteria.

Table 21. MDN Analytical Limits and Batch Run Sample Sequence

Sequence #	Sample/Control Type	Criteria
1	Calibration Blank 1	<0.25 ng/L
2	Calibration Blank 2	<0.25 ng/L
3	Calibration Blank 3	<0.25 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 22** for all Litterfall QA/QC samples and associated criteria.

Table 22. 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. 2023 MDN and MLN MS/MSD Results

In 2024, 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 103.2% for MDN; the mean RPD was 1.82%. All matrix spikes met criteria for MLN (Litterfall) in the 2023-2024 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 2024, results for 240 DLRBs were reported. Three LRBs measured above the method detection limit (MDL) of 0.2 ng/L in 2024. In each case, the LRB was re-analyzed with acceptable results. The root cause of these failures is not known, but possibly instrument related. The average LRB result was 0.0004 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 2024, 80 DQCS samples were reported for MDN. No QCS samples exceeded the control limit. The average recovery was 99.7%. All NIST 1515 samples for MLN-Litterfall met criteria in the 2023-2024 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 24-27** show the run sequences for both the NTN and AMoN instruments and include all applicable criteria.

Table 23. 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 24. 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 50^{th} 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 25. 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 50th 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 26. 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 27. 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 NAL 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 28**, and results for the numbers of samples in 2024 are shown in **Table 29** and **Table 30**.

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 the EHD NADP LAB QA/QC 200 SOP "NTN and MDN Supply Quality Control" – 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 28.**

Table 28. 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 29. NTN Lot Approval QC Samples and Failures

Item tested	# of 2024 QC Samples	Number Individual Samples Failed	Lots Tested	Lots Rejected	Lots Approved
Bottles	30	5 (retests passed)	3	0	3
Large NTN Disk Filters	20	0	1	0	1
Syringe Filter	10	3	1	0	1
Syringes Only	20	0	1	0	1
Test Tubes - ICP and FIA	120	0	12	0	12
Total	200	8	18	0	18

Table 30. MDN Lot Approval QC Samples and Failures

Bottle Size Tested	# of 2024 QC Samples	# of Individual Exceedances	Lots Tested	Lots Rejected	Lots Approved
PETG 1L	0	0	0	0	0
PET 1L	20	8	1	0	1
PETG 2L	5	0	1	0	1
PETG 250 mL	0	0	0	0	0
PETG 500 mL	0	0	0	0	0
Total	25	8	2	0	2

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.

15.7. Litterfall Collector QC

The collector materials that are used for capturing, storing, and transporting MLN samples are extracted in a solution of 0.5% 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 future seasons. All material blanks were below the detection limit in 2020. Supply testing began again for the 2023-2024 season, in which new collector netting was extracted as described above. This initial sampling exceeded acceptance criteria for netting blanks. Follow up sampling was performed, in which the sampled netting was cut from deeper in the roll of material. This was again extracted and produced acceptable QC results, suggesting that the storage of the netting material, and not the material itself, was the reason for elevated mercury results.

15.8. Litterfall Process Blanks

MLN-Litterfall laboratory processing blanks were prepared at a rate of at least one blank per five sites for the 2023-2024 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 2024.

15.9. Ongoing Supply Assessment

Ongoing supply testing protocols for NTN and MDN are listed in **Table 31**. 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 2024 ongoing supply QC testing are shown in **Table 32** 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; however, there was a single instance of an MDN sample train blank being above acceptance criteria. This failure was investigated by testing the MQ water and acid baths and no systematic issues were discovered. It was not a continuous issue going forward.

Table 31. 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 32. NTN Ongoing Supply QC Exceedances

Item Tested	Ca	Na	K	Mg	Cl	SO_4	NO3	NH4	PO4
Used 1L Bottles (n=181)	0	0	0	0	0	0	0	0	0
60 mL Bottles (n=24)	0	1	0	0	0	0	0	0	0
Used Buckets (n=1)	0	0	0	0	0	0	0	0	0
New Buckets (n=0)	0	0	0	0	0	0	0	0	0
Bags(n=25)	0	0	0	0	0	0	0	0	0
Used Lids (n=193)	1	4	3	0	2	0	0	0	0
New Lids (n=0)	0	0	0	0	0	0	0	0	0
Disc Filters (n=234)	1	6	6	1	1	0	0	0	0
Syringe Filters (n=12)	8	0	0	0	0	0	0	0	0

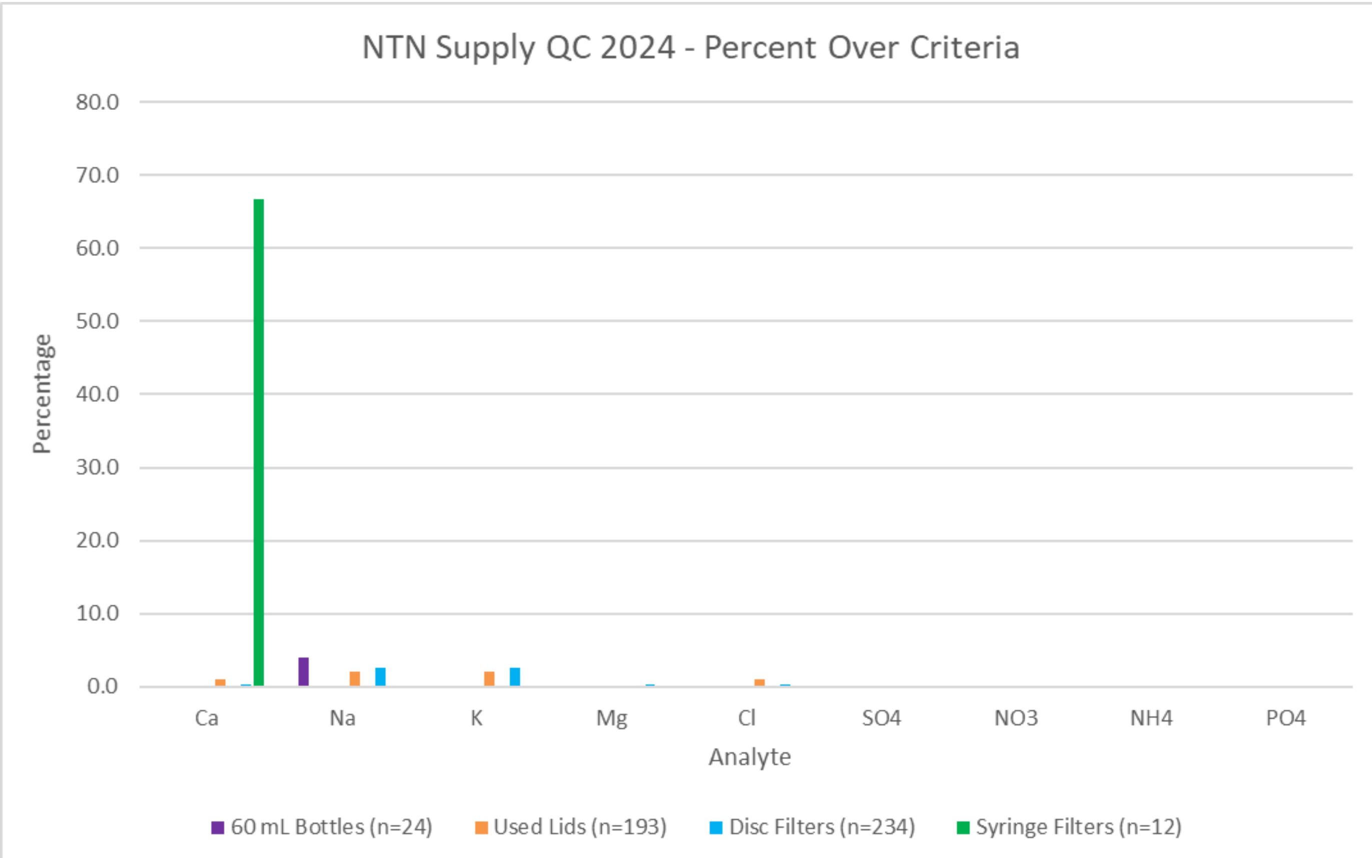

Figure 24. Percent of 2024 Ongoing Supply QC Tests that Exceeded NTN Network MDLs

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 33**, “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 33. AMoN Supply Quality Control 2024

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 zero out of the 49 tested were over the criteria. All details are provided in **Table 34.**

Table 34. AMoN Supply QC Summary 2023-2024 and results in mg/L NH_4.

QC Type	2023 Mean (mg/L)	2024 Mean (mg/L)	Nubmer Tested in 2023	Nubmer Tested in 2024	Number of exceedances in 2023	Number of exceedances in 2024	2023 % Exceedance	2024 % Exceedance	Criteria for 2023
Preparation Blanks	0.014	0.008	45	49	1	0	2.22%	0.00%	0.036 mg/L NH_4
Core Blanks	0.008	0.001	24	32	0	0	0.00%	0.00%	0.036 mg/L NH_4
2 Week Hood Blanks	0.236	0.249	50	52	3	5	6.00%	9.62%	0.400 mg/L NH_4
Water Blanks	0.001	0.000	97	99	0	0	0.00%	0.00%	0.014 mg/L NH_4
Jar Blanks	0.012	0.008	49	54	0	0	0.00%	0.00%	0.036 mg/L NH_4
Total			**265**	**286**	**4**	**5**	**1.51%**	**1.75%**	

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. Nonconforming Events (NCE) are reviewed bimonthly at staff meetings and corrective actions are detailed, implemented and verified before the entry can be closed out.

Nonconforming Events Management (NCEM) 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 NCE metrics is provided in **Table 35**.

Table 35. Summary of Nonconforming Events for 2024

Number of Occurrences	Category of Issue
4	Recording Protocol Deviation/Change
1	Sample Handling
9	Analytical QC
1	Supply QC
5	Data/Reporting
5	Instrumentation/Equipment
25	**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 2024 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. Testing is complete – now performing statistical analysis of data set.
- Pilot study for MDN passive samplers (MerPAS)
- Method verification of Total Nitrogen/Total Phosphorus on the FIA instrument
- Pilot study for 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 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 2024 are shown in **Table 36**. Fees are incurred for special study requests and NADP data needs are always the first priority.

Table 36. NADP Samples Provided to Outside Research Groups January through December of 2024

Cooperator and Affiliation	Network	# Of Samples Provided	Notes
Ty Coplen (USGS)	NTN	49 excess filtered samples	Measure stable hydrogen and oxygen isotopic abundances to generate a historic timeline of these data in the subject area.
Ross Edwards (WI State Lab of Hygiene)	NTN	87 unfiltered excess samples	Black carbon and levoglucosan analysis. Also working with John Walker and the EPA.
Tom Butler (Cornell University)	AMoN	208 newly prepped samplers	Gathering information from multiple test site locations around the Skaneateles Lake in NY.
Todd Royer (Indiana University)	NTN	253 frozen archive sample	All available active archive samples for IN22. Studying dissolved SiO_2.
Deni Murray and Adam Wymore (University of New Hampshire)	NTN	6470 frozen archive sample	All samples that are available from the expired archive samples that are set to be discarded – year 2018 samples. Testing DOC and DON from expired archived samples.
Andrew Jackson (Texas Tech)	NTN	1247 frozen archive sample	Active and expired (set to be disposed) archive samples from 94 sites for the time frame around 4th of July. Investigating the occurrence of perchlorate in lakes and reservoirs following fireworks displays.

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 2024, our turnaround times (TAT) have seen a steady decrease to reach our target of 90 days. This is due to streamlining the NTN process to allow multiple staff to work on a data set simultaneously and review it for approval. Refer to **Figure 25** for Data Review TATs.

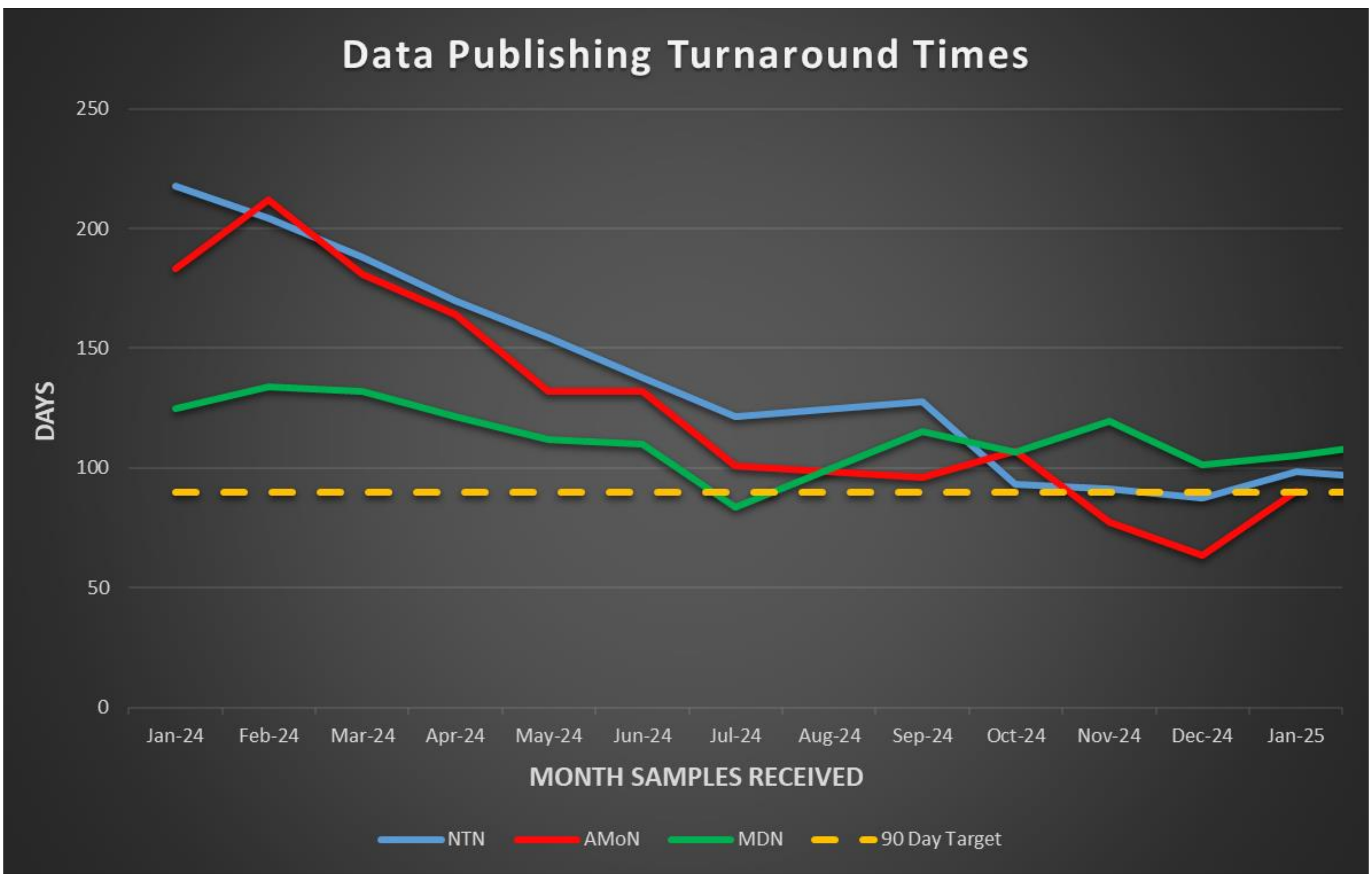

Figure 25. Monthly data set turnaround times for WSLH NAL data published to the NADP website for public use. Note: 90 days is our target TAT.

22. References

- Applicable NADP SOPs for instrumentation methods and laboratory procedures and requirements (managed in the WSLH document storage platform, OnBase, and available on request) https://nadp.slh.wisc.edu/wp-content/uploads/2025/09/NADP-SOP-list-2025.pdf
- 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): External QA Report - External quality-assurance project report for the National Atmospheric Deposition Program National Trends Network and Mercury Deposition Network, 2021–22 and ScienceBase data releases - U.S. Geological Survey Precipitation Chemistry Quality Assurance Project Data 2021 – 2022 - ScienceBase-Catalog

23. Approvals

- 2024 NAL QAR Prepared by Nichole Miller, Laboratory QA Specialist; Chris Lepley, Chemist II; Walter Ballesteros, Chemist I on: 6/2025
- Shared with NADP Management for review as draft on: 8/1/2025
- Approved by the NADP Program Coordinator David Gay on: 8/1/2025
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