# 2020 Quality Assurance Report

## January 01 – December 31, 2020

## National Atmospheric Deposition Program

## Mercury Analytical Laboratory (HAL)

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## Mercury Analytical Laboratory Quality Assurance Report 2020

### 1. Overview

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

The WSLH took over the operations of the NADP HAL on June 1, 2019 from Eurofins Frontier Global Sciences (EFGS) in Bothell, WA. The Litterfall initiative operations were taken over in January 2020 from USGS in Madison, WI, and in Spring 2021, the Litterfall initiative formally transitioned to an official NADP network.

To ensure data continuity and comparability between EFGS and the WSLH, a Readiness Validation Plan (RVP) was developed and approved by the Quality Assurance Advisory Group (QAAG) on March 4, 2019. WSLH employees visited EFGS in 2019 to discuss the RVP and transition of the lab/services to the WSLH. An agreement was reached for the purchase and transfer of MDN equipment from EFGS to the WSLH. Details of the RVP/Final report as well as instrument/method validations are available upon request.

An inter-comparison study between WSLH/HAL and USGS (the Litterfall analytical laboratory prior to 2019) was also performed for the Litterfall Initiative, as well as a formal instrument verification for the newly acquired Nippon MA-3000 THg instrument. Details of the RVP and instrument and method validations are available upon request.

An MDN specific Laboratory Information Management System (LIMS) was developed by WSLH for use by HAL sample receiving, analytical and data review staff. This was a significant project as an MDN-LIMS did not previously exist within NADP and required substantial NADP and WSLH-IT staff effort to complete. This QAR report covers the period from January 1, 2020 to December 31, 2020 for MDN samples.

All Litterfall Initiative samples are currently managed in a spreadsheet format. This report covers the 2019 Litterfall season (Fall 2019 to Winter 2019/2020). Litterfall samples are always collected in the fall (through early Spring for some southern sites) of the calendar year and dried, processed, analyzed, and reported in the following calendar year after all samples have been received.

### 2. 2020 HAL Staff

- Laboratory Manager - Mark Olson
- HAL Analytics/Trace Element Clean Lab Supervisor - Christa Dahman
- Chemist - Kirsten Widmayer
- Sample and Data Processing Manager (Shared with Central Analytical Lab, CAL) – Amy Mager
- QA Manager (Shared with CAL) – Camille Danielson
- Assistant Data Manager – Dana Grabowski
- Associate Chemists (Shared w/CAL) – Margaret Johnson, Erin Pierce, Jim Sustachek, and Chris Lepley

## 3. HAL Sample Counts

The number of network samples received and processed by the HAL is tracked in real-time; however, the percentage of valid samples can only be determined after data are published to the Program Office (PO). The COVID-19 pandemic in 2020 had an impact on sample numbers due to the temporary closure of some sites and some invalidation of samples due to field issues, such as long collection periods. Sample counts in **Table 1** include dry and wet samples. A dry sample is defined as a field collection with less than 1.5 mL of precipitation. 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. A QR of C means a sample is invalid.

**Table 1.** MDN Total Sample Counts (Last 5 years)

| Year | Active Sites | Total Samples | Wet Samples | | Dry Samples | | Valid Samples | |
|---|---|---|---|---|---|---|---|---|
| | | | Number | Percent | Number | Percent | Number | Percent |
| 2016 | 115 | 5551 | 4805 | 86.6 | 694 | 12.5 | 5145 | 92.7 |
| 2017 | 99 | 5042 | 4383 | 86.9 | 659 | 13.1 | 4582 | 90.9 |
| 2018 | 98 | 4766 | 4193 | 88.0 | 540 | 11.3 | 4318 | 90.6 |
| 2019 (EFGS) 1/19-5/19 | 92 | 1880 | 1741 | 92.6 | 127 | 6.8 | 1702 | 90.5 |
| 2019 (WSLH) 6/19-12/19 | 92 | 2536 | 2261 | 89.2 | 263 | 10.4 | 2374 | 93.6 |
| 2020 | 80 | 4039 | 3474 | 86.0 | 514 | 12.7 | 3671 | 90.9 |

In 2020, seven sites requested MeHg analysis on their MDN samples. MeHg sites require an aliquot of sample to be removed prior to sample oxidation. MeHg samples are composited on a monthly basis for each site. After monthly composites are complete, the samples are distilled to neutralize the pH, and then analyzed by CVAFS. There were 93 methyl composites collected in 2020. Due to insufficient volume and a few distillation issues, only 68 of these samples were successfully analyzed. Of the samples analyzed, less than 3% measured above the MDL (0.1 ng/L).

There were 22 Litterfall sites for the 2019 season. Each site consists of four collectors and each collector consists of at least two retrievals every season (under normal circumstances). There were 487 individual samples collected for the 2019 sample season. After grinding compositing, there were a total of 86 samples measured for THg (four per site, except for WI95, which had only two due to minimal season collections) and 22 composite samples (one composite per site) measured for MeHg. All MeHg concentrations made up less than 1% of the total mercury measured.

## 4. Network Operations

The COVID-19 pandemic caused substantial disruptions to MDN sites over the course of 2020. Numerous sites were closed for several weeks to months due to field staff health and safety concerns. The average number of weeks of a COVID-19 related suspension at an MDN site was 12 weeks. One site, SD18, was permanently closed in October 2020. By 6/30/2020, 80% of sites had resumed sampling and by 9/30/2020,

91% had resumed. Despite some increased safety measures, laboratory operations were not significantly impacted by the pandemic.

**Table 2**. MDN COVID-19 Site Impacts

| Total Suspended | Total Resumed (as of 4/27/21) | % Suspended | Missed Samples | % of Total Samples |
|---|---|---|---|---|
| 18 | 17 | 21% | 202 | 7% |

**Table 3.** Total Number of Samples in the History of NADP by Network (All Samples Received Prior to End of sample year)

| Network/Initiative | Year Network Began | Number of Years in Operation | Total Samples |
|---|---|---|---|
| MDN - THg | 1996 | 24 | 109,364 |

### 4.1. Active Sites

The number of sites in each network varies from year to year. MDN sites (**Figure 1**) have steadily declined since 2016 – the 80 active sites in 2020 represents a 30% decline from site numbers in 2016. This is mostly attributed to site sponsor budget cuts. The Litterfall initiative active sites (**Figure 2)** has varied from year to year since its beginnings in 2007. There were 22 sites for the 2019 season.

**Figure 1**. MDN Operational Sites 2016-2020

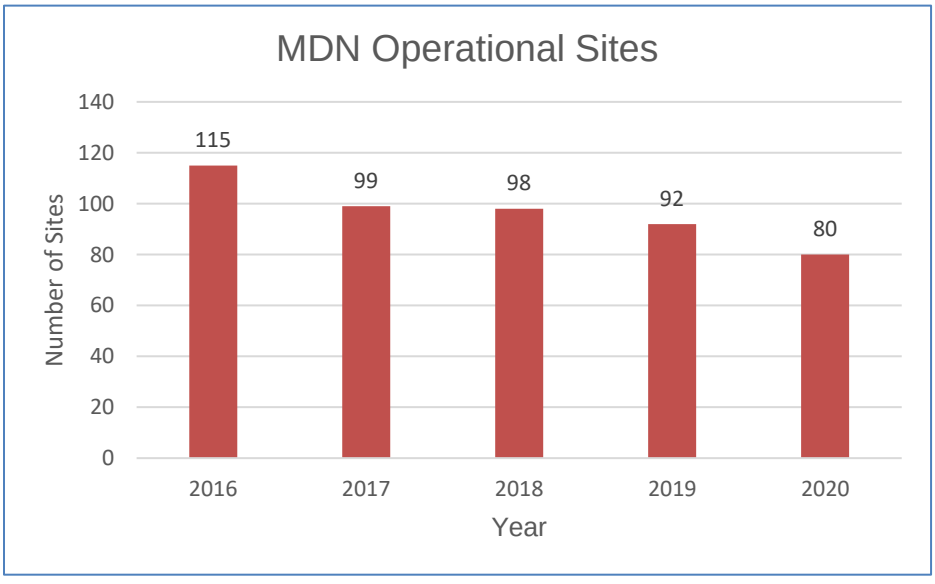
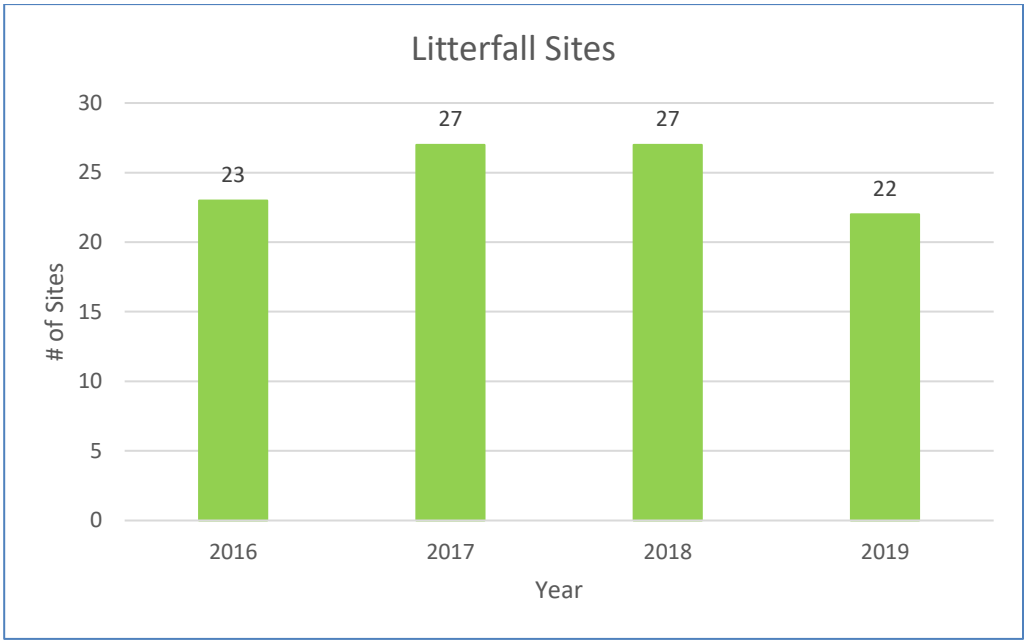


**Figure 2. Litterfall Operational Sites 2016-2020**




## 5. Major Changes

The HAL has attempted to track all dates of major changes in network operations, sample processing, analysis, and supply preparation that might affect sample results. Major Changes are noted in **Table 3**. There were very few major changes to the HAL in 2020.

**Table 3.** Major Changes January 1, 2020 – December 31, 2020.

| Date | Change | Reason | Highest Approval |
|---|---|---|---|
| **1/1/2020** | HAL begins processing Litterfall Samples | End of first season WSLH is responsible for analysis | WSLH Management |
| **9/1/2020** | Direct Mercury Analyzer (DMA) Verification Study Complete | DMA to be used for Litterfall | HAL Management |

## 6. Annual Management Review

### 6.1. Staff

The HAL strives to continuously improve processes and efficiencies. HAL staffing consists of one full-time analytical chemist (Kirsten Widmayer), a HAL supervisor (Christa Dahman), a HAL laboratory manager (Mark Olson), and four sample receiving staff (shared with the CAL). Kirsten began working full-time for the HAL in April 2020. Sample receiving brought-on two new associate chemists in August 2020, Chris Lepley and Margaret Johnson, after Kirsten Widmayer and Nichole Davis were promoted to HAL and CAL chemists in the spring.

### 6.2. Audits

Camille Danielson (QA Manager) conducted an internal audit of our QA systems in place for the HAL. No external audits were performed in 2020. An external audit is scheduled for September 2021. See **Section 18** of this report for a summary of the internal audit findings.

### 6.3. Equipment

No major equipment was purchased in 2020. The Direct Mercury Analyzer was validated in September 2020 and was used for the analysis of all 2019 Litterfall samples for total mercury.

### 6.4. Samples

There were no major changes to sampling procedures for the HAL in 2020. Sample loads were temporarily affected by the COVID-19 pandemic. See **Section 4** (Network Operations) for more details.

### 6.5. Data Management

In January 2020, the NADP LIMS was completed and data review for June 2019 and subsequent samples using this new platform began. Turn-around time (TAT) was at 208 days at the beginning of the year. Despite some complications with the new LIMS and the pandemic, the TAT for MDN samples was reduced to ~100 days by the end of 2020. The MDN data management team is on track to reduce TATs to <90 days in 2021.

### 6.6. Client Feedback

Camille Danielson and Martin Shafer worked on a Data Quality Objectives survey that was sent out to many of our primary data users. Results of the survey were used to help guide our first Data Quality Objective Summit, which was held in early 2021. Survey results are available upon request.

### 6.7. NADP-Wide Improvements and Recommendations

#### **6.7.1.** Items in Progress

- Establish Data Quality Objectives (DQOs)
- Evaluate results from DQO survey and summit.
- Create a more user friendly NADP mobile website
- Identify data user priorities (engage stakeholders)
- Improve website data interfacing
- Individual site data: Summary, trends, fact sheet to be provided to site funders, managers, operators
- Mapping options- more time resolution, other modeling options (seek input on this)
- Newsletter or other more general communication regarding data, network changes and operator highlights

## 7. Staff Training

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

Analytical staff also complete an annual analytical demonstration of capability (DOC) for each platform they operate (THg – Tekran 2600, MeHg – Tekran 2700, THg – Nippon MA-3000). New staff undergo even more rigorous DOC, initial document review and training protocols.

## 8. Instrumentation

The HAL currently has three instruments dedicated to Hg analysis. The CVAFS instruments are also used for analyzing surface waters and research samples for other programs, including the Wisconsin Department of Natural Resources.

**Table 4**. Major Analytical Equipment

| Analysis | Species | Instrument |
|---|---|---|
| Automated Cold Vapor Atomic Fluorescence (CVAFS) | Total Hg | Tekran 2600 with IVS |
| Automated Cold Vapor Atomic Fluorescence (CVAFS) with Chromatographic separation | Methyl Hg | Tekran 2700 with IVS |
| Thermal Decomposition, Gold Amalgamation, and Atomic Absorption Spectroscopy (AAS) | Total Hg (solids) | Nippon MA-3000 |

## 9. QA Documents

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

### 9.1. Standard Operating Procedures

The HAL has prepared the standard operating procedures (SOPs) outlined in **Table 5** as of the QAR date. SOPs are available upon request. The analytical SOPs are revised as necessary in a time-sensitive manner when method updates are introduced and tracked using version control. Staff that work on a particular task are required to review the SOPs annually for those tests or processes and to affirm completion of their reviews.

**Table 5**. NADP HAL Standard Operating Procedures Table of Contents

| SOP # | Rev # | Original Effective Date | Current Effective Date | Title |
|---|---|---|---|---|
| 100 | 2 | 3/20/2019 | 7/6/2020 | Sample Login and Data Entry |
| 104 | 0 | 8/16/2021 | 8/16/2021 | MDN Supply Shipping and Receiving |
| 200 | 2 | 10/1/2018 | 7/30/2020 | NTN and MDN Supply QC |
| 202 | 1 | 4/3/2019 | 12/7/2020 | Analytical QC Audit |
| 405 | 2 | 7/18/2019 | 6/25/2021 | MDN Supply Preparation |
| 406 | 0 | 10/15/2020 | 10/15/2020 | Litterfall Sample Processing |
| 506 (ESS 541.2) | 2 | 9/11/2019 | 3/18/2021 | Total Mercury by Oxidation, Purge & Trap, and CVAFS |
| 508 | 0 | 9/23/2020 | 9/23/2020 | Total Hg in Solids by Thermal Decomposition, Gold Amalgamation, and AAS |
| 507 (ESS 545.2) | 1 | 1/29/2020 | 8/5/2021 | MeHg in Water by Auto-CVAFS |

## 10. Method Detection Limits

### 10.1. MDN and Litterfall Method Detection Limits (MDL)

Calculations of MDN and Litterfall mercury 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 6** below. The LOD and LOQ for MDN did not change from 2019.

**Table 6**. Network MDLs

| Network | Analyte | 2019 LOD | 2020 LOD | 2019 LOQ | 2020 LOQ |
|---|---|---|---|---|---|
| MDN | THg | 0.2 ng/L | 0.2 ng/L | 0.667 ng/L | 0.667 ng/L |
| MDN/Litterfall | MeHg | 0.1 ng/L | 0.1 ng/L | 0.3 ng/L | 0.3 ng/L |
| Litterfall | THg | NA | 0.1 ng* | NA | 0.33 ng |

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

#### 10.1.1. 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) the QA staff will calculate the lab detection limit for use in assessing data for the following 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 provide on the website data. There is no flagging of samples that are below the lab MDL. The HAL will consider developing a Network MDL that takes into account some of uncertainty in the sample handling and processing.

### 10.2. Ongoing MDL Verification

MDN MDLs are verified by analyzing a spiked solution, prepared with 0.5% HCl (v/v) and 1% BrCl (v/v), at a concentration between 1-5x (currently 2.5x) the initial MDL with every analytical run. Annually, these spiked samples and all of the batch method blanks are assessed. The Lab MDL is calculated and compared to the previous MDL. The lab MDL may remain unchanged if all of the following criteria are met: 1) the new MDL is within 2x the current established MDL, 2) fewer than 3% of the method blanks are above the established MDL, and 3) fewer than 5% of the spiked samples fail to meet recovery criteria (per 40 CFR 136, Appendix B, Vol. 82, No. 165, Aug. 28, 2017, U.S. Environmental Protection Agency). Litterfall Network MDLs are verified by performing a complete MDL study annually because the instrument for this network is used infrequently.

#### 10.2.1. MDN MDL Adjusted by Dilution

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

## 11. External and Internal Field QA Programs

Information for Sections 11.1 – 11.3 is extracted from the U.S. Geological Survey (USGS) External Quality Assurance Project Report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network and preliminary 2020 report by Greg Wetherbee at the USGS.

The USGS has historically used two programs to provide external quality assurance monitoring for the MDN. The system blank program assesses the effects of onsite exposure, sample handling, and shipping on the chemistry of MDN samples. The inter-laboratory comparison program assesses the bias and variability of the chemical analysis data from HAL, and other participating laboratories that analyze precipitation samples for mercury.

### 11.1. Field QC System Blank Program

The MDN site operators normally receive system blank samples from the USGS Precipitation Chemistry Quality Assurance project (PCQA). When operators receive field system blanks from PCQA they wait until there is a week without wet deposition at their site. The operator then pours one-half of the volume of the system blank solution (reagent grade water) through the glass sample train. The glass sample train consists of the collector funnel, which collects the precipitation sample, and a thistle tube, which drains the precipitation into the sample bottle. On a dry week, the operators use the solution provided to them and wash ~half of it through the sample train. This is called the system blank sample (also known as "DF"), and the solution remaining in the original sample bottle is called the bottle blank sample (also known as "DK"). Both system blank and bottle samples are sent to the HAL for total mercury (Hg) analysis. Reports of this data are prepared every two years by the USGS. From the most recent report, the maximum contamination in MDN samples during 2015–17 was not greater than 1.02 ng/L with 90-percent confidence, and no more than 10 percent of the MDN samples had contamination concentrations exceeding 1.02 ng/L with 90 percent confidence. This concentration is approximately equal to the first percentile of all MDN weekly Hg concentrations from 2016–18.

In 2020, USGS also sent two aliquots of system blank solution directly to the lab to ensure the original water used in the field blanks for analysis was not contaminated. Both blanks measured well below the established blank limit (<0.2ng/L). The 2020 data from the CAL LIMs indicates some contamination in the field but also some bottle blanks that were higher than might be expected. Sometimes the reportedly processed sample is much lower than the unprocessed water. This, as well as reports from log in staff that sample identity is not always clear, casts some uncertainty on the validity of these results. In 2022, the HAL will be managing the shipment of the DF/DK bottles and hopes to improve the clarity on which sample has been processed. The results are displayed in **Figure 3** and **Figure 4**.

**Figure 3.** Total mercury results for the 41 unprocessed bottle blanks (DK) returned from the sites in 2020.

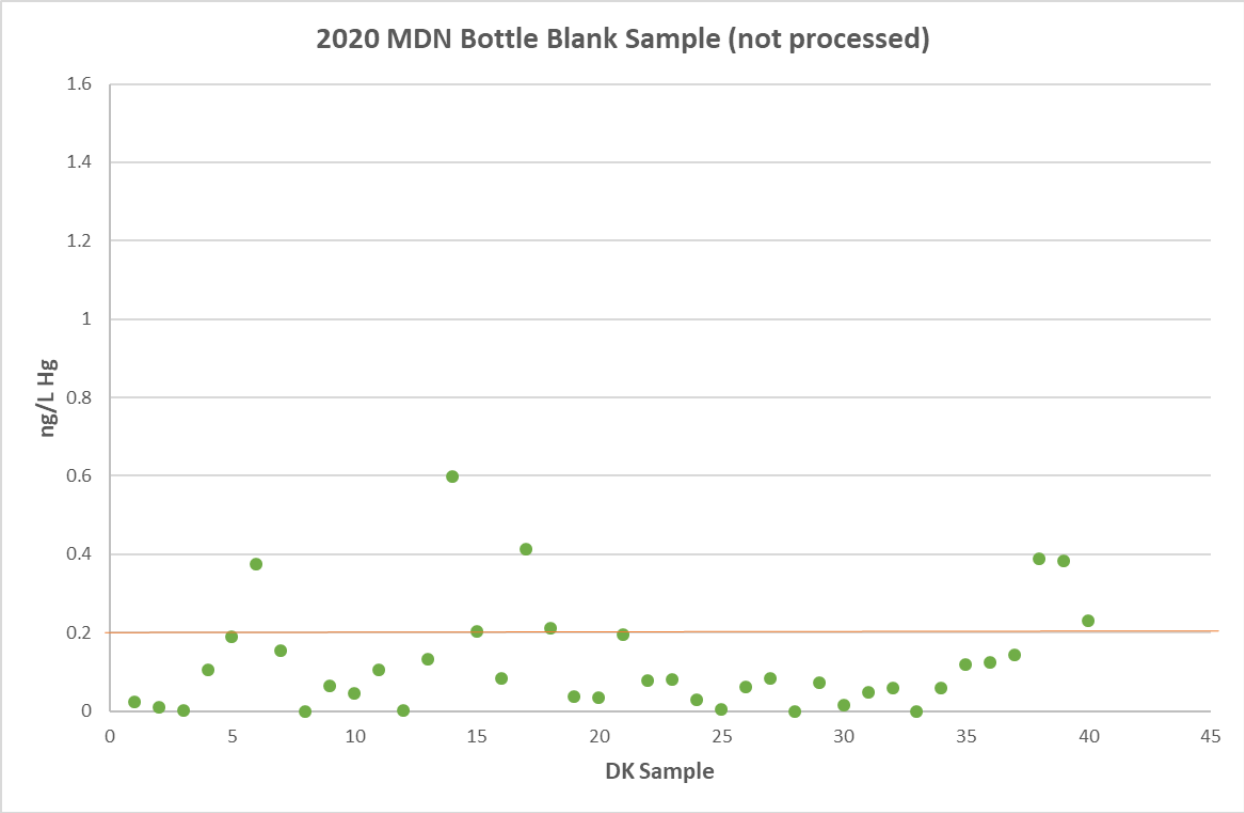
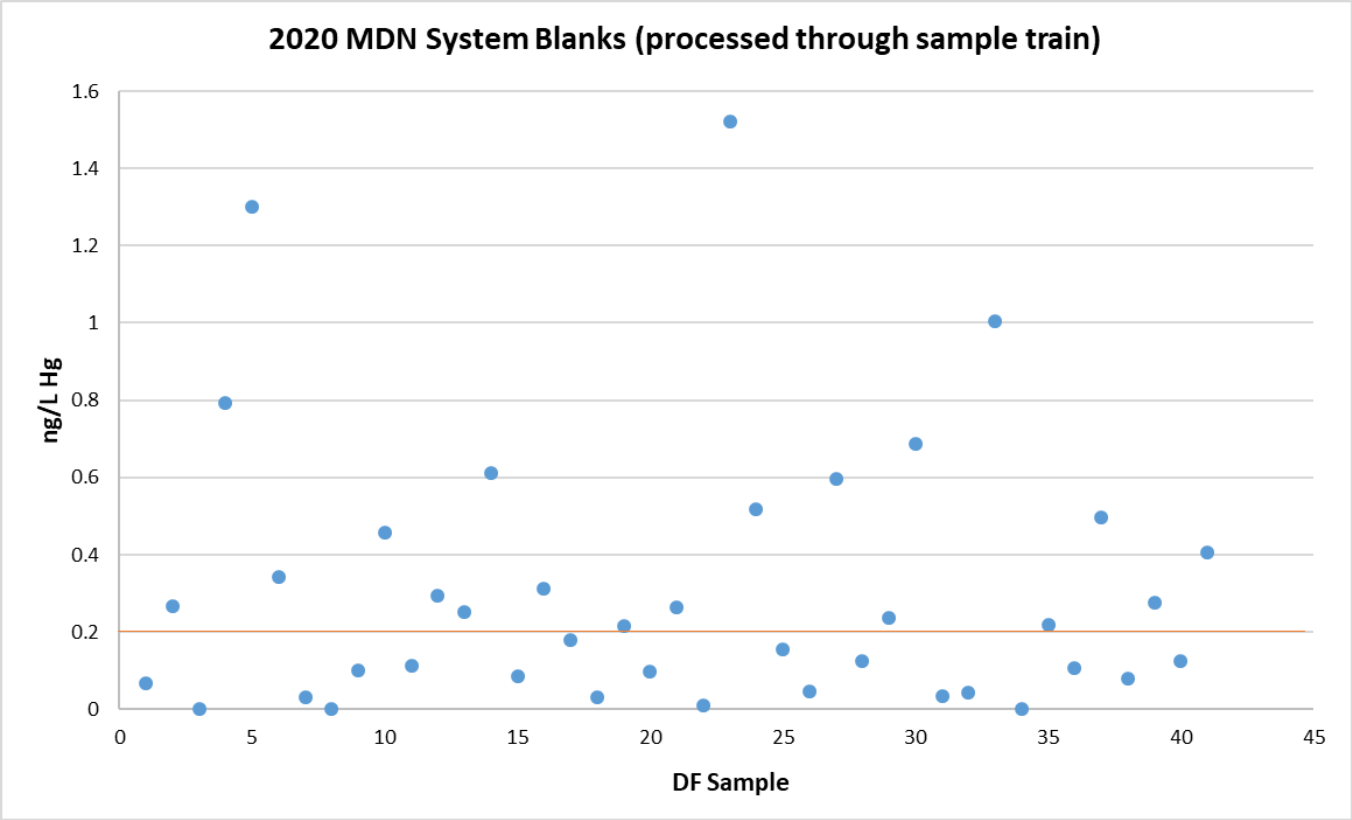


**Figure 4**. Total mercury results for the 41 system blanks (DF) that were processed through the sample train and returned from the sites in 2020.




### 11.2. USGS Proficiency Testing Studies

The HAL participates in the monthly THg Proficiency Testing (PT) program run by the USGS. Normally, two PT samples are provided and analyzed each month. Due to the COVID-19, this schedule was hindered due to USGS laboratory closures. Despite the irregular schedule, 24 PT samples were still received and analyzed in 2020. Of the 24 2020 PT samples, 16 of the results were acceptable by USGS criteria and were within the 80-120% recovery guidelines set for the method. The other eight samples did not meet criteria. It should be noted that other participating laboratories had similarly poor results for many of the PT samples. This likely skewed the most probable values (MPVs). A USGS PT program representative indicated that there may have been issues with the standards used to prepare the PT samples for 2020. Excluding the extreme outliers, the 2020 PT results suggest that the HAL has a low bias for Hg [USGS MDN Preliminary Field Assessment 2020].

**Table 7: USGS PT Sample Results: January 2020 - December 2020**

| LIMS ID | USGS ID | Date Analyzed | Result ng/L | MPV ng/L | % REC | RPD |
|---|---|---|---|---|---|---|
| 20000638 | 2020015019 | 3/3/2020 | 11.92 | 13.30 | 89.62 | 10.9 |
| 20000639 | 2020015020 | 3/3/2020 | 0.30 | 0.09 | - | <MDL |
| 20001246 | 2020044019 | 3/11/2020 | 4.40 | 5.31 | 82.77 | 18.9 |
| 20001247 | 2020044020 | 3/11/2020 | 6.08 | 7.65 | 79.50 | 22.8 |
| 20001858 | 2020070019 | 3/26/2020 | 18.47 | 19.30 | 95.70 | 4.4 |
| 20001859 | 2020070020 | 3/26/2020 | 0.00 | 0.09 | - | <MDL |
| 20003467 | 2020162019 | 6/23/2020 | 4.82 | 5.24 | 92.03 | 8.3 |
| 20003468 | 2020162020 | 6/23/2020 | 7.22 | 7.60 | 94.97 | 5.2 |
| 20003469 | 2020162039 | 6/23/2020 | 9.77 | 19.60 | 49.83 | 67.0 |
| 20003470 | 2020162040 | 6/23/2020 | -0.01 | 0.09 | - | <MDL |
| 20003471 | 2020162057 | 6/23/2020 | 6.98 | 7.34 | 95.15 | 5.0 |
| 20003472 | 2020162058 | 6/23/2020 | 17.28 | 18.70 | 92.41 | 7.9 |
| 20004054 | 2020198019 | 7/29/2020 | 3.12 | 3.26 | 95.66 | 4.4 |
| 20004055 | 2020198020 | 7/29/2020 | 18.97 | 20.20 | 93.90 | 6.3 |
| 20004654 | 2020225019 | 9/23/2020 | 14.70 | 24.50 | 59.98 | 50.0 |
| 20004655 | 2020225020 | 9/23/2020 | 1.31 | 1.75 | 75.03 | 28.5 |
| 20005433 | 2020260019 | 9/24/2020 | 8.43 | 10.30 | 81.82 | 20.0 |
| 20005434 | 2020260020 | 9/24/2020 | 0.04 | 0.09 | - | <MDL |
| 20006233 | 2020324019 | 11/2/2020 | 24.71 | 24.50 | 100.85 | 0.8 |
| 20006234 | 2020324020 | 11/2/2020 | 13.62 | 20.20 | 67.43 | 38.9 |
| 20007344 | 2020342019 | 12/17/2020 | 4.05 | 5.54 | 73.14 | 31.0 |
| 20007345 | 2020342020 | 12/17/2020 | 5.79 | 7.99 | 72.50 | 31.9 |
| 20007346 | 2020344019 | 12/17/2020 | 4.87 | 5.54 | 87.84 | 12.9 |
| 20007347 | 2020344020 | 12/17/2020 | 14.75 | 19.60 | 75.26 | 28.2 |

From the USGS MDN Preliminary Field Assessment 2020:

- Negative analytical bias ~ 1 ng Hg /L indicated for HAL
- HAL variability ~ 62% higher than overall among labs
- Hg Network Max Contamination ~ 0.09 ng / sample

## 12. Analytical QA and Acceptance Criteria

Each QC solution has a set target value and acceptable range of values based on the applicable criteria (some are +/-15%, MDL etc.).

**Table 8**. MDN Analytical Limits and Batch Run Sample Sequence

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

**Table 9**. 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 |

### 12.1. Analytical Sample Matrix Spikes and Duplicates

A second and third aliquot from a randomly chosen (from those with >400 mL) MDN sample are analyzed with a spike level of 15 ng/L and the precision between the two results is evaluated. A matrix spike (MS) and matrix spike duplicate (MSD) pair are prepared for every group of 10 or fewer samples. Therefore, approximately 10% of samples are spiked. Matrix spikes must recover between 75%-125% and the two spike results must have an RPD<24% (per EPA Method 1631). Please refer to **Table 8** for all HAL QA/QC samples and associated criteria.

For Litterfall, a duplicate and matrix spike are analyzed every 10 samples or fewer. Samples are chosen at random. Duplicates must have an RPD <20%. Litterfall samples are analyzed with a spike of 5 ng. The spike recovery must be within 80-120%. For each analysis date, one sample must be randomly selected for triplicate analysis at three different masses (20 mg, 30 mg, and 40 mg). The percent RSD (of the ng/g data)

must be within 10%. Daily calibration is not required; a check standard must be recovered 80-120% and a blank must measure below the MDL. Please refer to **Table 9** for all Litterfall QA/QC samples and associated criteria.

#### 12.1.1. 2020 MS/MSD Results

In 2020, there were no MS recovery failures and no MS/MSD failures associated with reported samples for MDN or Litterfall. Infrequent failures may occur due to instrument instability or analyst errors. In such a case, all samples in the control group are promptly reanalyzed and documented. The mean recovery for accepted matrix spikes was 105.6% for MDN; the mean RPD was 1.85%. All matrix spikes met criteria for Litterfall in 2020.

#### 12.1.2. 2020 Litterfall %RSD Results

In 2020, 2 sets of triplicates were analyzed for Litterfall. The percent RSD of both sets measured within 10%.

## 13. Digested Lab Reagent Blanks (DLRB)

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

### 13.1. DLRB Results

In 2020, results for 256 DLRBs were reported. No LRBs measured above the method detection limit (MDL) of 0.2 ng/L in 2020. The average LRB results was 0.012 ng/L.

## 14. Digested Quality Control Standard (DQCS)

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

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

### 14.1. DQCS Results

In 2020, 84 DQCS samples were reported for MDN. None of the samples exceeded the control limits, and the average recovery was 98.4%. All NIST 1515 samples for Litterfall met criteria in 2020.

## 15. Network Supply QC

Each network within the NADP long-term monitoring program requires very specific sampling supplies, all cleaned and prepared using established specialized protocols to maintain high data quality and consistency throughout the networks. The NADP must supply materials of identical quality to those being replaced at the sites. The HAL cleans and provides supplies for MDN. All network supplies must meet Supply QC criteria listed in **Table 10**.

**Table 10. MDN Network Supply QC Criteria**

| Total Hg Run ID | LIMS ID | Target Value (ng/L) | Criterion (ng/L) Total Hg |
|---|---|---|---|
| **Sample Train Blank** | 2000XXXX | 0.0 | <0.8 ng/L (<0.08 ng per train) |
| **Acid Bath Blank** | 2000XXXX | 0.0 | None – monitor in conjunction with other QC |
| **1L PETG Bottle Blank** | 2000XXXX | 0.0 | Mean bottle batch <0.2 ng/L (No bottle >0.667 ng/L) |
| **2L PETG Bottle Blank** | 2000XXXX | 0.0 | Mean bottle batch <0.2 ng/L (No bottle >0.667 ng/L) |
| **Acid Preservative Blank** | 2000XXXX | 0.0 | <0.4 ng/L (15 mL sample) |
| **THg Type I Water Blank** | 2000XXXX | 0.0 | <0.2 ng/L |

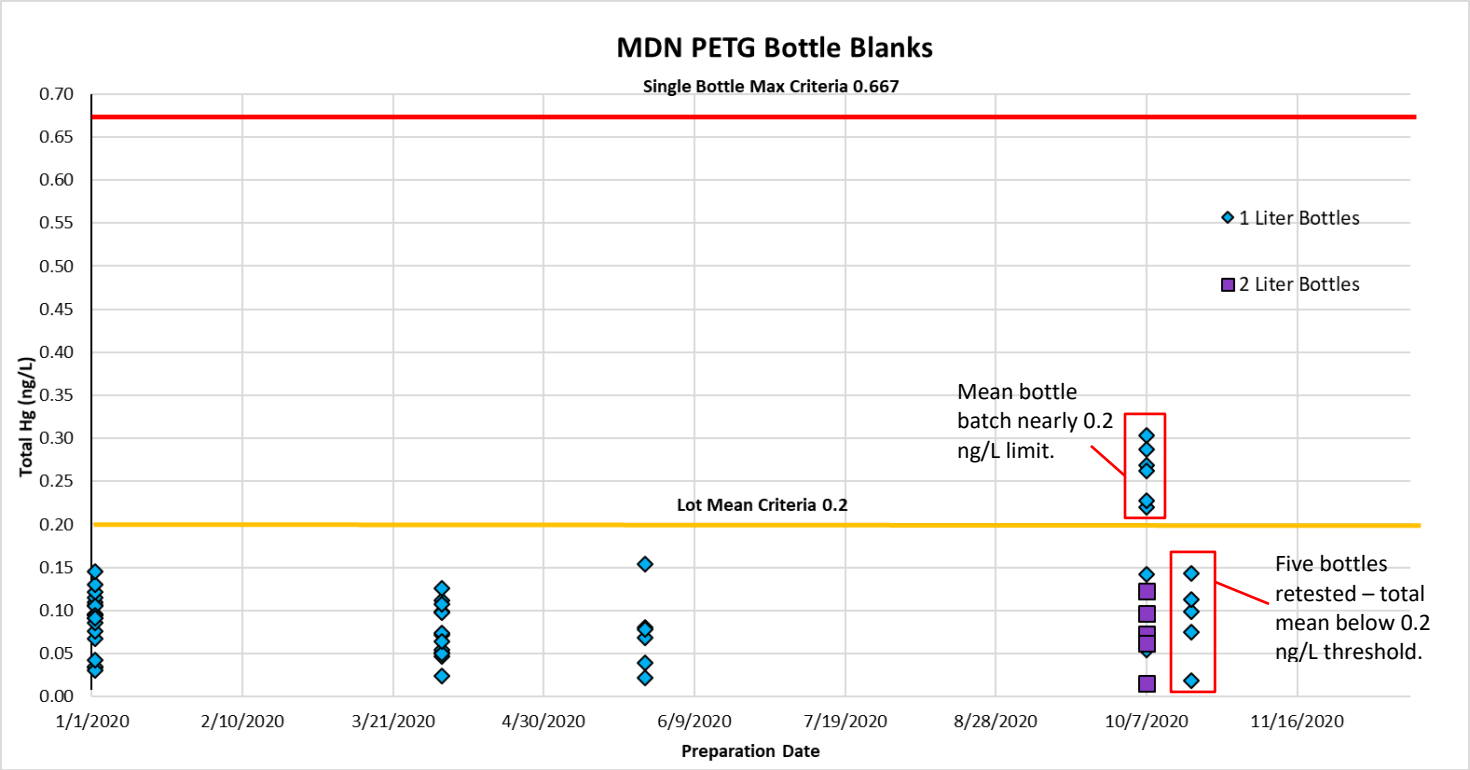
### 15.1. New Supply Assessment

New lots of MDN 1L and 2L PETG bottles must meet established “Lot QC” based criteria before use within the network. Details are provided in NADP SOP 200 “NTN and MDN Supply QC”, and a brief summary is provided below.

#### 15.1.1. New PETG Bottle Testing

PETG (Polyethylene terephthalate glycol) bottles are purchased in batches from common lots and tested for background mercury concentrations. PETG bottles replaced glass bottles for MDN sample collection in July 2018. New PETG bottle lots are blank tested without bottle rinsing by filling the bottle with a weighed quantity of Type I water. Samples are then brominated to a level of 1% v/v BrCl and left to sit overnight before being analyzed. Currently, 2L and 1L bottles are in use for sample collection. One lot of 1L bottles required retesting in October 2020. Initial testing resulted in a mean bottle batch blank of nearly 0.2 ng/L (just at the threshold value). Five additional bottles from the lot were tested, and these additional bottles all measured below 0.2 ng/L and reduced the batch mean to acceptable levels. It is suspected that the initial bottle blanks were contaminated during preparation. All lot checks of bottles in 2020 met criteria as shown in **Figure 5.**

**Figure 5. MDN PETG Bottle QA 2020 Results**




### 15.1.2. Lot Testing Criteria

The HAL lot testing criteria states that the mean of at least 10 samples per lot must be <MDL and none of the supply blanks in the batch tested may exceed 3 times the MDL. 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 supplies greater than 1000 a minimum sample set of 20 QC checks are analyzed. Lot approval criteria are listed previously in **Table 10**, and results for the numbers of samples that exceeded criteria in 2020 are shown in **Table 11**.

**Table 11**. Lot Approval QC Samples and Failures

| Bottle Size Tested | # of 2020 QC Samples | # of Individual Exceedances | # mean Lot Exceedances (≥0.2 ng/L) | Lots Tested | Lots Rejected | Lots Approved |
|---|---|---|---|---|---|---|
| **PETG 1L** | 63 | 6 | 1 (retests lowered avg to 0.16 ng/L) | 6 | 0 | 6 |
| **PETG 2L** | 15 | 0 | 0 | 3 | 0 | 3 |
| **Total** | 78 | 0 | 0 | 9 | 0 | 9 |

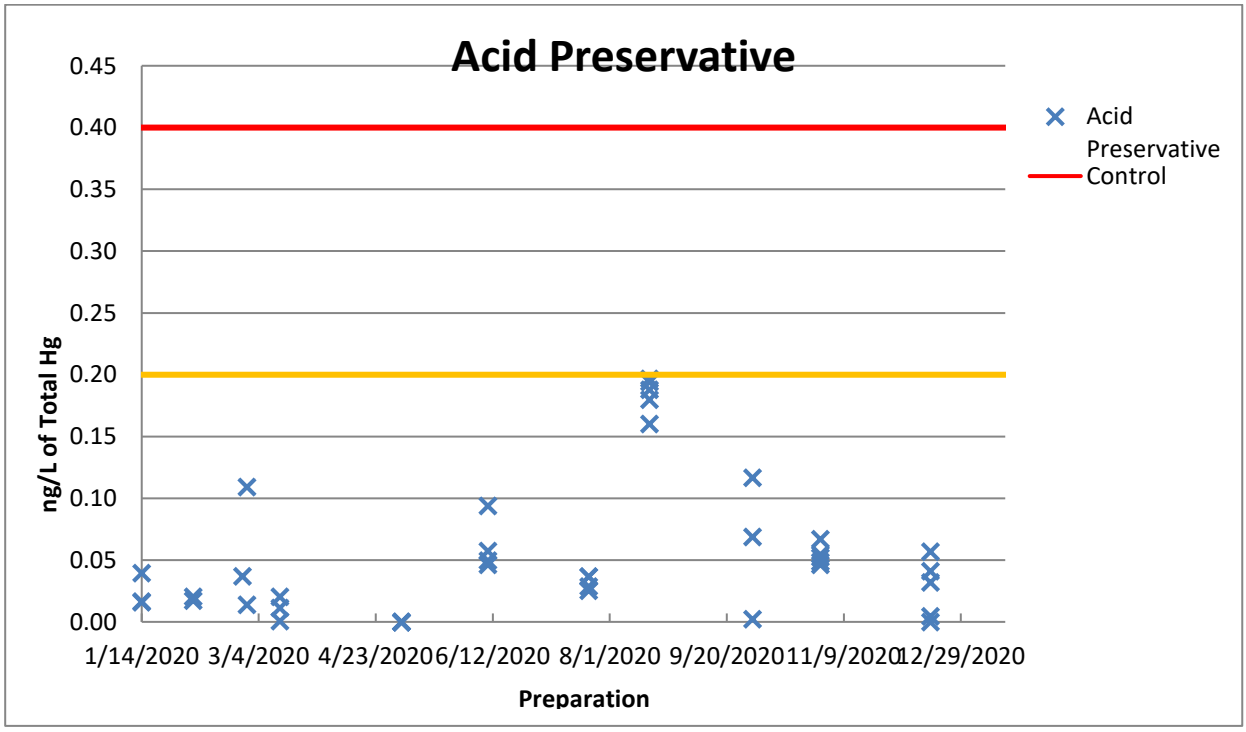
### 15.1.3. New Acid Preservative Testing

Acid preservative is prepared by MDN sample receiving staff. Acid preservative is 1% v/v HCl (~1.2M, Trace Metal Grade), prepared in 2L batches. All MDN 1L bottles are pre-charged with 20 mL of acid preservative and all 2L bottles are pre-charged with 40 mL of preservative before being shipped to sites for field use (**Table 12**). Acid preservative must be <0.4 ng/L in order to be approved for official use. All acid preservative batches prepared in 2020 met criteria as shown in **Figure 6.**

**Table 12**. New Acid Lot Supply QC for MDN

| Item | Solution | Frequency & Amount | Project Login | LIMS Description |
|---|---|---|---|---|
| **PETG 1L Bottle Blank** | 20 mL 1% HCl + 100 mL MQ (30 mL analyzed) | 10/new lot (unless <200, then 5) | MDN Bottle Blanks | Bottle Type, Lot #, Bottle # (i.e. 1L MDN LOT44348 1 OF 10 |
| **PETG 2L Bottle Blank** | 40 mL 1% HCl + 100 mL MQ (30 mL analyzed | 5/new lot | MDN Bottle Blanks | Bottle Type, Lot #, Bottle # (i.e. 2L MDN LOT44349 1 OF 10 |
| **Acid Preservative Blank** | 30 mL (15 mL analyzed) | 1/batch acid preservative, prior | Acid Checks | Acid Lot # + Batch ID |

**Figure 6. MDN Acid Preservative Testing, 2020**



### 15.2. Ongoing Supply Assessment

Data from the ongoing supply QC program (**Table 13**) is assessed, at a minimum, on a quarterly basis. Trends are investigated and corrective action taken as needed. Analysts must notify the QA Manager if they notice high supply blanks in analytical runs so that they can be followed up on as quickly as possible. Reused supplies are assessed for blank values above the supply criteria (which are set to the HAL MDL).

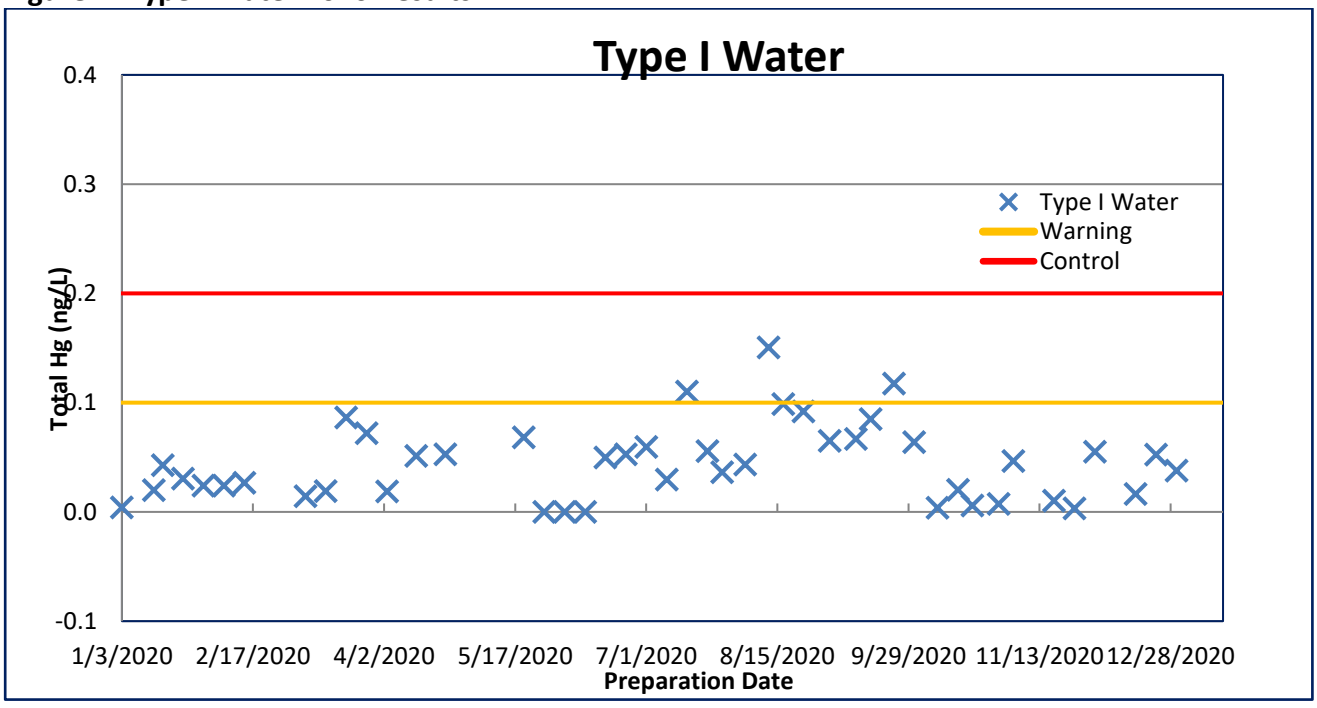
**Table 13**. MDN Ongoing Supply QC, Performance Test Solutions, and Standards

| Item | Solution | Frequency + Amount | Project Login | LIMS Description |
|---|---|---|---|---|
| **MDN Type I Water** | 100 mL MQ | 1/purifier/week | MQ Water System Blanks | Type I Blank, Building, RM # |
| **MDN Sample Train** | ~100 mL MQ | 1/week (in bag ≥2 days) | Sample Train Blanks | Sample Train, Week # |
| **MDN Acid Bath/Crock** | 10 mL (from reservoirs) | 1/acid bath/month | Acid Checks | Acid Bath Blank, Bath ID # |
| **MDN USGS PTs** | As Sent | 2/month | MDN PT Samples | USGS MDN PT X of X |
| **USGS System Blanks** | High Purity $H_2O$ | 2/quarter | USGS System Blanks | USGS ID, Blank X of X |

#### 15.2.1. Type I Water

Type I water (deionized water routed through a water polisher) is tested for THg weekly by collecting 100 mL of Type I water in a 250 mL PETG bottle. There were no exceedances in 2020 for Type I water blanks as shown in **Figure 7**. Note that negative values may occur because all peak areas are blank-subtracted by the mean calibration blank for the run.

**Figure 7. Type I Water 2020 Results**

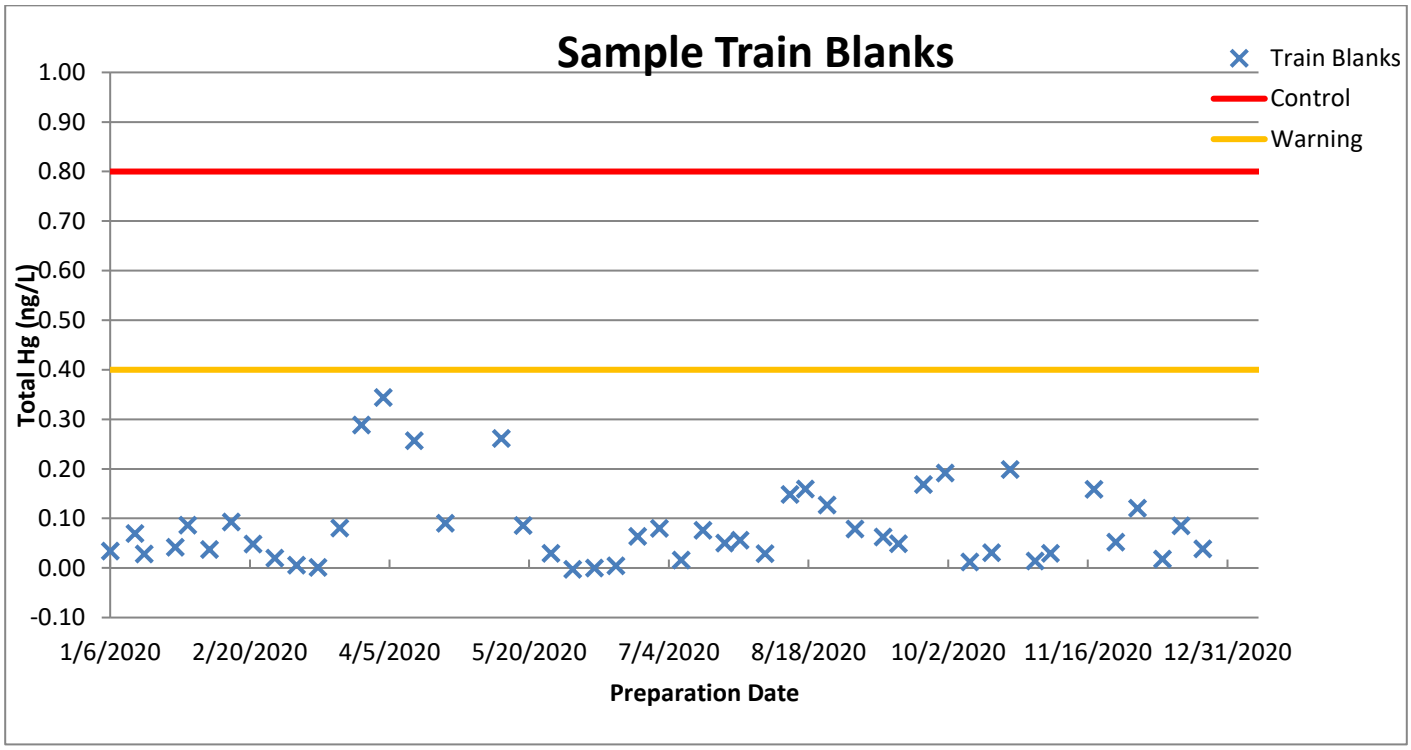


### 15.2.2. Sample Train Blanks

Sample train blanks are collected and tested weekly to monitor background concentrations of Hg in sampling glassware. Sample train glassware components, which have been cleaned, bagged, and stored, are randomly selected. The glass sample trains components are assembled, and approximately 100 mL of Type I reagent water is passed from the funnel, through the thistle tube, and collected in a weighed PETG bottle. The samples are then labelled, bagged, brominated, and analyzed according to procedures for natural samples.

No sample train blanks exceeded criteria in 2020. The limit for sample train blanks is 0.8 ng/L (**Figure 8**). Further MDN supply criteria are outlined in NADP SOP 405 MDN Supply Preparation. See Appendix A for MDL and supply QC criteria.

**Figure 8. Sample Train 2020 Results**




### 15.2.3. Acid Baths

Two acid soaking tubs are used to clean glassware, both containing 25% v/v HCl (3M). Funnels are immersed in a 70 L vat of 25% acid, and thistle tubes are immersed in a 25 L crock of 25% acid for at least 24 hours. Both baths were tested for total Hg weekly until 2020. The HAL is continuing to monitor the baths, but there does not appear to be a direct correlation to the sample train blanks. Acid bath solutions will be replaced as needed, based on results of blank controls from sample trains and informed by acid bath trends (**Figures 9 and 10**).

**Figure 9. Acid Bath Vat (Funnels) 2020 Results**

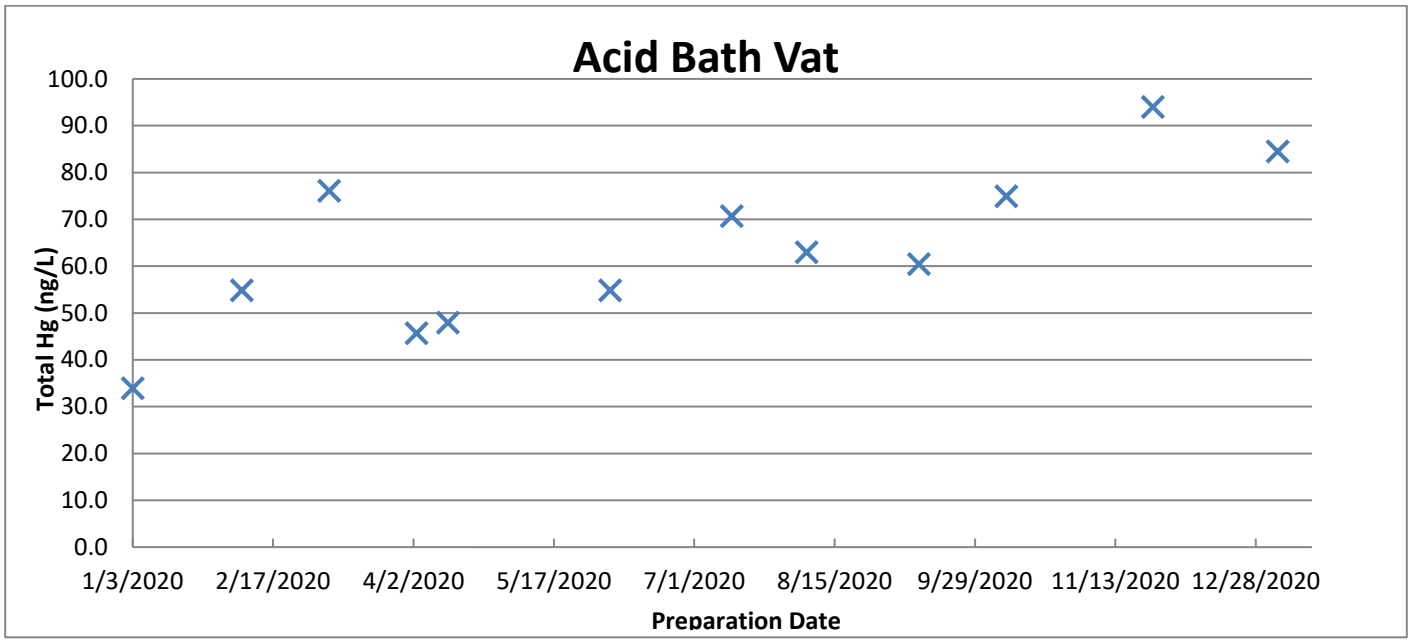
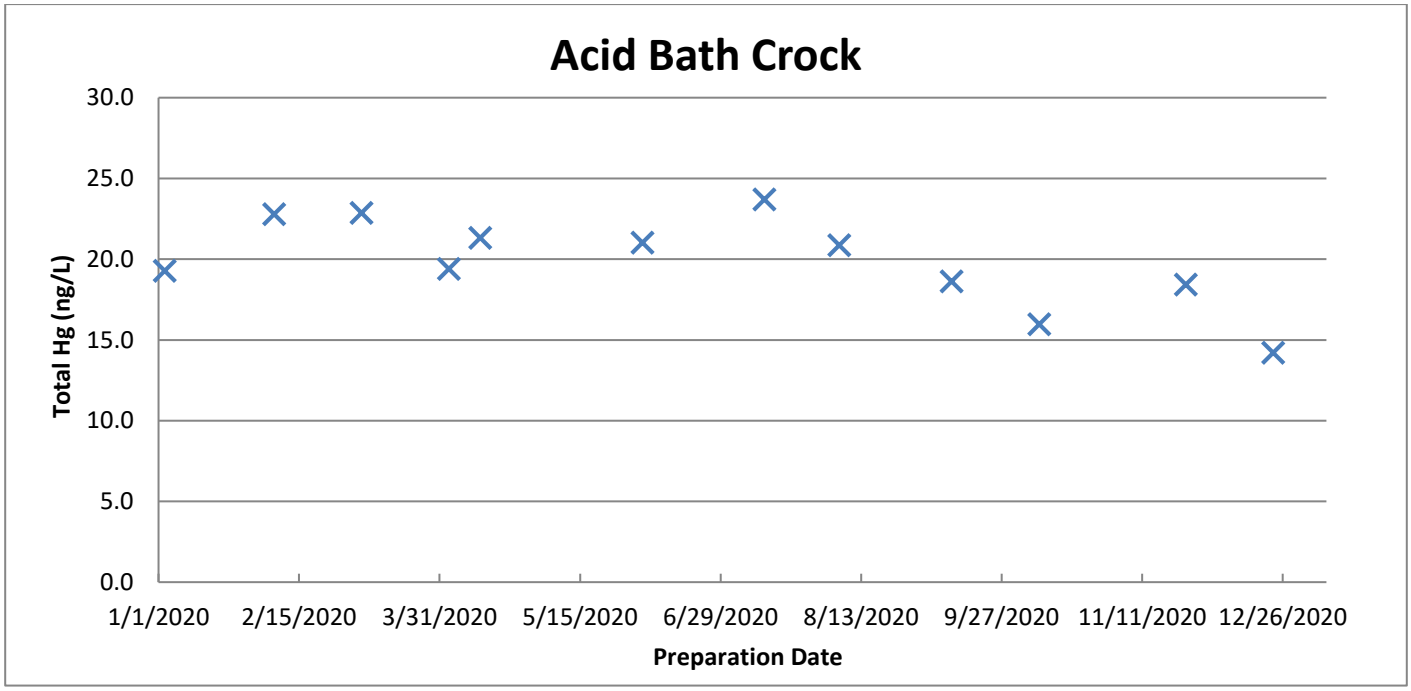



**Figure 10. Acid Crock (Thistle Tubes) 2020 Results**



## 16. Litterfall Collector QC

All laboratory supplies and materials were provided and prepared by USGS for the 2019 collection season. No field materials were tested by the WSLH for the 2019 season. WSLH does test material blanks for Litterfall; these results will be summarized in the next QAR.

## 17. Litterfall Process Blanks

Litterfall process blanks were prepared at a rate of one blank per three sites for the 2019-20 Litterfall season samples. Process blanks consisted of running ~50 mg of dry milk powder through the grinder used for all Litterfall samples. All process blanks measured below the MDL in 2020.

## 18. Audits

### 18.1. Internal Audits

Internal Systems Audit – November 2020

#### 18.1.1. Internal Systems Audit Findings

- Finding 1: NADP Data Review SOPs 301 and 302 need to be reviewed and updated. MDN Data review SOP needs to be completed as soon as possible. SOP on writing and managing SOPs to be written once Onbase is functional. A table of contents of all NADP spreadsheets needs to be put together.
- Finding 2: Need to develop a survey regarding lab/data reporting performance.
- Finding 3: Issues with MDN sample traceability. MDN sample IDs are not provided on the NADP website. MDN is lacking in adjusted MDLs and dilution factors on the website. There are inconsistencies with provision of QR C data on the web. MDN is provided on the web in two ways - with and without QR C results (with a disclaimer). There is a need for consistency, transparency, and more robust qualifying for all the networks.
- Finding 4: Lacking SOP on internal audit procedure.
- Finding 5: Need procedures for estimating uncertainty.
- Finding 6: Equipment list is not up to date.
- Finding 7: Thermometers were overdue for verification and lacking documented procedures for these tasks.
- Finding 8: The NADP electronic laboratory notebook (ELN) was reviewed as part of this process and some errors in records were found.
- Finding 9: MDN and metadata on the website is outdated and has no document control (i.e. revision date or ID) and does not include definition of “q” notes code and may need other updating.

### 18.2. External Audits

No external audits were performed during this period. An external audit is scheduled for September 2021.

## 19. Occurrence Management

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

### 19.1. HAL Occurrences 2020

There was one major occurrence in 2020, concerning a suspected carryover issue with the Tekran 2600 used to analyze MDN THg samples. The issue was first identified in July 2020 and persisted through February 2021. As a temporary workaround, a Type I Water blank was measured between each sample to monitor for contamination. The manufacturer was contacted in August 2020 and a series of troubleshooting procedures took place between then and the date of resolution. In February 2021, it was discovered that the issue was reagent based. The Hydroxylamine-HCl reagent was incompletely consuming the excess bromine in the sample. Residual bromine was being purged into the analytical system as a gas, damaging the gold traps and causing the gold to be released to the detector, causing a positive interference. The problem was resolved by increasing the amount of Hydroxylamine-HCl used for sample preparation and storing hydroxylamine in a desiccator to ensure that the hydroscopic reagent was not impacted by adsorbed water. This occurrence (#3985) was closed 2/2021.

## 20. Method Improvement Projects

The HAL has continued to test and assess new techniques and supplies that might improve outcomes for the networks. Some of the initiatives pursued in 2020 include:

- Method development of Litterfall MeHg analysis by distillation and CVAFS
- Method development of Litterfall THg analysis by Thermal Decomposition, Gold Amalgamation and AAS.
- Began exploration of alternative Litterfall processing procedures (oven drying, subsampling, etc.)
- Began exploration of alternative sampling options (e.g., passive carbon sampling) for MDN.
- MDN field spiking experiments to determine if Hg loss is occurring
- MDN field duplicate program to quantify real-world sampling precision at sites WI06 and WI31.

## 21. Data Review

### 21.1. Analytical Data Review

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

- Peer review – a second analyst reviews all data packets prior to results being uploaded to LIMS and released.
- Possible Qualifiers spreadsheet – a record of all anomalies associated with samples during preparation/analysis.

- Duplicate failures spreadsheet – record of all duplicate failures even those corrected by rerun to assess trends.
- LIMS Compare – monthly data packet review per method compared to LIMS analytical data. Extra checks on dilutions, matrix spikes, and duplicates.

### 21.2. Network Data Review

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

MDN THg samples are analyzed well within the hold time (3 months from receipt), and data is peer reviewed promptly after analysis and uploaded to the NADP LIMS. Typically, MDN samples are analyzed within one month of receipt. Data delivery from the HAL to the sites is current as of January 2021 in **Table 14**. The HAL data turnaround time (TAT) is calculated from the end of the month in which a sample was received to the date that preliminary reports were sent to the sites. Publishing on the website is the responsibility of the program office (PO). MDN transitioned to the WSLH in June of 2019, requiring the development of a completely new LIMS for sample/data management, assessment and reporting by the HAL. The HAL LIMS component was completed in January 2020. The development of the HAL LIMS caused significant delays in the MDN data review process due to review staff efforts in developing the HAL LIMS. A 90-day TAT or less will be attained in 2021.

## 22. Data Management

**Table 14.** WSLH MDN Data Deliverables: Preliminary Reports Sent to Sites of Month Year.

| Network | Data Month | Prelim Reports Sent | HAL Avg TAT (days) |
|---|---|---|---|
| MDN | June 2019 | January 2020 | 208 |
| MDN | September 2019 | April 2020 | 212 |
| MDN | February 2020 | July 2020 | 152 |
| MDN | June 2020 | October 2020 | 106 |
| MDN | September 2020 | January 2021 | 113 |

## 23. References

- ESS INO Method 541.2 Mercury by Auto-CVAFS. Revision 1, July 30, 2020.
- ESS INO Method 545.2 MeHg in Water by Auto-CVAFS. Revision 1, June 25, 2020.
- National Atmospheric Deposition Program Laboratory Quality Assurance Plan, Mercury and Central Analytical Laboratories. Revision 1, June 25, 2020 (http://nadp.slh.wisc.edu/lib/qaPlans.aspx)
- NADP SOP 200 NTN and MDN Supply QC. Revision 2, July 30, 2020.
- NADP SOP 405 MDN Supply Preparation. Revision 2, June 25, 2020.

- NADP SOP 406 Litterfall Processing. Revision 0, October 15, 2020.
- NADP SOP 508 Hg in Solids by Thermal Decomposition. Revision 0, September 23, 2020.
- Wetherbee, G.A., and Martin, RoseAnn, 2020, External quality assurance project report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network, 2017–18: U.S. Geological Survey Scientific Investigations Report 2020-5084

## 24. Approvals

- 2020 HAL QAR Prepared by Kirsten Widmayer, Reviewed by Mark Olson HAL Manager, Christa Dahman HAL Supervisor and Camille Danielson, NADP CAL/HAL QA Manager Completed Draft: 8/30/2021
- Shared with External Review Team as Draft on: 9/1/2021
- Approved by the NADP Program Office: 9/5/2021
- Reviewed and revised by Systems QA and Special Projects Manager Martin Shafer: 9/19/2021
- Shared with the QAAG for review on: 9/30/2021
- Approved by QAAG by vote: 10/19/2021
- Shared at Fall 2021 NADP Technical Meeting