# 2019* Quality Assurance Report

## National Atmospheric Deposition Program (NADP)

## Mercury Deposition Network (MDN)

## Mercury Analytical Laboratory (HAL)

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

Analytical Laboratory Address:
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Madison, WI 53718

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

Revision Date: 8/28/2020

*Covering the period: June 01, 2019 to December 31, 2019

# 1 Contents

## 2 MDN Background

The Mercury Analytical Laboratory (HAL) prepares and provides field-sampling supplies, and performs sample processing, chemical analysis, and data validation services for precipitation samples collected by the NADP/Mercury Deposition Network (MDN). The MDN field operators and analytical laboratory staff must adhere to strict quality assurance (QA) and quality control (QC) procedures to ensure data quality. The HAL chemical analysis 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.

The WSLH took over the operations of the NADP HAL on June 1, 2019. The HAL was previously located at Eurofins Frontier Global Sciences (EFGS) in Bothell WA. To ensure data continuity 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. To ensure a smooth transition, in February 2019, WSLH employees visited EFGS 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 and final report 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. Samples collected after June 1, 2019 were shipped to and analyzed at the WSLH. Therefore, this QAR report covers the period from June 1, 2019 through December 31, 2019 and not a full year.

## 3 2019 HAL Staff

- HAL Manager – Mark Olson
- HAL Analytics/Trace Element Clean Lab Supervisor – Christa Dahman
- HAL (Shared with CAL) Associate Chemists - Nichole Davis, Kirsten Widmayer, James Sustacheck, Erin Pierce
- QA Manager (Shared with CAL) – Camille Danielson
- Sample and Data Processing Manager (Shared with CAL) – Amy Mager
- Assistant Data Managers (Shared with CAL) – Zac Najacht and Dana Grabowski

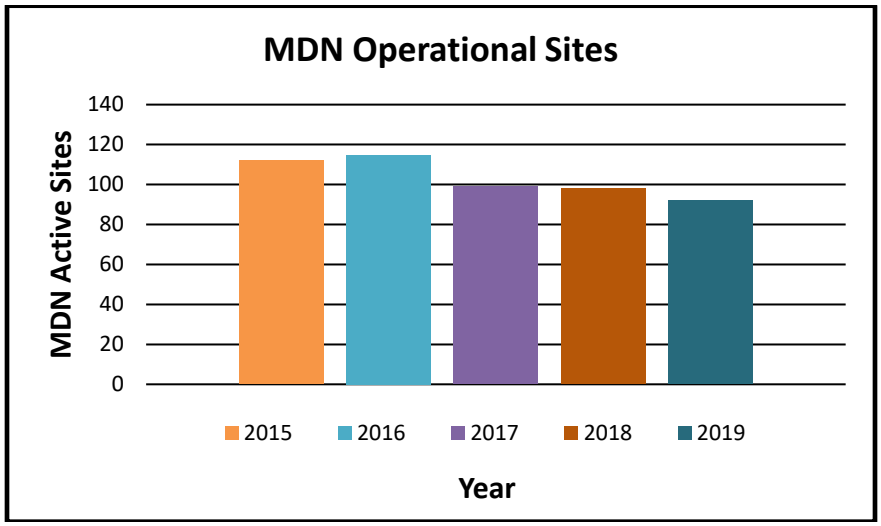
## 4 MDN Sample Counts

The WSLH began receiving MDN samples at the end of the 2rd quarter of 2019 and the number of samples received at the WSLH in 2019, as shown in ***Table 1***, reflects that start date. See ***Figure 1*** for number of sites over last 5 years.

**TABLE 1. MDN Sample Count 2015-2019**

| Year | MDN Active Sites | Total Samples | Number of Valid Samples | % Valid |
|---|---|---|---|---|
| 2015 | 112 | 5978 | 5495 | 91.9 |
| 2016 | 115 | 5617 | 5227 | 93.1 |
| 2017 | 99 | 5042 | 4583 | 90.8 |
| 2018 | 98 | 4705 | 4310 | 91.6 |
| 2019 January – May (EFGS) | 92 | 1875 | 1694 | 90.3 |
| 2019 June – December (WSLH) | 92 | 2559 | 2395 | 93.6 |

**FIGURE 1. MDN Operational Sites 2015-2019**




# 5 HAL Instrumentation

Major HAL instrumentation is shown in ***Table 2***. All instruments used for MDN sample analysis are verified and/or calibrated before use. Calibration verification standards must meet criteria (Appendix A) before analysis proceeds (refer to ***Table 5*** for a detailed description of batch run design and QC).

**TABLE 2. HAL Analytical Equipment**

| Analytical Objective | Species | Instrument |
|---|---|---|
| Total Mercury in Precipitation | Total Hg | Tekran 2600 with IVS |
| Methyl Mercury in Precipitation | MeHg | Tekran 2700 with IVS |
| Total Mercury in Solids | Total Hg | Nippon MA-3000 |

# 6 QA Documents

## 6.1 QAP/Standard Operating Procedures (SOPs)

The NADP Laboratory QAP includes both the HAL and the CAL. The current version is available on the NAPD website (see Section 12). Staff have prepared the necessary HAL SOPs as listed in ***Table 3*** and on the NADP website.

**TABLE 3. HAL Standard Operating Procedures**

| SOP # | Rev # | Original Effective Date | Current Effective Date | Title |
|---|---|---|---|---|
| 100 | 1 | 3/20/2019 | 4/8/2020 | Sample Login and Data Entry |
| 200 | 1 | 10/1/2018 | 2/28/2019 | NTN and MDN Supply QC |
| 202 | 0 | 4/3/2019 | 4/3/2019 | Analytical QC Audit |
| 405 | 1 | 7/18/2019 | 3/5/2020 | MDN Supply Preparation |
| 506 (ESS 541.2) | 0 | 9/11/2019 | 9/11/2019 | Total Mercury by Oxidation, Purge & Trap, and CVAFS |
| ESS 545.2 | 0 | 1/29/2020 | 1/29/2020 | MeHg in Water by Auto-CVAFS |

### 6.2 Annual Management Review

The annual management review (MR) of the HAL for calendar year 2019 was completed on January 27, 2020. The MR covers all major changes in the HAL laboratory over the previous year. The HAL MR is compiled along with reviews from the other sections of the WSLH Environmental Health Division (EHD) into one document which the division director reviews and approves (see Section 11). Significant operational changes in the HAL are also summarized below.

HAL-Agriculture Drive: The HAL continues to focus on improving processes and efficiencies. With the integration of the HAL and Litterfall initiative a small percentage of CAL staffing resources was allocated to this area in 2019. Katie and Kirsten are now devoting 20-40% of their time to the HAL (Litterfall and MDN samples). The shift in staff resources is being monitored to ensure CAL functions are not negatively impacted. No external audits were performed during the applicable period of this QAR. An external audit of the HAL is being considered for late 2020 (or as soon as can be safely carried out given COVID-19 policies). An internal audit was conducted in December 2019 by Camille Danielson.

HAL-Data Management: The HAL integration included Zac's training Dana (HAL Data review staffer). Zac and Dana have been cross-training (blending between the CAL/HAL) and expect to reduce turnaround times from >90 days in 2019 to 60 days in 2020. Zac and Amy (and the HAL) continue to look for avenues to improve data quality, the data review process, and the communication of results to the customer.

HAL-Henry Mall (sample receiving):): The HAL sample receiving team began receiving MDN samples on June 1, 2019. Erin Pierce was initially hired to handle this responsibility. All the associate chemists (from the CAL) have learned receiving procedures and now share the responsibility of these new networks (Litterfall and MDN). Multiple areas within Henry Mall are currently being remodeled to accommodate the HAL (i.e.g., supply prep, shipping, and receiving).

## 7 Analytical QA

### 7.1 MDN MDLs

7.1.1 Calculations of MDN mercury MDLs for waters 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 4***.

7.1.2 MDN MDL Establishment

7.1.3 Initially, a minimum of seven method blanks and seven spiked samples are prepared and analyzed over three days. The spiked sample concentration is prepared at 1-5 times the estimated MDL, using a second-source standard. Both blank and spike samples are prepared in-bottles with all reagents that are used to prep and analyze natural matrix samples. The MDL of spikes is calculated by multiplying the standard deviation of the measured concentration of the spiked samples by the students' t-value at the 99th percentile. The MDL of the blanks is calculated by multiplying the standard deviation of the measured concentrations of the blanks samples by the students' t-value at the $99^{th}$ percentile and adding the mean of the blank concentrations. The selected MDL is the greater of the MDLs calculated from the blanks and spikes.

7.1.4 Ongoing MDN MDLs

7.1.5 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 "annual" MDL is again calculated and 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.

7.1.6 MDN MDL Adjusted by Dilution

7.1.7 Because mercury methods for waters are pre-concentrated, the MDL changes with the volume analyzed. The standardized (maximum) volume is 30mL. If a smaller volume is used, the MDL is multiplied by the dilution factor to define the MDL for an individual sample.

**Table 4. MDN 2019 MDLs**

| Analyte - Platform | Limit of Detection as Mass (pg) | Standard Sample Volume (mL) | Method Detection Limit (ng/L) | Limit of Quantitation (ng/L) |
|---|---|---|---|---|
| Total Hg - Tekran 2600 | 6 | 30 | 0.2 | 0.667 |
| Methyl Mercury - Tekran 2700 | 3 | 30 | 0.1 | 0.333 |

## 7.2 Digested Lab Reagent Blanks (DLRB)

Every batch of 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.

7.2.1 DLRB Results

In 2019, 180 DLRBs were reported. Of those, two were above the method detection limit (MDL) of 0.2 ng/L but below the limit of quantitation (LOQ) of 0.667 ng/L. As a result of the two exceedances, 19 sample results were qualified by the HAL.

## 7.3 Digested Quality Control Standard (DQCS)

Every batch of 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 into bottles, oxidized with the same BrCl lot used in sample processing, and analyzed alongside the samples to confirm the calibration and ensure that the sample preparation and analytical procedures produce reliable results. The DQCS recoveries between 80%-120% result in a run within control limits.

7.3.1 DQCS Results

In 2019, 59 DQCS samples were reported. None exceeded the control limits, and average recovery was 96.1%

## 7.4 Sample Matrix Spikes

A second and third aliquot of MDN from a randomly chosen (from those with >400 mL) sample are analyzed at a spike of 15 ng/L and the precision between the three results are evaluated. Matrix spikes (MS) are performed for every group of 10 or fewer samples and include a matrix spike and matrix spike duplicate (MSD). Therefore, approximately 10% of samples are spiked. Matrix spikes must be recovered between 75%-125% and the two spike results must have an RPD<24%. Please refer to Appendix A for all HAL QA/QC samples and associated criteria.

### 7.4.1 MS/MSD Results

In 2019, there were no MS recovery failures and no MS/MSD failures associated with reported samples. Infrequent failures may occur due to instrument instability or analyst errors. In such a case, affected samples are promptly reanalyzed and documented. The mean recovery for accepted matrix spikes was 104%. The mean RPD was 2.08%.

**TABLE 5. Typical Analytical Sequence and Criteria**

| 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 75%-125% |
| 11 | DLRB 1 | <0.2 ng/L |
| 12 | DLRB 2 | <0.2 ng/L |
| 13 | DLRB 3 | <0.2 ng/L |
| 14 | DQCS | Recovery 75%-125% |
| 15 | MDL Verification Sample | Recovery 70%-130%; 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 75%-125% |
| 29 | Continuing Calibration Blank | <MDL |

# 8 Supply Assessment

The MDN program requires very specific sampling supplies; all cleaned and prepared using established specialized protocols to maintain data consistency throughout the network. The laboratory cleans and provides supplies for the MDN and tests to verify that supplies are adequately clean. New MDN bottles, preservation acid and sample trains must meet QC requirements per NADP SOP 405 MDN Supply Preparation and NADP SOP 200 NTN and MDN Supply QC.

## 8.1 Lot Testing Criteria

The lot testing criteria states that the mean of at least 10 sample bottle blanks per lot must be < MDL and none of the supply (bottle) 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 rejected and returned to the manufacturer. If the second test is performed and fails criteria again, the lot must be rejected.

## 8.2 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, 1L and 250 mL bottles are in use. All lot checks of bottles in 2019 met criteria and no lots required additional testing.

**FIGURE 2: 2019 MDN PETG Bottle QA Results**

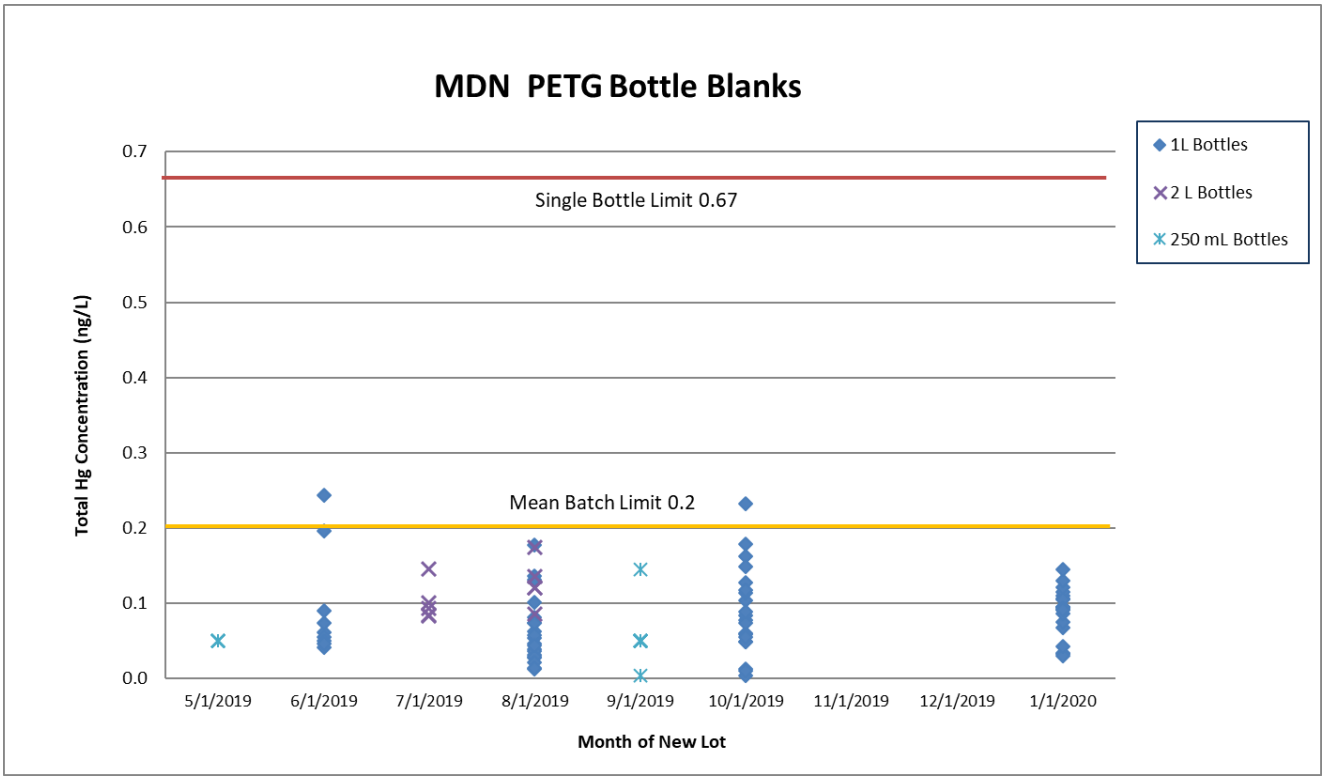


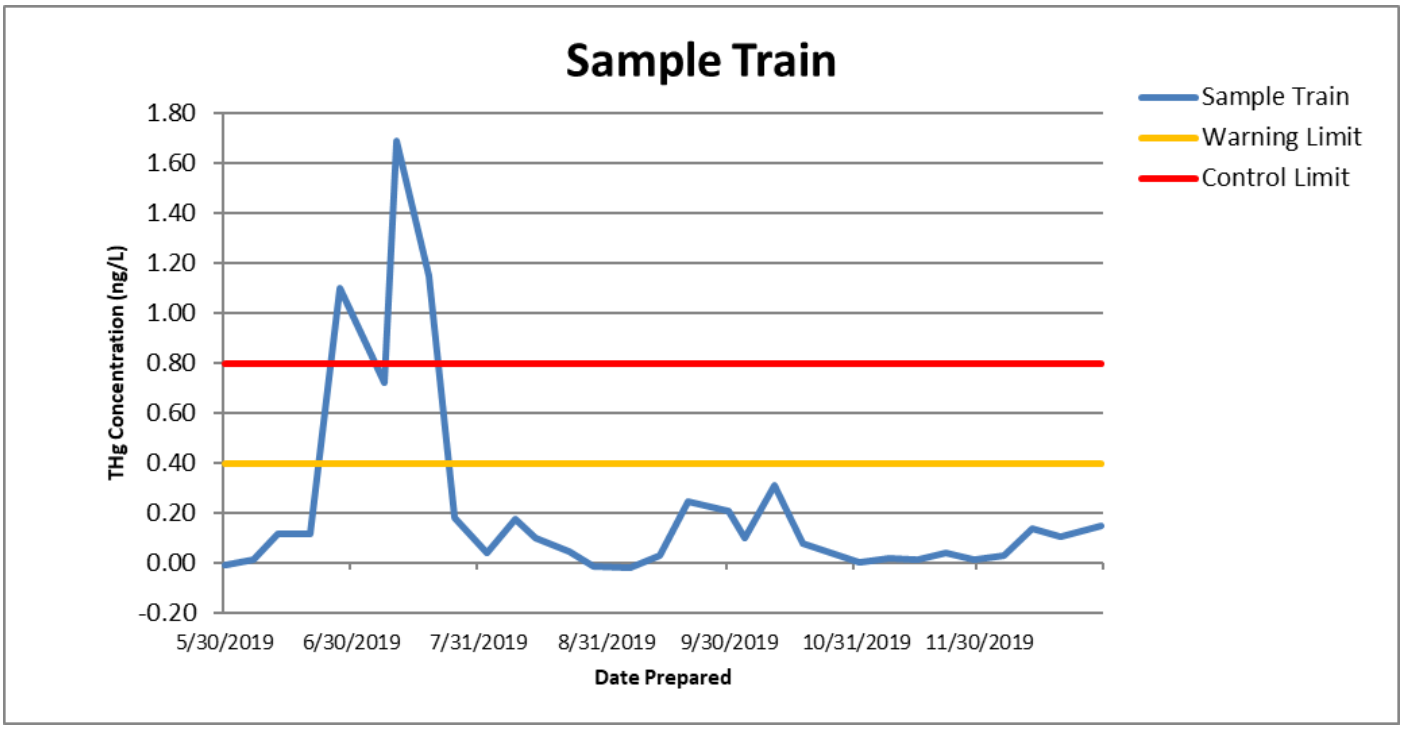
**TABLE 6. MDN Bottle Lot Approval QC**

| Bottle Size Tested | # of 2019 QC Samples | # of Individual Exceedances | Lots Tested | Lots Rejected | Lots Approved |
|---|---|---|---|---|---|
| Bottles – 1 L | 70 | 3 | 4 | 0 | 4 |
| Bottles – 2 L | 10 | 0 | 2 | 0 | 2 |
| Bottles – 250 mL | 30 | 0 | 2 | 0 | 2 |
| Total | 110 | 3 | 8 | 0 | 8 |

## 8.3 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 has 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. From June 27 to July 19, 2019 four sample train blanks exceeded criteria (1.10, 0.72, 1.69 and 1.15 ng/L respectively). The limit for sample train blanks is 0.8 ng/L (***Figure 3***). These exceedance values coincided with high concentrations of HgT measured in the Type I water at the time (refer to ***Figure 4)***. Therefore, it is believed the Type I water used to prepare the sample train blanks was the primary contributing factor. No additional exceedances occurred in 2019. Further MDN supply criteria are outlined in NADP SOP 405 MDN Supply Preparation. See Appendix A for MDL and supply QC criteria.

**FIGURE 3: Sample Train 2019 QA Data**

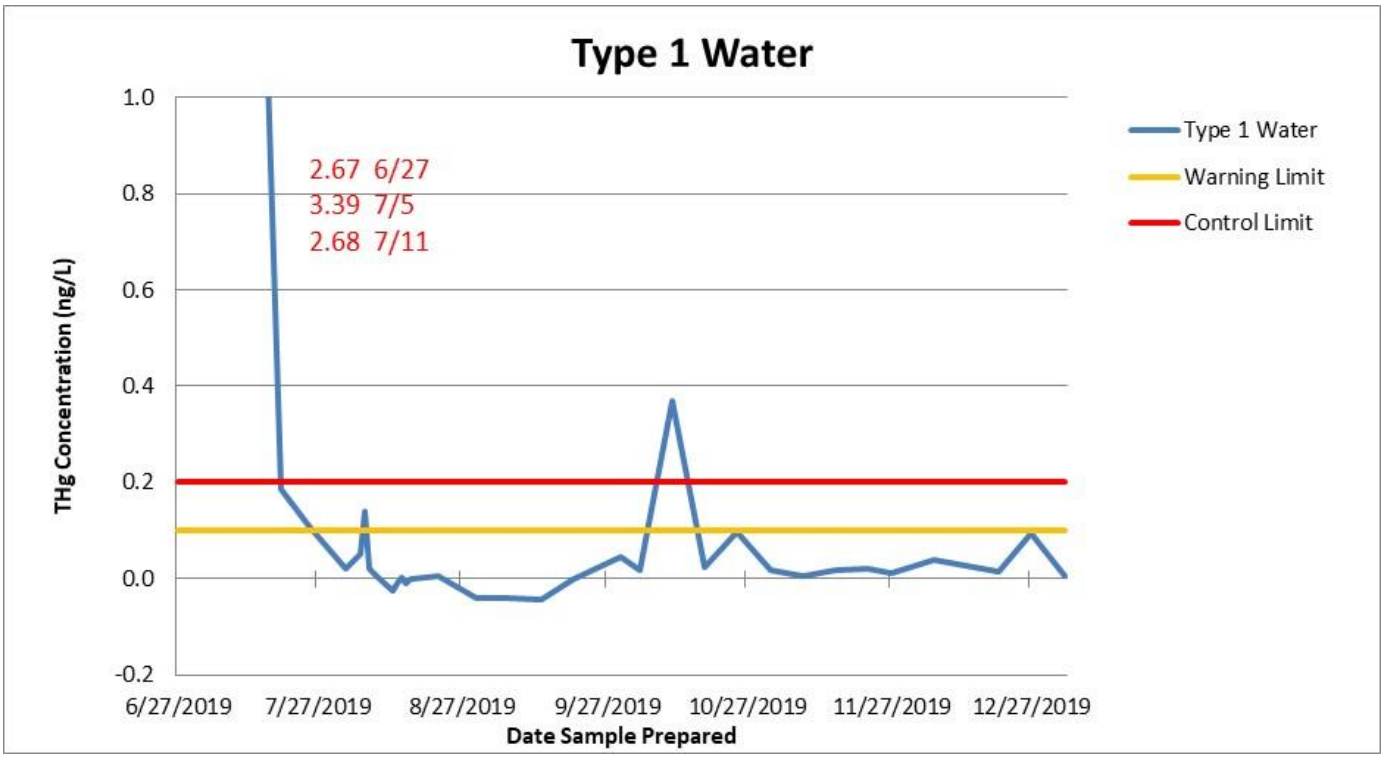



## 8.4 Type I Water

Type I water (deionized water routed through a water polisher) is tested for HgT weekly by collecting 100 mL of Type I water in a 250 mL PETG bottle. Initial tests resulted in exceedances for June and July 2019. After these exceedances,

a daily log and weekly blank collection was put into place to monitor the Type I water more effectively. After the July 2019 exceedances, one sample, in October 2019, exceeded the control limit of 0.2 ng/L (0.37 ng/L). Note that negative values occur because all peak areas are blank-subtracted by the mean calibration blank for the run.

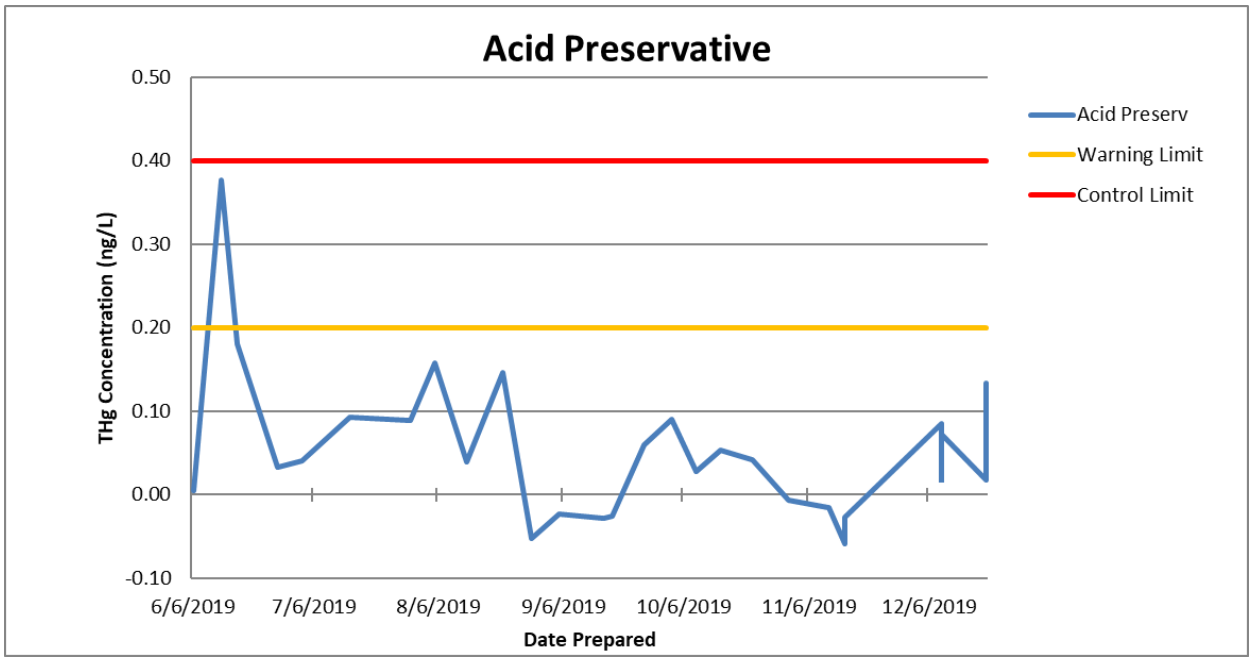
**FIGURE 4: TYPE I DI Water 2019 QA Results**




## 8.5 Acid Preservative

Sample acid preservative is made weekly and is used to pre-charge the MDN sample collection bottles sent into the field. Acid preservative is 1% v/v HCl (12M); 1L bottles are pre-charged with 20 mL of preservative and 2L bottles are pre-charged with 40 mL of preservative. Acid preservative must be <0.4 ng/L. Initially, acid preservative was prepared and dispensed into sample bottles immediately before shipping bottles to the field, before QA analysis was complete. In November 2019, the policy was changed so that acid is analyzed before being dispensed and sent into the field. There were no exceedances in 2019 (***Figure 5***). Note that negative values occur because all peak areas are blank-subtracted by the mean calibration blank for the run.

**FIGURE 5: Acid Preservative 2019 QA Results**




## 8.6 Acid Baths

Two acid soaking tubs are used to clean glassware, both containing 25% v/v HCl (12M) in Type I water. Funnels are immersed in a 40 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 6 and 7***).

**FIGURE 6: Acid Bath Vat (for MDN Funnels) 2019 QA Results**

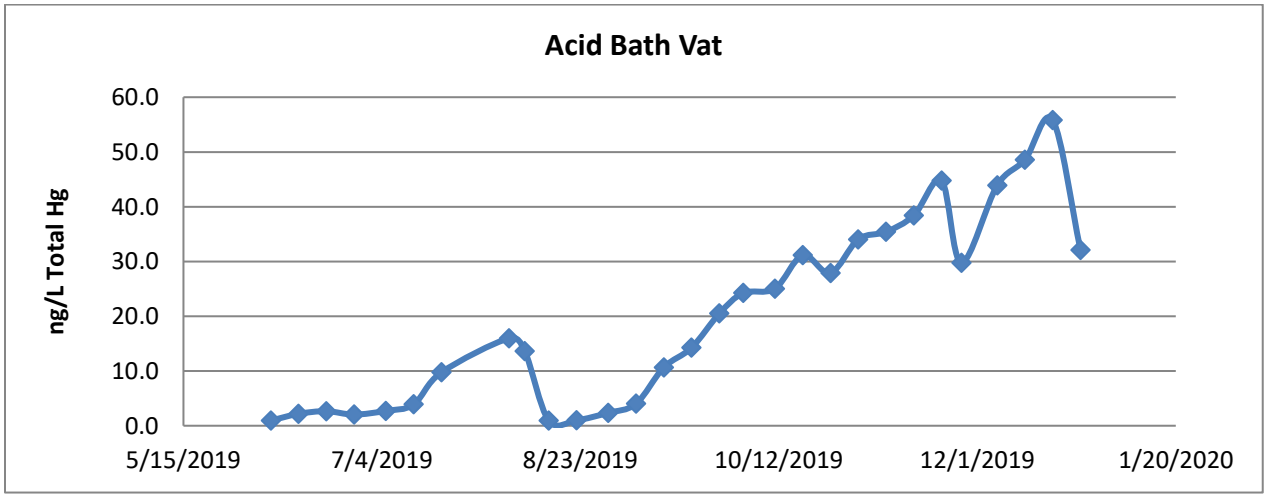
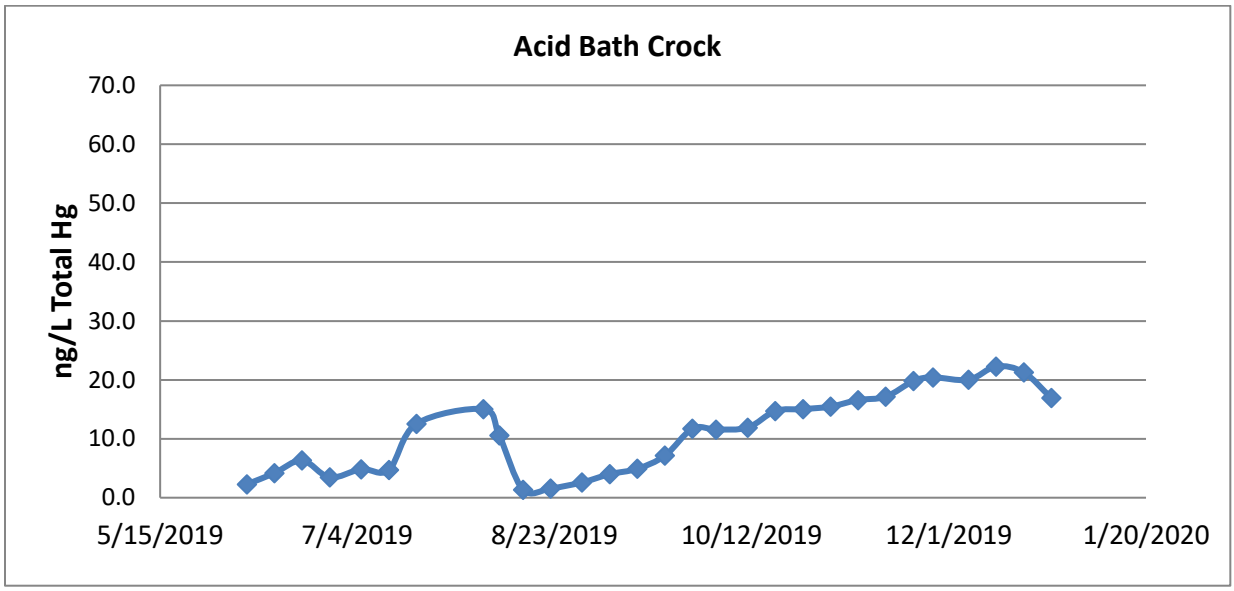


**FIGURE 7: Acid Bath Crock (for MDN Thistle Tubes) 2019 QA Results**




# 9 External and Internal QA Programs

Information for Section 9.1 – 9.3 was modified from the USGS External Quality Assurance Project Report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network, 2017–18 By Gregory A. Wetherbee and RoseAnn Martin (Section 11.0).

The U.S. Geological Survey (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.

## 9.1 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. The solution that washed through the sample train is called the system blank sample, and the solution remaining in the original sample bottle is called the bottle sample. 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.

## 9.2 USGS Proficiency Testing Studies

The HAL participates in the monthly HgT Proficiency Testing (PT) program run by the USGS. Two PT samples are provided and analyzed each month. All results for 2019 PT spike samples have been acceptable by USGS criteria and

were within the 80-120% recovery guidelines set for the method. The outcomes of six HgT blank PTs were well below the detection limit indicating low background Hg in the lab, reagents, and overall processing. These USGS PT results demonstrate good accuracy and precision of the total mercury analysis at the HAL. The HAL purchased and validated a Tekran 2600 during the transition period. The manual system was used to measure readiness verification plan samples (including some PT samples) but not actual MDN field samples. The network samples have all been analyzed using the Tekran.

**TABLE 7. Outcomes of USGS Proficiency Testing Samples: February 2019–December 2019**

| LIMS ID | USGS ID | Description | Result (ng/L) | MPV | %Recovery | Notes |
|---|---|---|---|---|---|---|
| 19001104 | 2019045037 | USGS Feb PT 1 of 4 | **5.89** | **5.45** | **108** | Measured on Brooks Rand Model III Manual Instrument |
| 19001105 | 2019045038 | USGS Feb PT 2 of 4 | **9.15** | **8.24** | **111** | Measured on Brooks Rand Model III Manual Instrument |
| 19001106 | 2019045039 | USGS Feb PT 3 of 4 | **15.2** | **14.0** | **109** | Measured on Brooks Rand Model III Manual Instrument |
| 19001107 | 2019045040 | USGS Feb PT 4 of 4 | **19.0** | **19.7** | **96** | Measured on Brooks Rand Model III Manual Instrument |
| 19001636 | 2019073019 | USGS March PT 1 of 2 | **6.33** | **5.45** | **116** | Measured on Brooks Rand Model III Manual Instrument |
| 19001637 | 2019073020 | USGS March PT 2 of 2 | **0.06** | **0.00** | **-** | Measured on Brooks Rand Model III Manual Instrument |
| 19002690 | 2019101019 | USGS April PT 1 of 2 | **7.88** | **8.24** | **96** | Switch to Tekran 2600 Automated Instrument |
| 19002691 | 2019101020 | USGS April PT 2 of 2 | **13.08** | **14.00** | **93** | Tekran 2600 Automated |
| 19003076 | 2019129019 | USGS May PT 1 of 2 | **18.44** | **19.70** | **94** | Tekran 2600 Automated |
| 19003077 | 2019129020 | USGS May PT 2 of 2 | **0.06** | **0.00** | **-** | Tekran 2600 Automated |
| 19003831 | 2019164020 | USGS June MDN PT 1 of 2 | **7.00** | **8.24** | **85** | Tekran 2600 Automated |
| 19003832 | 2019164019 | USGS June MDN PT 2 of 2 | **4.92** | **5.45** | **90** | Tekran 2600 Automated |
| 19004284 | 2019190019 | USGS July MDN PT 1 of 2 | **11.32** | **14.00** | **81** | Tekran 2600 Automated |
| 19004285 | 2019190020 | USGS July MDN PT 2 of 2 | **15.86** | **19.70** | **80** | Tekran 2600 Automated |
| 19005389 | 2019227019 | USGS Aug. MDN PT 1 of 2 | **5.16** | **5.45** | **95** | Tekran 2600 Automated |
| 19005390 | 2019227020 | USGS Aug. MDN PT 2 of 2 | **19.60** | **19.70** | **100** | Tekran 2600 Automated |
| 19005715 | 2019227001 | USGS Sept. MDN PT 1 of 2 | **4.67** | **5.45** | **86** | Tekran 2600 Automated |
| 19005716 | 2019227002 | USGS Sept. MDN PT 2 of 2 | **17.40** | **19.70** | **88** | Tekran 2600 Automated |
| 19006004 | 2019255019 | USGS Oct. MDN PT 1 of 2 | **13.27** | **14.00** | **95** | Tekran 2600 Automated |
| 19006005 | 2019255020 | USGS Oct. MDN PT 2 of 2 | **0.00** | **0.00** | **-** | Tekran 2600 Automated |
| 19006328 | 2019269001 | USGS Oct. MDN PT 1 of 2 | **-0.01** | **0.00** | **-** | Tekran 2600 Automated |
| 19006329 | 2019269002 | USGS Oct. MDN PT 2 of 2 | **-0.02** | **0.00** | **-** | Tekran 2600 Automated |
| 19006655 | 2019283019 | USGS Oct. MDN PT 1 of 2 | **7.80** | **8.24** | **95** | Tekran 2600 Automated |
| 19006656 | 2019283020 | USGS Oct. MDN PT 2 of 2 | **-0.01** | **0.00** | **-** | Tekran 2600 Automated |
| 19007681 | 2019318019 | USGS Nov. MDN PT 1 of 2 | **8.30** | **8.24** | **101** | Tekran 2600 Automated |
| 19007682 | 2019318020 | USGS Nov. MDN PT 2 of 2 | **19.36** | **19.70** | **98** | Tekran 2600 Automated |
| 19008525 | 2019345019 | USGS Dec. MDN PT 1 of 2 | **5.33** | **5.45** | **98** | Tekran 2600 Automated |
| 19008526 | 2019345020 | USGS Dec. MDN PT 2 of 2 | **13.60** | **14.00** | **97** | Tekran 2600 Automated |

### 9.3 Audits: June 2019–December 2019

In December 2019, the first full scale internal audit of the HAL lab was completed. Findings were identified and promptly addressed. Detailed audit and corrective action reports are available upon request. An external audit of the HAL will be planned as soon as feasible (COVID-19 pandemic is delaying this).

### 9.4 Internal Audit Findings

9.4.1 SOPs have not been completed: Methyl Mercury Analysis.

9.4.2 QAP for HAL needs to be developed.

9.4.3 The repipettor used for pre-charging MDN sample bottles is not calibrated at least quarterly.

9.4.4 MDN reagent preparation log needs preparation date and clearer link to NADP IDs.

9.4.5 MDN sample contamination noted at analysis is not consistently recorded.

9.4.6 MDN sample preparation spreadsheet policies for manual changes to volumes are not well documented.

9.4.7 Current policy of analyzing only 5 mL of MDN THg sample for some low volume samples is leading to over-dilution of some samples.

9.4.8 USGS MDN PT samples on 11/20/19 were found to have incorrect dilution factors of 3.03 in the analytical run and data packet which led to incorrect results in LIMS.

9.4.9 Failed THg lab reagent blank in packet 9/26/19 analytical date not noted on possible qualifiers spreadsheet and samples not rerun.

9.4.10 Methyl Hg method validation documentation needs to be completed.

9.4.11 Methyl mercury composite samples will be over 6 months old soon and analysis is not fully in place.

9.4.12 Methyl Hg LIMS system and report needs to be completed.

9.4.13 Customer satisfaction is not actively assessed – although the NADP Executive Committee/QAAG and NOS are all involved in CAL and HAL issues/changes the end data users and operator satisfaction is not addressed.

9.4.14 Analysts are not aware of location of MSDS for chemicals they work with.

9.4.15 Safety training for CAL/HAL crossover analysts not documented for work in HAL.

## 10 Major HAL Changes June 2019–December 31, 2019

| Date | Change | Notes |
|---|---|---|
| **5/27/2019** | Moved all Sample Receiving and Shipping to HM | CAL, HAL and AMoN Networks |
| **6/1/2019** | HAL operations officially transitioned from Eurofins to WSLH and sample receiving begins at Henry Mall | E. Pierce hired to help with HAL receiving operations |
| **6/1/2019** | Same day turnaround shipping schedule established | Keeps supplies in rotation more efficiently |
| **10/1/2020** | Created new LIMS for MDN data | Significant effort to build this |
| **10/16/2019** | Began receiving Litterfall samples at WSLH | |
| **10/31/2019** | MeHg LOD Verification Study Completed | No MDN samples for MeHg were run in 2019. Holding times exceeded for some 2019 samples. |
| **11/20/2019** | Changed MDN dry sample definition to < 1.5 mL | 1.5 mL = 0.004 in of precipitation |

# 11 Data Review

A custom designed LIMS system was created to manage MDN data including field sample receiving, precipitation data, and reporting of the analytical data. This was a major undertaking handled by NADP/WSLH Information systems staff. The custom LIMS also was patterned after LIMSs already in place for the other NADP networks and will allow efficiencies in the area of precipitation review for co-located NTN/MDN sites.

## 11.1 Analytical Data Review

A second analyst peer reviews all data packets prior to results being uploaded/released to the LIMS. The reviewer verifies that the all reagent, sample, and instrument QC meet criteria and confirms that the sample calculations (such as dilution factor), peak area, peak shape, and concentration are correct. Support equipment and reagent lots associated with each batch must be within calibration or expiration. Batch comments by the analyst are reviewed individually and a "Possible Qualifiers" spreadsheet is used as a record of all anomalies with samples during analysis.

## 11.2 Network Data review

Review of all MDN sample data for completeness and consistency is done prior to releasing reports to operators/funders of the sampling sites and publishing data to the PO. The review includes comparison to historical site values and analysis of possible analytical qualifiers.

# 12 References


- National Atmospheric Deposition Program Laboratory Quality Assurance Plan, Mercury and Central Analytical Laboratories. Revision 1, June 25, 2020 (http://nadp.slh.wisc.edu/lib/qaPlans.aspx)
- NADP SOP 405 MDN Supply Preparation
- NADP SOP 200 NTN and MDN Supply QC
- Webb, David, 3/31/2020, WSLH Summary of Management Reviews by Departments - Annual Management Review 2019
- Wetherbee, G.A., and Martin, RoseAnn, 2020, External quality assurance project report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network, 2017–18: U.S. Geological Survey Scientific Investigations Report XXXX–XXXX, In Press


# 13 Acknowledgments

Thank you to all the NADP CAL and HAL staff who contributed to the transition and implementation of the Mercury Analytical Lab at the Wisconsin State Laboratory of Hygiene. In addition, a special thanks to Eurofins Frontier Global Sciences for providing supplies and insight during the transition period.

# 14 Authors/Approvals

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Reviewed by: Martin Shafer and Mark Olson
Submitted for QAAG review: 8/10/2020
Approved by QAAG pending revisions on 8/24/2020
Finalized by: Camille Danielson 8/28/2020

## Appendix A: HAL QA Criteria

| HAL Analytical QC | As of 5/21/2020 | | | | | |
|---|---|---|---|---|---|---|
| **Total Hg Run ID** | **True Value (ng/L)** | **Criterion (% or ng/L)** | **Frequency of Testing** | **LIMS Criteria CL (1/3 criteria = WL)** | | |
| **Calibration blank (CB)** | 0.0 | Mean < 0.5 ng/L | 3 each analytical run | 0.5/0.166 | | |
| **Continuing Calibration Blank (CCB)** | 0.0 | <0.2 ng/L | After calibration; Every 10 samples | 0.2/0.0667 | | |
| **Ongoing Precison and Recovery (OPR5)** | 5.0 | 80-120% (must be 90-110% for calibration verification or recalibration required) | Prior to analyzing samples; Every 10 samples | 1.0/0.333 | | |
| **Digested Lab Reagent Blank (DLRB)** | 0.0 | <0.2 ng/L | 3 each analytical run | 0.2/0.0667 | | |
| **Digested Quality Control Standard (DQCS - 2nd source)** | 8.0 | 80-120% | 1 each analytical run | 1.6/0.533 | | |
| **Matrix Spike/Matrix Spike Duplicate MS/MSD** (Compare) | NA | 24% RPD | Every 10 samples | NA | | |
| **MS Recovery** | 15.0 | 75-125% | Every 10 samples | NA | | |
| **Method Detection Limit (MDL) Standard** | 0.5 | 80-120% (not batch QC parameter) | Weekly | 0.1/0.033 | | |
| **Methyl Hg Run ID** | **True Value (ng/L)** | **Criterion (% or ng/L)** | **Frequency of Testing** | **LIMS Criteria CL (1/3 criteria = WL)** | | |
| **Calibration blank (CB)** | 0.0 | Mean < 0.05 ng/L | 3 each analytical run | 0.5/0.166 | | |
| **Continuing Calibration Blank (CCB)** | 0.0 | <0.1 ng/L | After calibration; Every 10 samples | 0.2/0.0667 | | |
| **Ongoing Precison and Recovery (OPR5)** | 0.3 | 65-135% | Prior to analyzing samples; Every 10 samples | 1.0/0.333 | | |
| **Distilled Lab Reagent Blank (DLRB)** | 0.0 | <0.1 ng/L | 3 each analytical run | 0.2/0.0667 | | |
| **Distilled Lab Fortified Blank (DLFB)** | 1.0 | 65-135% | 1 each analytical run | 1.6/0.533 | | |
| **Matrix Spike/Matrix Spike Duplicate MS/MSD** (Compare) | NA | 35% RPD | Every 10 samples | NA | | |
| **MS Recovery** | 0.5 | 65-135% | Every 10 samples | NA | | |
| **Distilled QC Standard** (2nd source)**/MDL Standard** | 0.5 | 65-135% (not batch QC parameter) | 1 each analytical run | 0.1/0.033 | | |
| **HAL Supply QC** | | | | **HAL Calibration QC** | | |
| **Run ID** | **True Value (ng/L)** | **Criterion (% or ng/L)** | **Frequency of Testing** | **Calibration QC** | **Criteria** | **Units** |
| **Sample Train Blank** | 0.0 | <0.8 ng/L (<0.08 ng per train) | 1/week in bag for ≥2 days - 100 mL MQ | **Calibration Coefficient RSD** | ≤15 | % |
| **Acid Bath Blank** | 0.0 | <50 ng/L | 1/Acid Bath/week | **Calibrator Recovery** | 85-115 (THg) 65-135 (MHg) | % |
| **1 L PTGE Bottle Blank** | 0.0 | Mean bottle batch < 0.2 ng/L (NO bottle > 0.667 ng/L) | 20/new lot (unless <200 then 10) | **Mean Cal Blank/System Blank** | <0.5 | ng/L |
| **2 L PETG Bottle Blank** | 0.0 | Mean bottle batch < 0.2 ng/L (NO bottle > 0.667 ng/L) | 10/new lot (unless <100 in lot then 5) | **Std. Dev. Calibration Blank** | <0.1 | |
| **Acid Preservative Blank** | 0.0 | <0.4 ng/L (15 mL sample) | 1/Batch Acid Preserv prior to use | **OPR** (as calibration verification) | 4.5 to 5.5 | ng/L |
| **THg Type 1 Water Blank** | 0.0 | <0.2 ng/L | 1/purifier/week | | | |