National Atmospheric Deposition Program

Mercury Analytical Laboratory

2018 Annual Quality Assurance Report

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Introduction

Eurofins Frontier Global Sciences Inc. (EFGS) has served as the Mercury Analytical Laboratory (HAL) and Site Liaison Center for the Mercury Deposition Network (MDN) since January 1996. MDN, which is coordinated through the National Atmospheric Deposition Program (NADP), was designed with the primary objective of quantifying the wet deposition of mercury in North America to determine long-term geographic and temporal distributions. The MDN consisted of 91 active sites in the United States and Canada at the end of 2018. In 2018, 7 sites were closed; no new sites were added and no sites were re-started.

The HAL analyzes weekly precipitation samples for total mercury from all active MDN sites and for methyl mercury from 9 sites. The analytical technique, a modified EPA Method 1631, was developed by Nicolas S. Bloom, one of FGS' founders. FGS also served as the referee lab for the EPA Method 1631 "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" final validation study.

EFGS continued to maintain and demonstrate acceptable quality control (QC) in 2018. EFGS demonstrated consistency and reproducibility in bottle blanks, preparation blanks, certified reference materials, matrix duplicates, and matrix spikes. Results for all of these QC samples are plotted in control charts and summarized in this report.

The following changes occurred at HAL in 2018:

- In January, the name of the HAL lab changed from Eurofins Frontier Global Sciences, Inc. to Eurofins Frontier Global Sciences, LLC. The HAL notified the Program Office of this change
- In January, the lab had to retire Hg-07, the bubbler system used to analyze MDN samples for MHg
- In January, the lab began to use the Tekran 2700 to analyze MDN samples for MMHg. The HAL notified the Program Office of this change.
- EFGS became certified by Kentucky for wastewater analysis using EPA Method 1631E
- 5S training was conducted and then implemented throughout the lab
- QA Specialist Allison Kazlauskas resigned in March
- Trace metals chemist Matthew Prolo was promoted to QA Specialist in April
- Nikita Pester, MDN equipment cleaning, resigned in April
- The lab installed a new commercial dishwasher and began cleaning process comparability studies in May
- Kaizen LEAN training was conducted in May and June and implemented throughout the lab.
- Jason Lindstrom, MDN Receiving, resigned in June
- Ted Pierce was hired for MDN equipment cleaning in June
- Disposable PETG sample bottles began to replace the re-usable glass collection bottles in July.
- The lab finished the cleaning process comparability studies in July that demonstrated the dishwasher cleaning method is as good as, if not better than, the acid vat cleaning method.
- The lab began cleaning MDN funnels and thistle tubes in the new dishwasher in July
- Two summer interns, Ariana Flournoy and Khadijah Pritchett, were hired in July to support S&R.
- NADP PO wants all lot testing of PETG bottles included in the report. First lot test was work order 1611429. Second lot test is logged in on WO 8G00372.
- Ryan Shannon was hired in August for MDN equipment cleaning.

- Lar Mittet, sample receiving manager, resigned in September.
  Rothboury Doung was hired in September for MDN equipment cleaning and MDN sample log-in.
- Summer interns Ariana Flournoy and Khadijah Pritchett resigned in September.
- Trace metals sample prep technician Lily-Anna LeCount was promoted to sample receiving manager in October.
- MDN equipment cleaning technician Ted Pierce transferred to sample prep in October
- Two technicians – Zahra Hannani and Sean McCord - were hired in November to support MDN Receiving and equipment cleaning.
- MDN Receiving and equipment cleaning technician Rothboury Doung transferred to sample prep in December.

1. Quality Assurance

1.1 Philosophy and Objectives

EFGS is committed to a rigorous quality assurance (QA) program and philosophy. Quality control begins at the bench level. Process improvements are solicited continuously from laboratory technicians and analysts. Management is active in evaluating and implementing feasible improvements. The QA program is a system for ensuring that all information, data, and interpretations resulting from an analytical procedure are technically sound, statistically valid, and appropriately documented.

HAL data quality is assessed against EFGS' Data Quality Objectives (DQO). Our DQOs consist of five components: ***Precision, Accuracy, Representativeness, Comparability, and Completeness.***

- **Precision** is a measure of data reproducibility. HAL assesses analytical precision using matrix duplicates. The acceptance criterion for both total mercury (THg) and methyl mercury (MMHg) matrix duplicates is a relative percent difference (RPD) less or equal to 25 percent (%).
- **Accuracy** is a measure of proximity to a "true" value. HAL assesses accuracy using certified reference materials and matrix spikes. The acceptance criterion for reference materials and matrix spikes varies by method. Therefore, acceptance criterion for accuracy is specified in Quality Control sections 2.2, 2.5 and 2.6.
- **Representativeness** is the degree to which a sample's characteristics reflect those of the population. It is demonstrated by accurate, unbiased sampling procedures and appropriate sample processing.
- **Comparability** is measured by comparing the variability of one set of data with respect to another. Control charts enable HAL to assess comparability over the course of an ongoing monitoring project such as MDN.
- **Completeness** is measured by the number of usable data points compared to the number of possible data points. The HAL DQO for the MDN project is at least 95% completeness.

1.2 Method Detection Limits

Method Detection Limits (MDL) are determined according to 40 CFR Part 136, Appendix B. At least seven replicates (t-1 degrees of freedom, where t is the Student's T-value for the number of replicates) of matrix-matched samples spiked at 1-10 times the expected MDL are analyzed. There is no recovery criterion for a MDL analysis, but the new calculated MDL value must be within 2 times of the previously established MDL. The standard deviation (σ) is taken from the resulting data and the MDL is determined as t * σ of the replicates. For ten replicates, the MDL is calculated as follows: MDL=2.821 * σ. This value should not be interpreted as the method reporting limit.

The Practical Quantitation Limit (PQL) is the reporting limit for the method and is included as the lowest calibration point (TNI Standard EL V1M4-2016-Rev2.0 section 1.7.1.1.g). The PQL is determined by running ten replicate samples with a concentration that must have the same recovery criteria as for the lowest calibration point.

The ratio between the True Value (TV) and the MDL shall be less than or equal to 10 for a MDL to be valid. A TV/MDL ratio greater than 10 indicates that the study was performed at too high of concentration. In other words, the standard deviation was low at the analyzed level and this does not produce enough variability to establish a realistic MDL. As such, the study would need to be reanalyzed at a lower concentration.

The HAL updates MDL studies periodically for the MDN project. See the summary in Table 1 for the MDL study results performed on the instruments that are used to analyze the MDN samples for THg and MMHg collected during 2018. All MDL and PQL studies are on file with the Quality Assurance department and are available upon request.

The MDL studies for THg for instruments 2600-2 (datasets THg26002-180725-1, THg26002-180726-1 and THg26002-180730-1) and 2600-3 (datasets THg26003-180725-1, THg26003-180726-1 and THg26003-180730-1), were performed at 0.30 ng/L (the PQL is 0.50 ng/L). The TV/MDL ratios for both instruments were less than 10. Since the TV/MDL ratios were in control for both sets of MDLs, both studies are valid and the highest MDL value, 0.095 ng/L, will be used to evaluate data.

The MDL study for MHg for instrument 2700-1 (datasets MHg27001-180223-1, MHg27001-180309-1 and MHg27001-180320-1) were performed at 0.078 ng/L (the PQL is 0.050 ng/L). The TV/MDL ratio was less than 10. Since the TV/MDL ratio was in control, the study is valid and the MDL value, 0.040 ng/L, will be used to evaluate data.

Table 1 - MDL Studies for 2018 Summary

Instrument	Dataset	MDL (ng/L)	PQL (ng/L)	True Value TV (ng/L)	TV/MDL
FI-AFS 2600-2	THg26002-180725-1, -180726-1 and -180730-1	0.095	0.50	0.30	3.16
FI-AFS 2600-3	THg26003-180725-1, -180726-1 and -180730-1	0.073	0.50	0.30	4.15
Tekran 2700-1	MHg27001-180223-1, -180309-1 and -180320-1	0.040	0.050	0.078	1.95

1.3 Accreditations

In 2018 Eurofins Frontier Global Sciences was accredited in eleven states and maintained ISO/IEC 17025:2005, NELAP, DOD ELAP and DOECAP accreditations:

Table 2 – Accreditation Summary for 2018

Accrediting Agency	Accreditation Type	Accreditation or Certificate Number
Perry Johnson Lab Accreditation	ISO/IEC 17025:2005	L17-540
Perry Johnson Lab Accreditation	DOD ELAP	L17-539
Perry Johnson Lab Accreditation	DOECAP	L19-46
Perry Johnson Lab Accreditation	TNI (NELAP)	L17-541
Louisiana DEQ	Primary NELAP	3073
Florida DOH	Secondary NELAP	E87575-20
New Jersey DEP	Secondary NELAP	WA014
New York DOH	Secondary NELAP	11662
Arkansas DEQ	State	16-059-1
California ELAP	State	2954
Kentucky EEC	State	KY98042
Maine DHHS	State	2016021 (105)
Nevada DEP	State	WA012732018-1
Washington DOE	State	C788-18
Wisconsin DNR	State	998348230

1.4 Laboratory Bottle Blanks and Lot Testing of PETG Bottles

1.4.1 Description

In 2018, the HAL switch from using reusable, cleaned glass bottles to disposable PETG bottles. Since the change was completed at the end of July, bottle blanks were only collected from January through July. Following cleaning, HAL glass bottles were charged with 20 mL of 1% hydrochloric acid. One sample bottle was randomly selected from each cleaning event and was analyzed for THg. On average, 1 to 2 laboratory bottle blanks were analyzed each week for THg. The 20 mL of 1% HCl is oxidized with 1% BrCl. The sample is shaken to ensure that all the walls of the bottles come into contact with the BrCl. The sample is then left for a minimum of 24 hours before analysis. At least one bottle blank was collected per month (from January through July) and analyzed for MMHg.

Before PETG bottles are shipped to the sites, each new lot of bottles is tested. 2L and 1L bottles selected for testing are filled with reagent-grade water, then preserved with 1% hydrochloric acid and finally oxidized with 1% BrCl. The sample is then left for a minimum of 24 hours before analysis. The number of bottles tested per lot depends on the lot size.

1.4.2 Purpose

Even in an ultra-clean laboratory, mercury exposure is inherent to the handling of reusable MDN glass sample bottles. Because such contamination is inevitable, it should be quantified for subtraction from final sample results. Final sample results for mercury only are corrected by the average bottle blank value from the previous quarter.

Disposable PETG sample bottles need to demonstrate that they're contamination-free, as received from the vendor. Since lots are rejected if the number of failures from the lot testing exceeds the limits assigned to a lot size, final results are not corrected for background levels.

1.4.3 Discussion

MDLs and PQLs for THg and MMHg Laboratory Bottle Blanks were converted to ng/bottle (using 20mL charge volume/bottle) in Table 3A to accommodate comparisons with the bottle blank data. Laboratory bottle blanks for THg exceeded the PQL about 30% of the time and generally exceeded the MDL all of the time (figure 1).

All six laboratory bottle blanks were less than the MDL for MMHg (figure 2). Laboratory bottle blanks are expected to be at, or near, the MDL (0.0.0008 ng/bottle, Table 3). Methyl mercury results are not bottle blank corrected.

For the lot testing of 1L and 2L PETG bottles, a total of 75 PETG bottles from five lots were tested between July and December. Because the PETG bottles were completely filled for the lot tests, it wasn't appropriate to report the results as ng/bottle as described above. The results from the lot tests were compared to the HAL control limit (0.25 ng/L or ½ the PQL). None of the 75 tested bottles exceeded the control limit and all except for two were less than the MDL. Therefore, none of the lots were rejected.

Table 3A - Laboratory Bottle Blank Summary

2018 Laboratory Bottle Blanks	n	Average (ng/bottle)	Standard Deviation	MDL (ng/bottle)	PQL (ng/bottle)
Total Mercury	34	0.009	0.006	0.0019	0.010
Methyl Mercury	6	0.0001	0.004	0.0008	0.001

Table 3B - Laboratory PETG Lot Test Summary

2018 PETG Lot Tests	n	Average (ng/L)	Standard Deviation	MDL (ng/L)	HAL Control Limit (ng/L)	PQL (ng/L)
Total Mercury	75	0.004	0.026	0.095	0.25	0.5

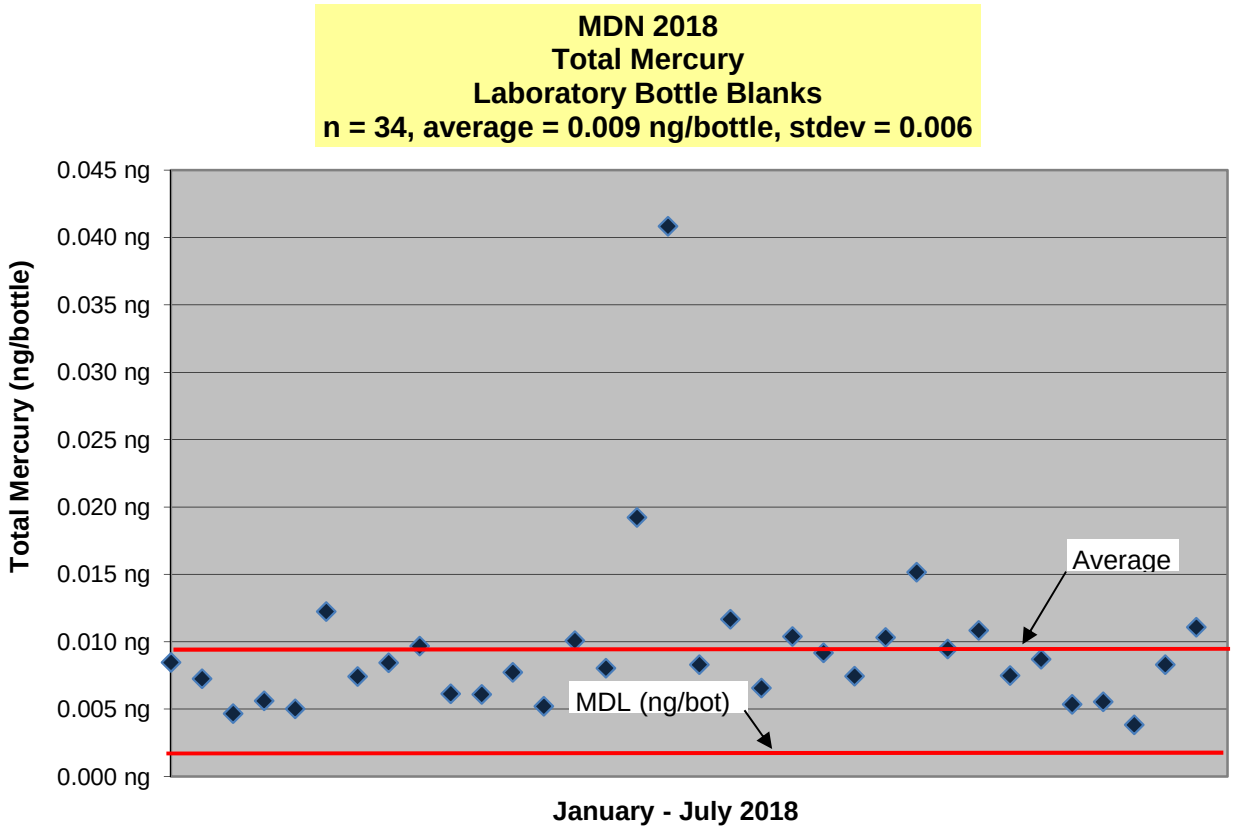


Figure 1 - Total Mercury Mass in Laboratory Bottle Blanks for 34 Samples, 2018

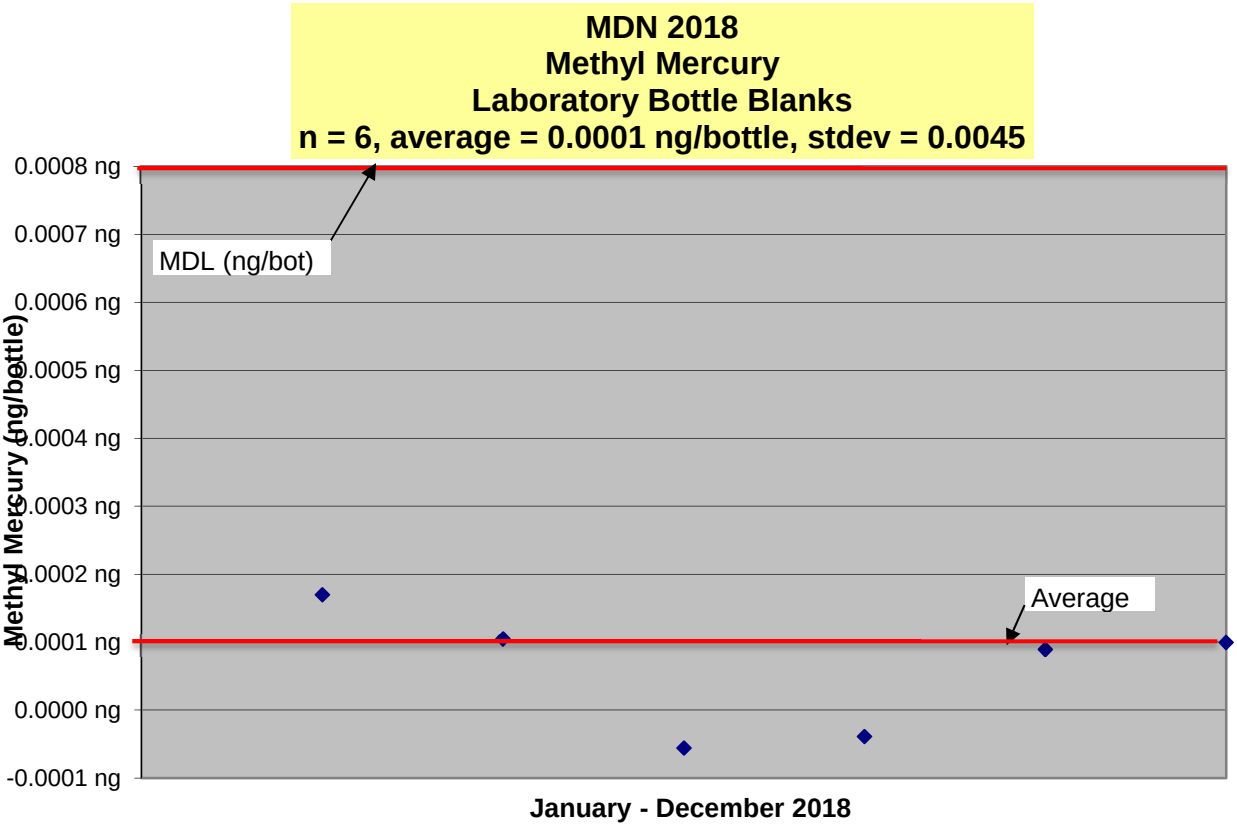


Figure 2 - Methyl Mercury Mass in Laboratory Bottle Blanks for 6 Samples, 2018

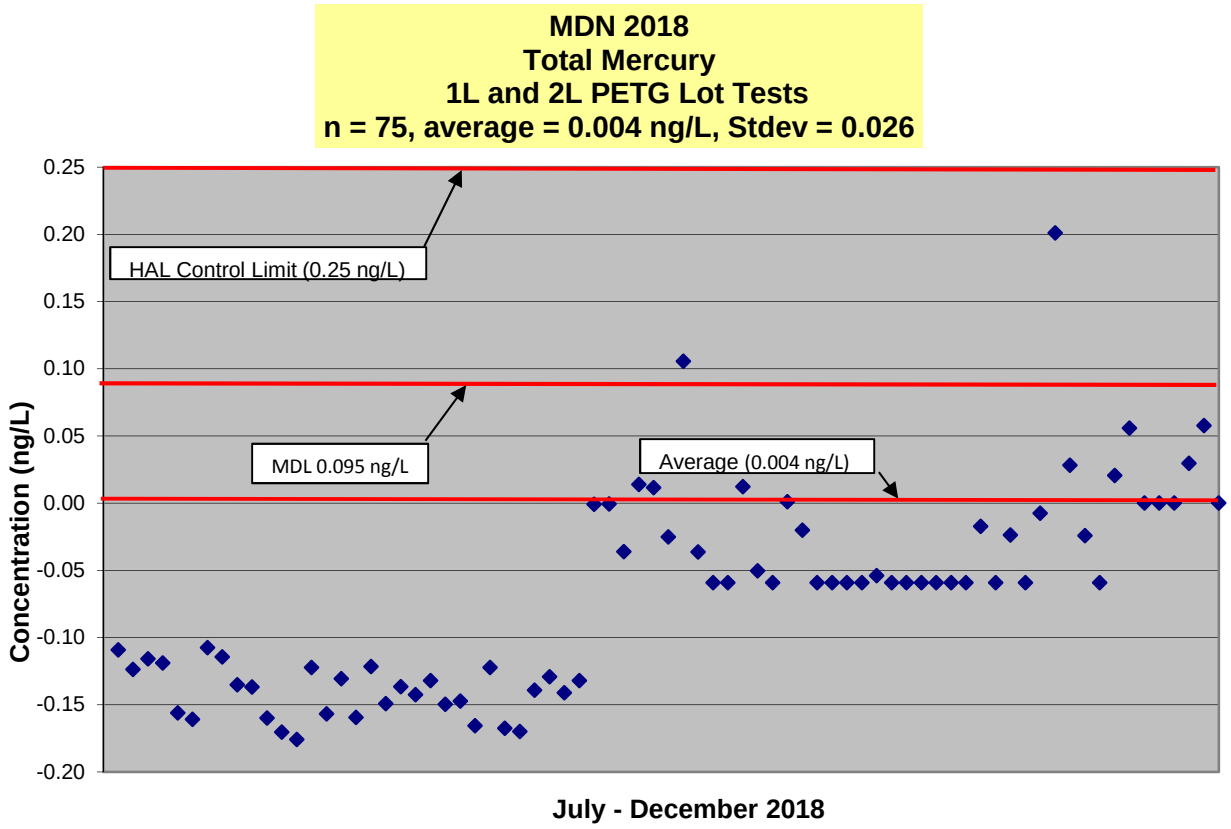


Figure 2' – Laboratory 1L/2L PETG Lot Tests for 75 Samples in 5 Lots, 2018

2. Quality Control

QC samples have expected target values that can be used to objectively assess performance of sample and reagent preparation and analytical methods. If performance on these known samples is acceptable, client sample results and other unknowns are assumed to be acceptable. Conversely, unacceptable QC results require immediate troubleshooting and re-assessment of affected sample results. The HAL utilizes eight types of QC samples for the MDN project:

- preparation blanks
- continuing calibration standards
- continuing calibration blanks
- matrix duplicates
- matrix spikes
- certified reference materials (blank spikes and blank spike duplicates for MMHg)
- field blanks
- system blanks

2.1 Preparation Blanks

2.1.1 Description

Preparation blanks for THg consist of bromine monochloride (1% BrCl) and hydroxylamine hydrochloride (0.025 mL) in 50 mL of reagent water. The HAL control limit for THg is 0.25 ng/L for each individual preparation blank. This limit is lower than the US EPA method 1631E method blank limit, which individually must be less than 0.50 ng/L (the same value as the HAL's PQL).

Preparation blanks for MMHg consist of 45 mL reagent water, hydrochloric acid (0.5%), ammonium pyrrolidine dithiocarbamate (0.200 mL of APDC) solution, ethylating agent (40 µL) and acetate buffer (0.300 mL). The HAL control limit for MMHg is set to 0.045 ng/L, which is the same as required by EPA method 1630. See Table 10 for a summary of QC Criteria for EPA 1630 and EPA 1631E.

2.1.2 Purpose

Mercury contamination is inherent in sample preparation and in analytical reagents in any laboratory setting. Preparation blank measurements determine how much of each sample result can be attributed to these necessary reagents. Preparation blanks are also used to investigate possible sources of contamination.

2.1.3 Discussion

All of the preparation blanks analyzed for THg during 2018 were less than the control limit of <0.25 ng/L used at the laboratory (table 4 and figure 3).

All of the preparation blanks analyzed for MMHg during 2018 were less than the EFGS control limit of 0.045 ng/L (table 4 and figure 4).

Table 4 - Preparation Blanks Summary

2018 Preparation Blanks	n	Average (ng/L)	Std Dev (ng/L)	MDL (ng/L)	HAL Control Limit (ng/L)	EPA 1631E/1630 Requirements
Total Mercury	501	0.014	0.055	0.095	0.25	< 0.50
Methyl Mercury	30	0.0072	0.0078	0.040	0.045	Mean <0.045 σ<0.015

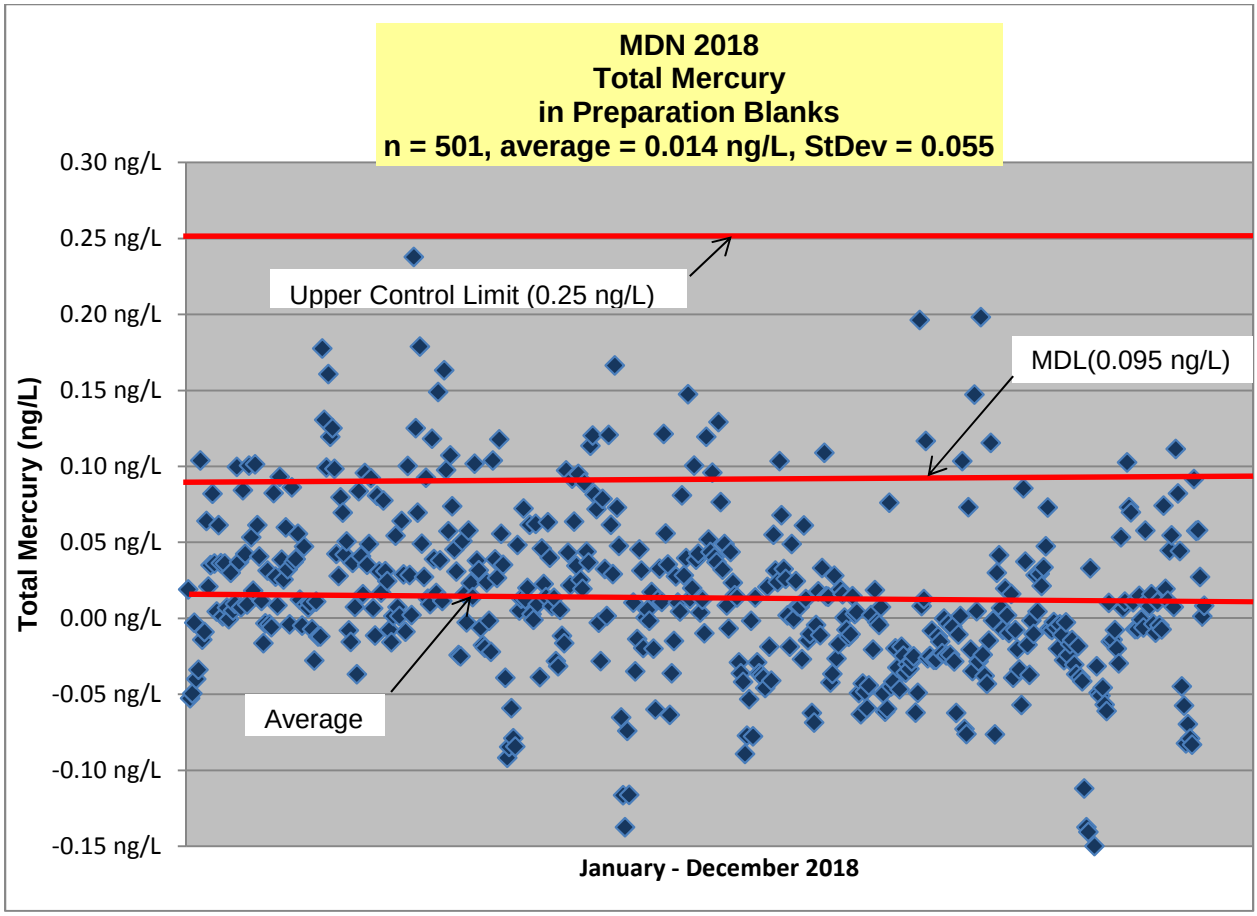


Figure 3 - Total Mercury Concentrations in Reagent Preparation Blanks, 2018

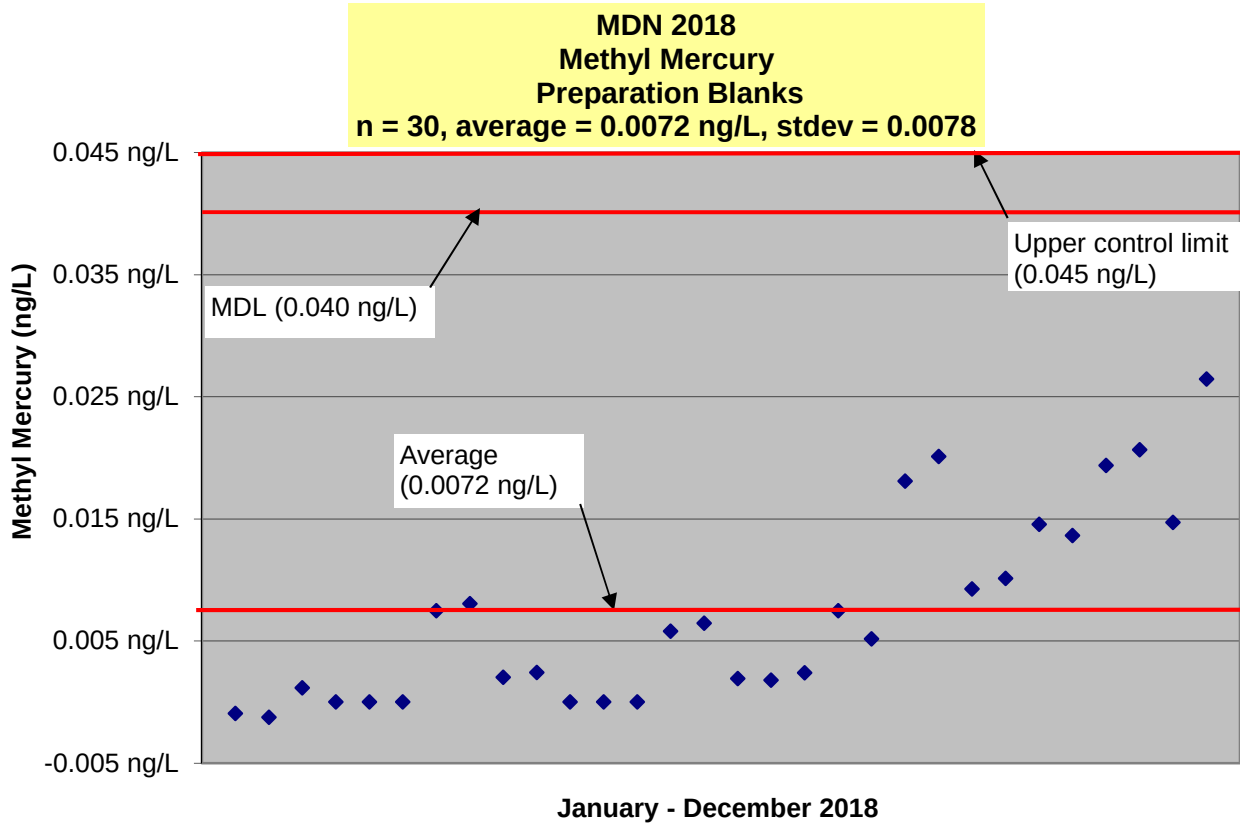


Figure 4 - Methyl Mercury Concentrations in Reagent Preparation Blanks, 2018

2.2 Initial and Continuing Calibration Verification Standards (ICVs & CCVs)

2.2.1 Description

The Initial Continuing Calibration Verification (ICV) is a solution made from a second source standard, independent of what is used in the primary standard solution. New working standards and standard dilutions are tested prior to use. Three replicates of the new standard are analyzed in the same run as three replicates of the current NIST standard. The mean percent recovery of the three standards should be +/- 5% (95-105%) of the true value and also within 5% of the average NIST recovery. For example, if the average NIST recovery is 97%, the acceptable range for the standards is 95-102%. For the MDN THg project, NIST 1641d and 1641e are the secondary source analyzed after the calibration curve and also after the second set of matrix spikes, and are discussed under the Certified Reference Material (CRM) section.

Continuing Calibration Verification (CCV) standards are analyzed intermittently during the course of sample analysis, after ten or fewer samples, and at the end of each analytical run. The CCV is a standard solution that is made from a traceable stock standard (usually the same source as the primary calibration stock). A 10 ng/L standard for THg and a 0.5 ng/L standard for MMHg are analyzed as ongoing calibration standards. The MDN control limits for ICVs are set to 80-120% recovery for THg, while the CCV limits are set to 77-123% recovery; the control limits for MMHg ICVs are set to 80-120% recovery, while the limits for CCVs are set to 67-133% recovery.

2.2.2 Purpose

An ICV is analyzed following each set of calibration curve standards to verify the accuracy of the primary standard solution and to validate the calibration curve. CCVs are used to verify that the analytical system is in control and to identify analytical drift. All ICV/CCVs reference a unique identification number and are traceable through Frontier's Laboratory Information Management System (LIMS). All raw data reference a unique laboratory ID number and include a unique identifier for each standard used in the analysis.

2.2.3 Discussion

No reportable CCV recoveries were outside the control limit of 77-123% for THg (table 5 and figure 5).

No reportable CCV recoveries were outside the control limit of 67-133% for MMHg (table 5 and figure 6).

Table 5 - Continuing Calibration Standard Summary

2018 Continuing Calibration Standard	n	Average recovery (%)	Std dev of recovery (%)	Control Limit (%)	EPA 1631E/1630 Control Limits (%)
Total Mercury	538	97.1	4.3	77-123	77-123
Methyl Mercury	39	90.1	10.9	67-133	67-133

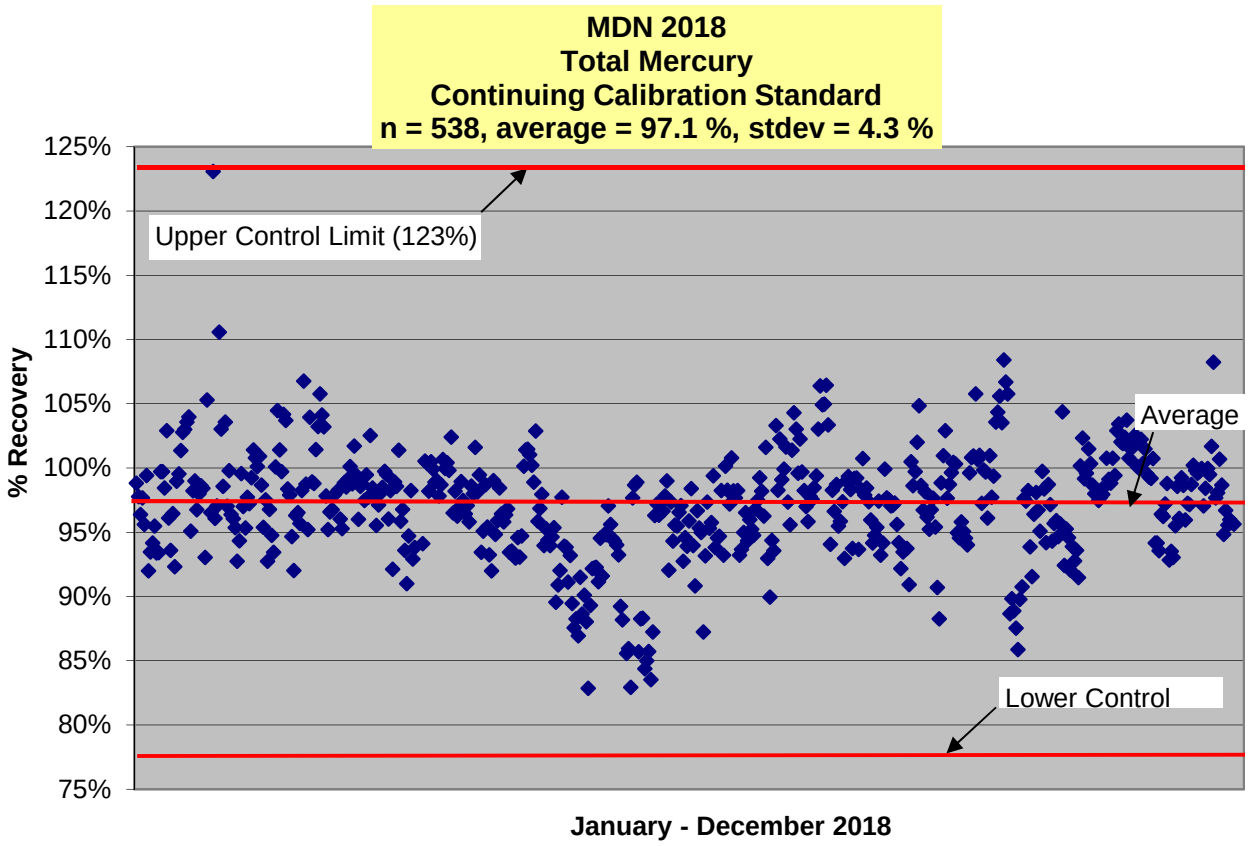


Figure 5 - Total Mercury Continuing Calibration Standard Percent Recovery, 2018

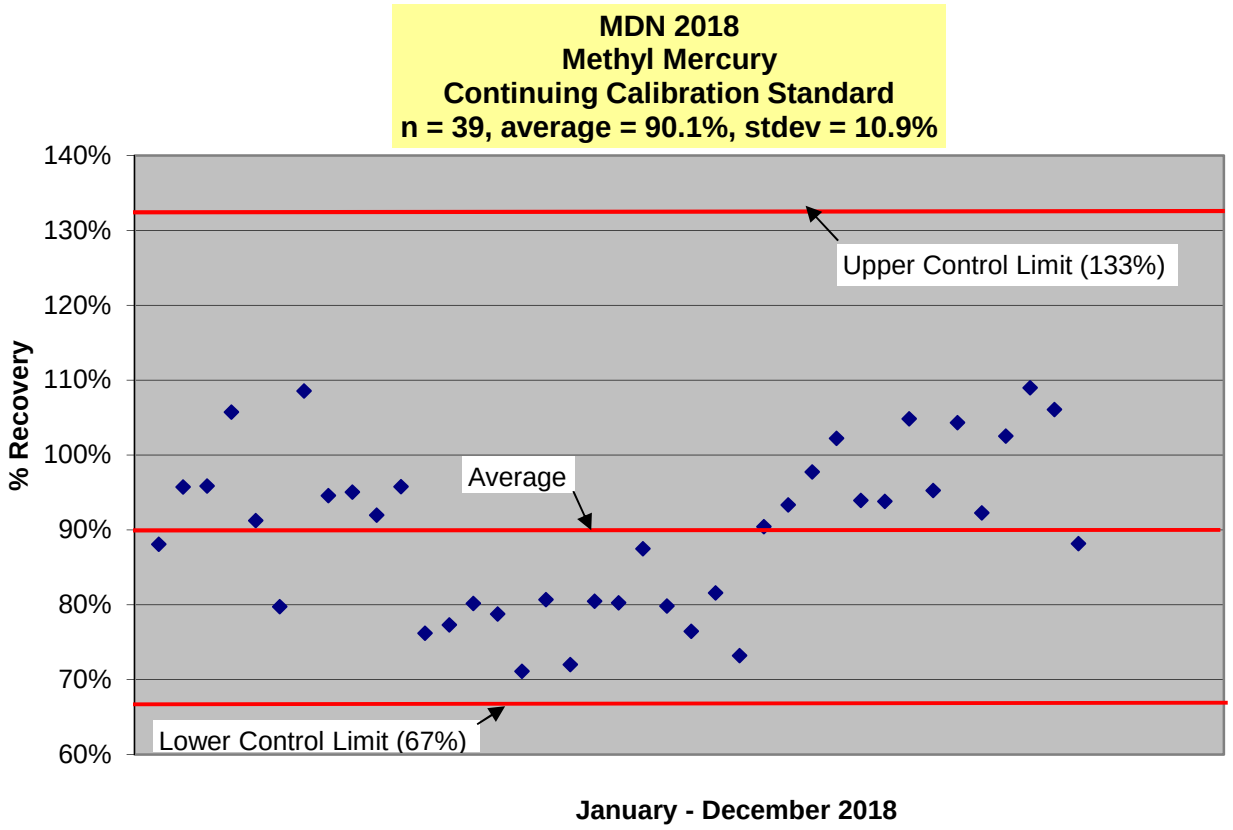


Figure 6 - Methyl Mercury Continuing Calibration Standard Percent Recovery, 2018

2.3 Continuing Calibration Blanks

2.3.1 Description

Continuing Calibration Blanks (CCBs) are analyzed every ten or fewer samples and at the end of each analytical run. Individual initial calibration blanks (ICB) and CCBs shall be less than 0.50 ng/L and their mean should be less than 0.25 ng/L with a standard deviation of less than 0.1 ng/L in order to be within control limits for THg. For MMHg, the mean of the ICB and CCB shall be less than 0.025 ng/L in order to be within control limits for MMHg.

2.3.2 Purpose

Instrument blanks are used to monitor baseline drift and to demonstrate freedom from system contamination and carryover.

2.3.3 Discussion

Three of the 569 ongoing CCBs for THg were greater than the individual control limit of 0.50 ng/L used for MDN analysis at HAL (table 6 and figure 7). The samples associated with this CCB were re-analyzed. The mean of all ongoing CCBs was less than the mean control limit of 0.25 ng/L and their standard deviation was less than 0.1 ng/L.

All of the ongoing CCBs for MMHg were less than the mean control limit of 0.025 ng/L used for MDN analysis at HAL (table 6 and figure 8).

Table 6 - Continuing Calibration Blanks Summary

2018 Continuing Calibration Blanks	n	Average (ng/L)	Std Dev (ng/L)	MDL (ng/L)	HAL Control Limits
Total Mercury	569	0.081	0.086	0.095	Individually <0.50 ng/L, mean <0.25 ng/L with a standard deviation <0.10 ng/L
Methyl Mercury	39	0.003	0.003	0.040	0.025 ng/L

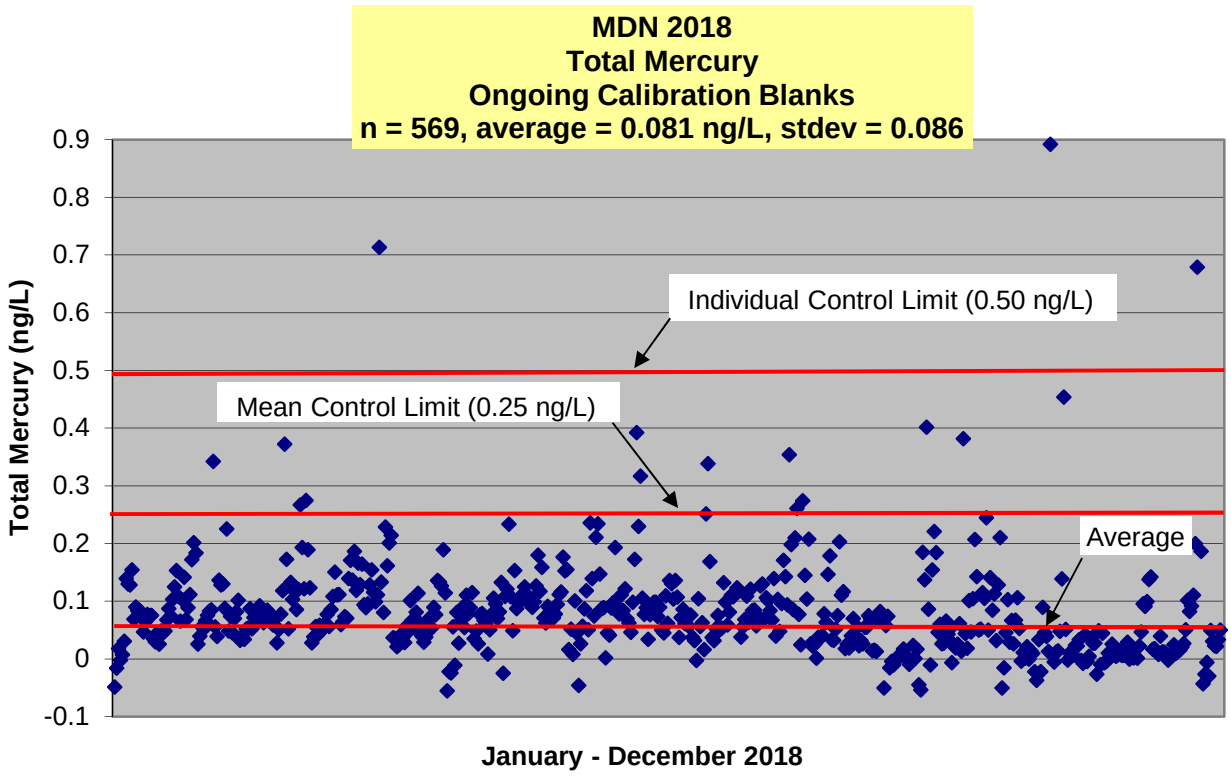


Figure 7 - Total Mercury Continuing Calibration Blanks, 2018

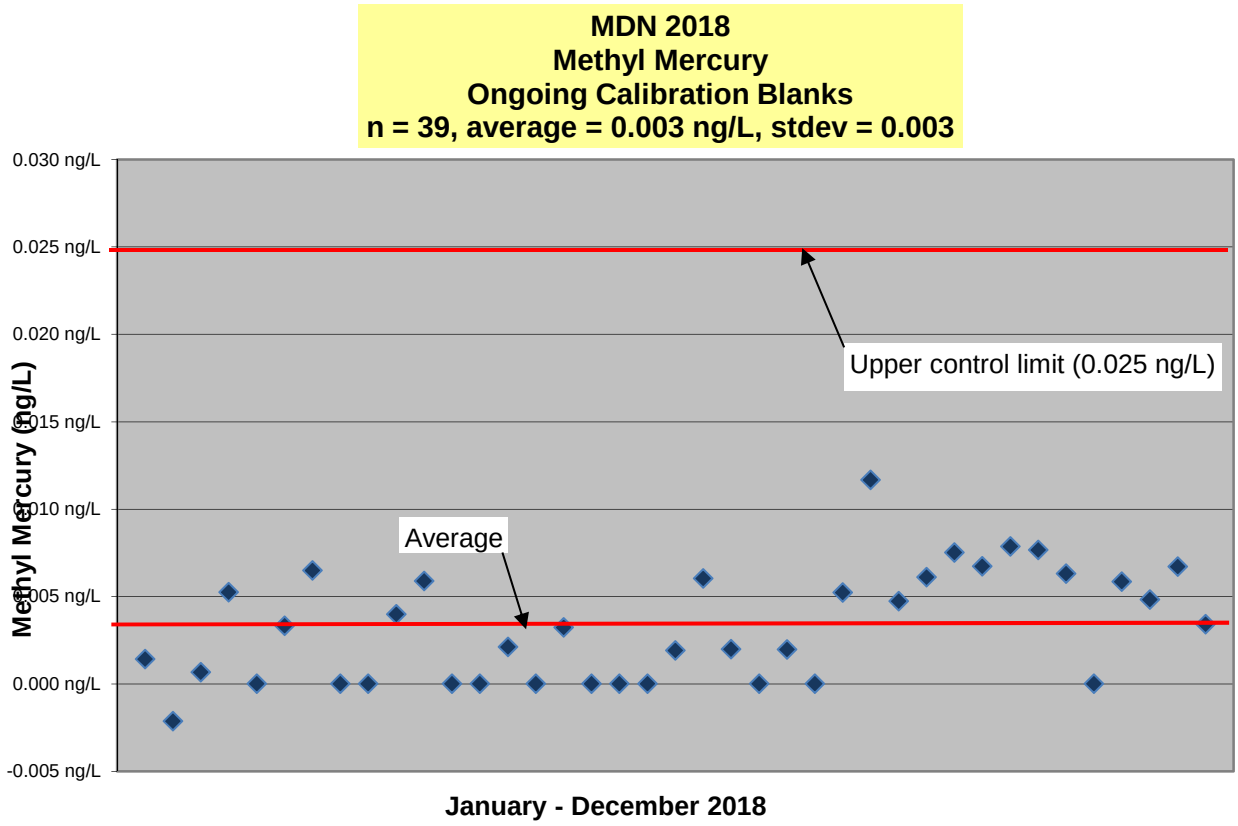


Figure 8 - Methyl Mercury Continuing Calibration Blanks, 2018

2.4 Matrix Duplicates

2.4.1 Description

Matrix Duplicates (MD) are created when an existing sample is split into two portions and then are compared analytically. The MDN control limit for the MDs is set at 25% RPD for THg and MMHg. US EPA methods 1630 and 1631 do not require a MD. One MD is performed for every ten analyzed samples and during a standard MDN THg analytical run, three MDs are analyzed. The source samples are selected depending on available volume. For THg analysis, 100 mL is needed for each source sample to obtain the MD, a Matrix Spike (MS), and for potential reanalysis of these QC samples. A smaller aliquot size can be used if needed.

2.4.2 Purpose

Replicate samples provide information about analytical precision. MDs are part of the same sample. As such, their Relative Percent Difference (RPD) is expected to be less than 25%. Out of control results are indications of a potential inhomogeneous sample matrix and/or poor analytical precision.

2.4.3 Discussion

For THg, all of the RPDs calculated for duplicate pairs were within the control limit of 25% RPD used at HAL (table 7 and figure 9).

For MMHg, four of the RPDs calculated for duplicate pairs were not within the control limit of 25% RPD used at HAL (table 7 and figure 10). The MMHg concentration in two of these pairs was lower than, or equal to, the reporting limit of 0.050 ng/L and was less than 5 times the reporting limit in the other two pairs. Low concentration can yield high RPDs. For example, the recovery criteria for the calibration point at the PQL (0.050 ng/L) level is 70-130%; the analytical values of 0.035 ng/L and 0.065 ng/L, corresponding to 70% and 130% of the PQL (0.050 ng/L), yield a RPD of 60.0%. MDN samples of low concentration that produce high RPD values can often be qualified in the final data. HAL applies the same type of qualifiers on MDN data as for any other analysis of EPA 1630 or 1631 E, if applicable.

Values for QC samples that were qualified for known problems were excluded from the control charts to avoid misrepresentation of actual precision. In general, data points that are flagged with QR-04 are rejected from the chart. This qualifier is defined as follows:

QR-04: RPD and/or RSD value exceeded the control limit. Sample concentrations less than 5 times the reporting limit and the difference between the QC values was less than the reporting limit.

Table 7 - Matrix Duplicates Summary

2018 Matrix Duplicates	n	Average RPD (%)	Std Dev (%)	HAL control Limit (%)	EPA 1631E/1630 Control Limits
Total Mercury	477	2.44	2.6	25	NA
Methyl Mercury	9	28.6	30.7	25	NA

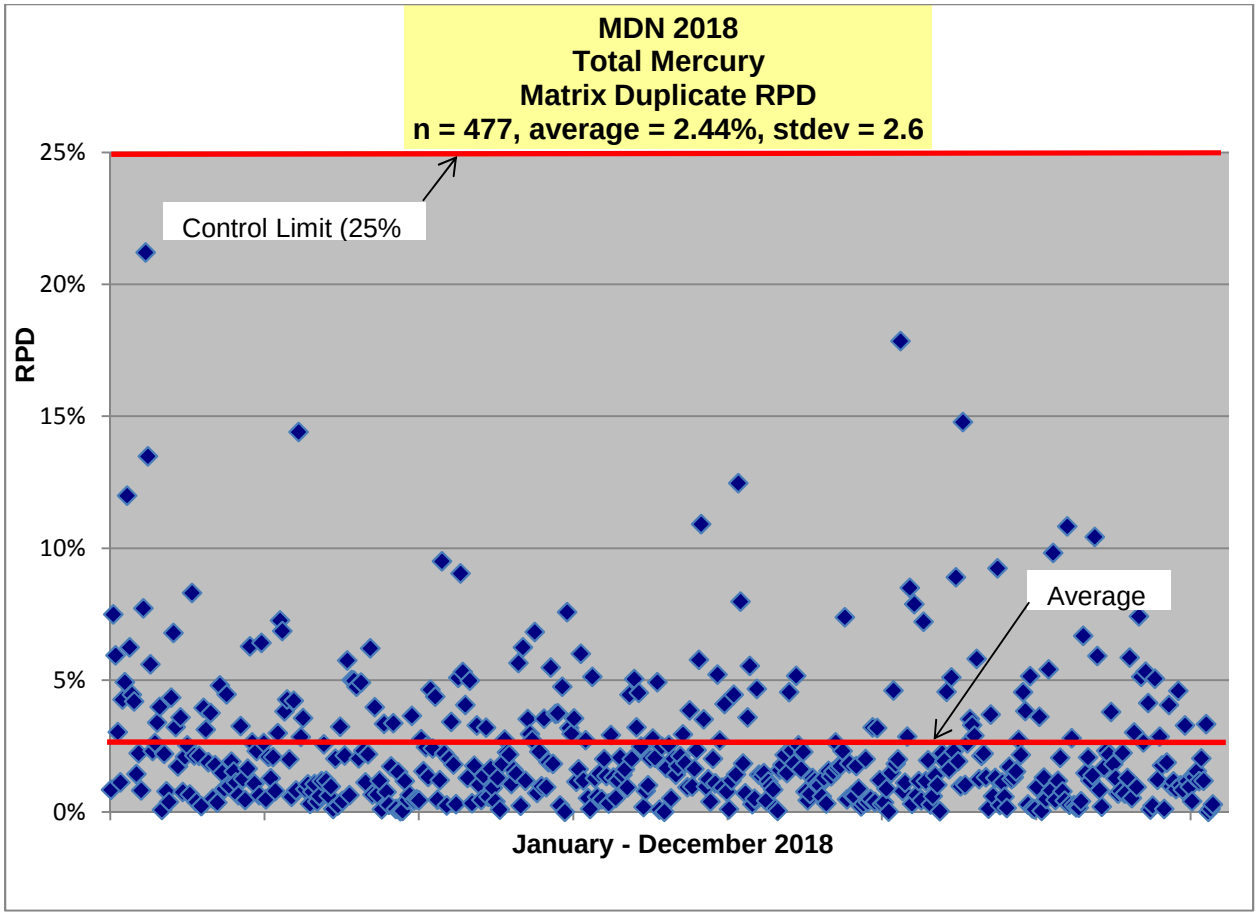


Figure 9 - Relative Percent Differences for Total Mercury Concentrations in Matrix Duplicates, 2018

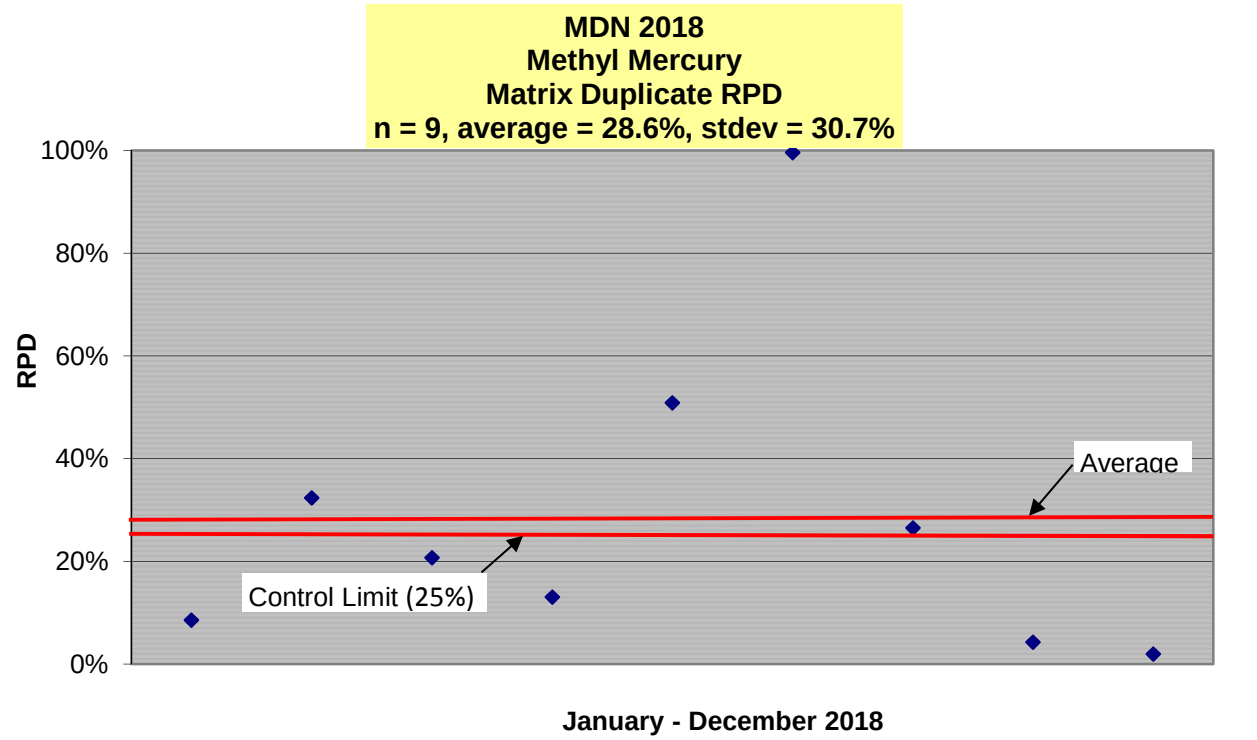


Figure 10 - Relative Percent Differences for Methyl Mercury Concentrations in Matrix Duplicates, 2018

2.5 Matrix Spikes

2.5.1 Description

A Matrix Spike (MS) for THg is created when an MDN sample with known mercury content is split in two fractions and one fraction is supplemented with an additional 1.00 ng of mercury standard.

For both EPA method 1631 and 1630, there must be 1 MS and 1 MSD sample for every 10 samples (a frequency of 10%) and the spiking level shall be at 1–5 times the background concentration or at 1-5 times the MRL (0.5 ng/L for THg and 0.05 ng/L for MMHg), whichever is greater. For MDN (THg) runs, due to limited sample volume, only one matrix spike (MS) is performed for every ten analyzed samples. During a normal analytical run, three matrix spikes are analyzed. The source samples are selected depending on available volume as 50 mL is desired for the source sample, the matrix duplicate and the matrix spike, and for potential reanalysis of these QC samples. No RPD data for MS/MSD is available for THg, since only a MS is analyzed. A MS/MSD is performed for MMHg and the control limit for the RPD is $\pm$25%.

2.5.2 Purpose

The purpose of analyzing a MS and MSD is to demonstrate the performance of the analytical method in a particular sample matrix, and to account for matrix interference. To prepare a MS/MSD, predetermined quantities of the analyte are added to a sample matrix before (when possible) extraction or digestion of samples, in this case preservation with BrCl for THg analysis and preservation with HCl and distillation for MMHg analysis. Because of the limited volume of sample that's usually available for MMHg quality control samples, the laboratory changed its approach to aliquoting for MD/MSD samples. Beginning in 2015, the laboratory attempted to use the same volumes for the matrix spike and matrix duplicate as it did for the source sample. If the sample is spiked with the analyte of interest after extraction or digestion, this is considered an analytical spike and an analytical spike duplicate (AS/ASD). If low recovery of a matrix spike indicates matrix interference, samples with sufficient volume are diluted and reanalyzed. The purpose is to determine the largest aliquot size that can be analyzed without matrix interference. The source sample is also reanalyzed at the same aliquot volume.

2.5.3 Discussion

For THg, all recovery values were within the 75-125% control limit used at HAL (table 8 and figure 11).

For MMHg, all recovery values are within the 65-135% control limit used at HAL (table 8 and figure 12).

Table 8 - Matrix Spike Recoveries for 2018 Samples

2018 Matrix Spikes	n	Average Recovery (%)	Std Dev of Recovery (%)	HAL Control Limits	EPA 1631E/1630 Control Limits (%)
Total Mercury	477	96.4	4.75	75-125	71-125
Methyl Mercury	32	101	11.1	65-135	65-135

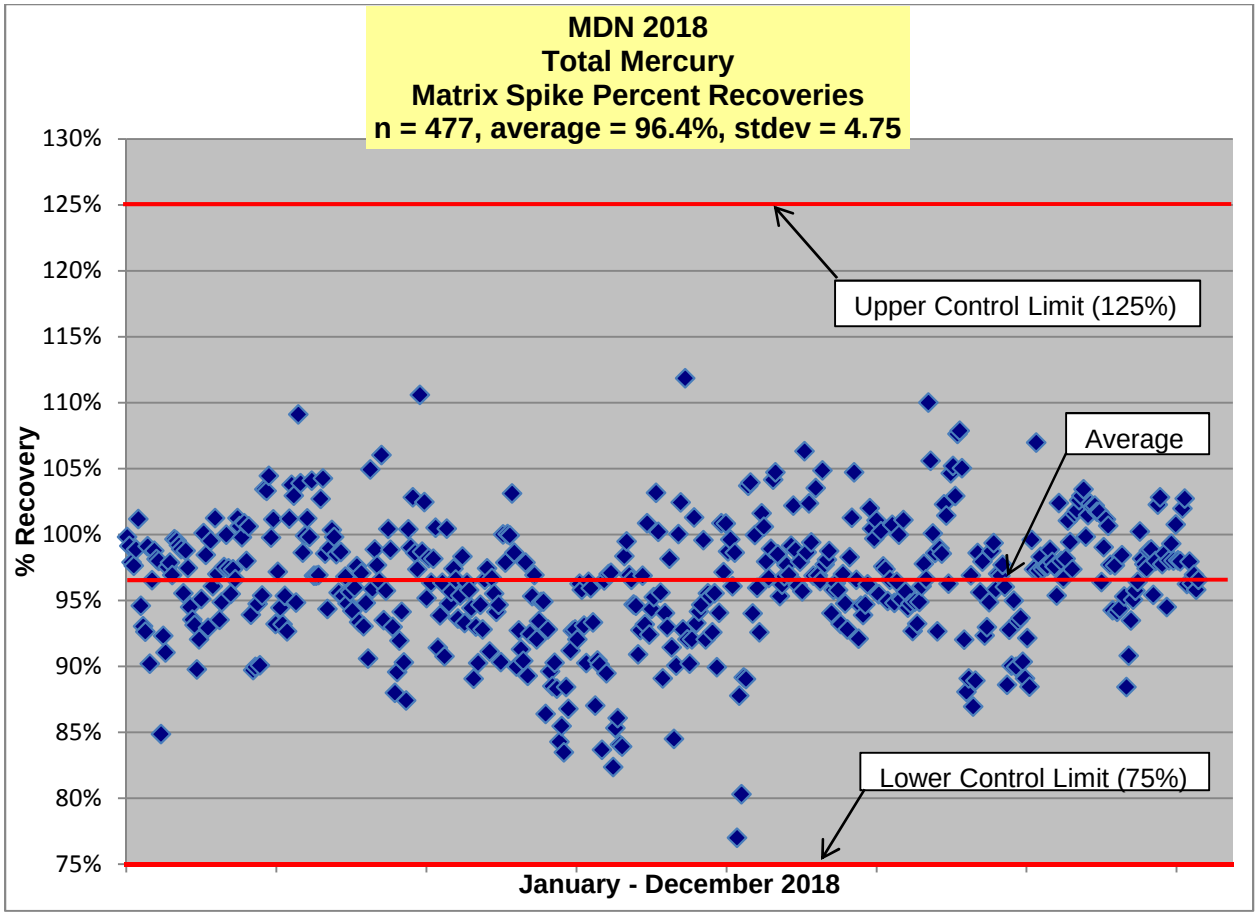


Figure 11 - Total Mercury Percent Recovery in Matrix Spikes, 2018

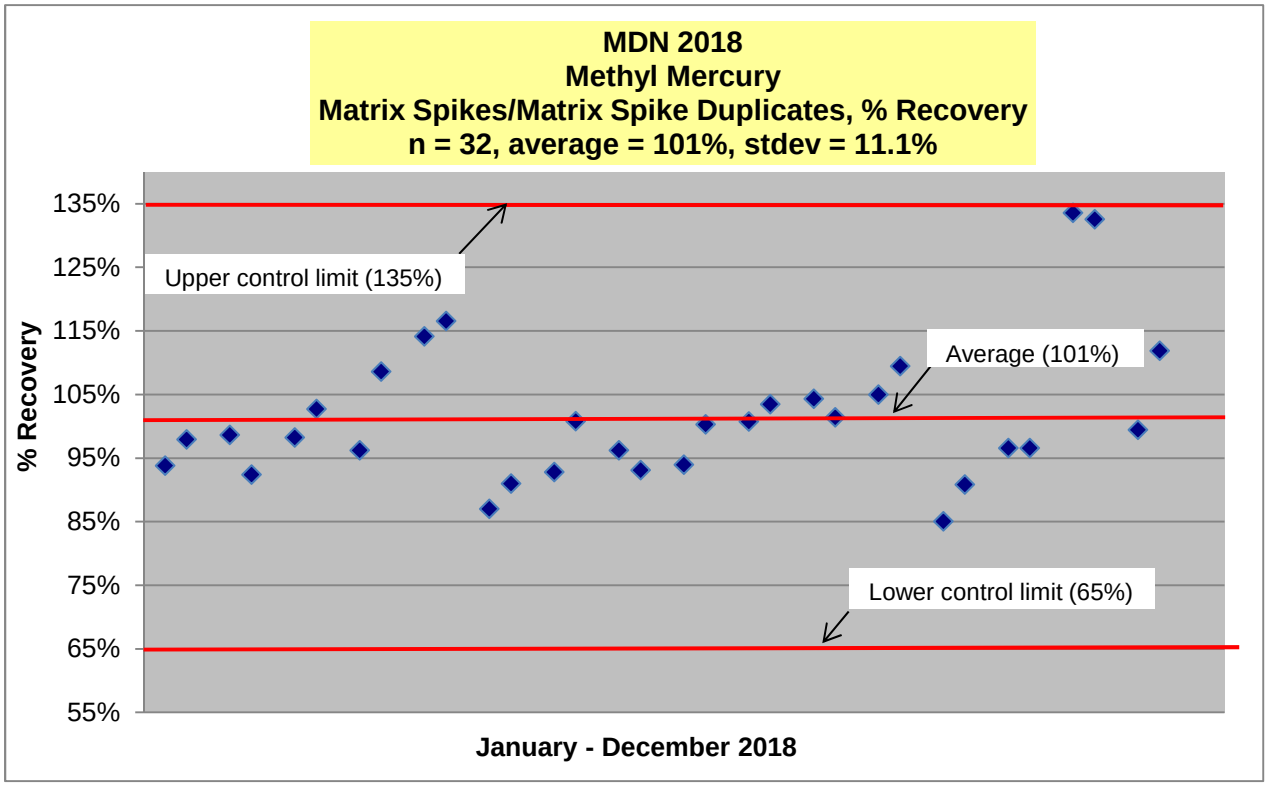


Figure 12 - Methyl Mercury Percent Recovery in Matrix Spikes, 2018

All RPD values for MMHg were within the 25% control limit used at HAL (table 9 and figure 13).

Table 9 - Matrix Spike/Matrix Spike Relative Percent Differences (RPD) for 2018 Samples

2018 Matrix Spike Duplicates	n	Average RPD (%)	Std Dev (%)	HAL Control Limits	EPA 1630 Control limits RPD (%)
Total Mercury	0	0	0	NA	<24
Methyl Mercury	16	5.1	3.5	<25	<35

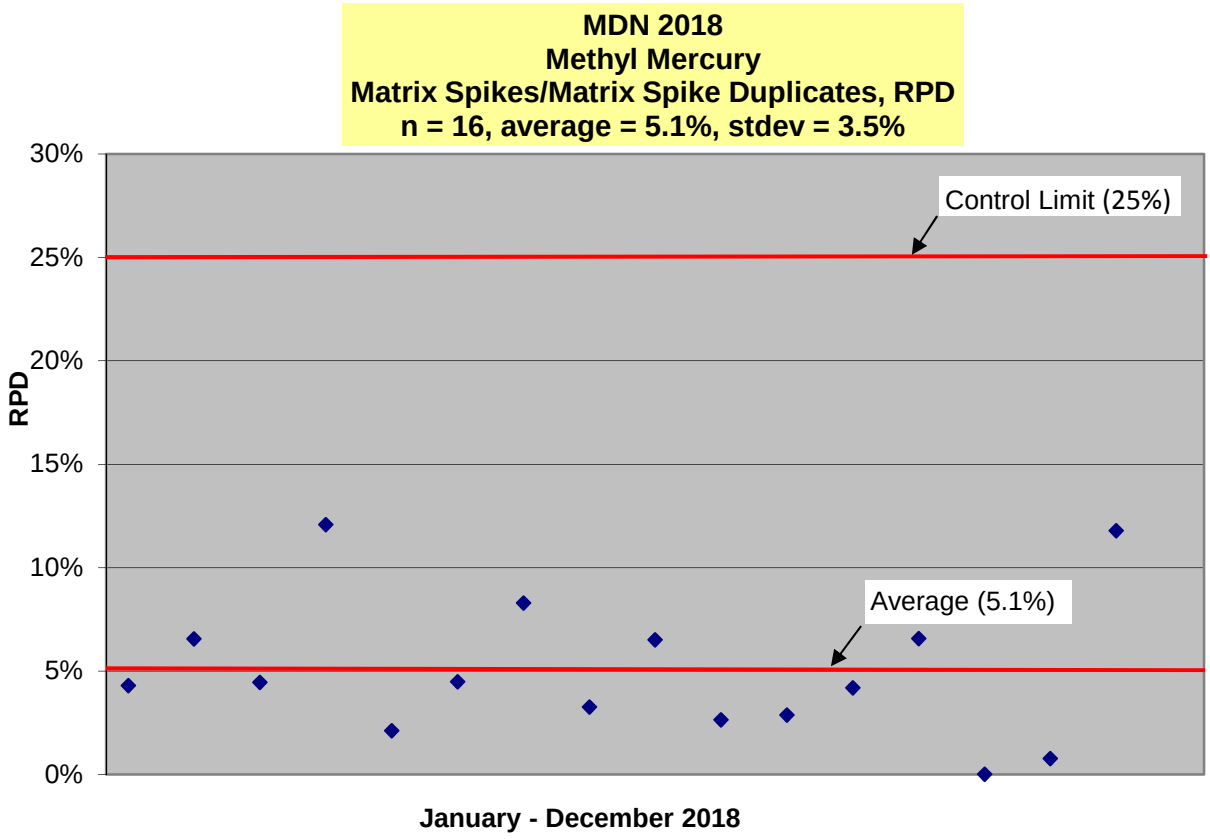


Figure 13 - Relative Percent Differences (RPD) for Methyl Mercury Matrix Spike/Matrix Spike Duplicate Pairs, 2018.

2.6 Certified Reference Materials

2.6.1 Description

Certified Reference Materials (CRMs) are matrix specific standards that are accompanied by a certificate of analysis for the analytes of interest. Eurofins Frontier generally purchases reference materials from the National Institute of Standards and Technology (NIST), the National Research Council of Canada (NRCC), or the International Atomic Energy Agency (IAEA). Eurofins Frontier maintains that matrix equivalent reference materials provide the best measure of precision and accuracy (bias) because they have a consistent, homogeneous matrix.

A CRM matching the MDN rainwater matrix has not been located. Therefore, HAL uses National Institute of Standards and Technology (NIST) reference material 1641d "Mercury in Water."

Because the availability of 1641d vanished early in 2018, the HAL also had to use NIST CRM 1641e later in the year. The percent recovery control limits for THg in both CRMs are currently set at 80-120% with a RPD of 24%. There is no CRM available for MMHg. Therefore, a Blank Spike and a Blank Spike Duplicate (BS/BSD) are analyzed for MMHg with acceptance criteria of 70-130%, with a RPD of 25%. US EPA methods 1630 and 1631 do not require a certified reference material.

2.6.2 Purpose

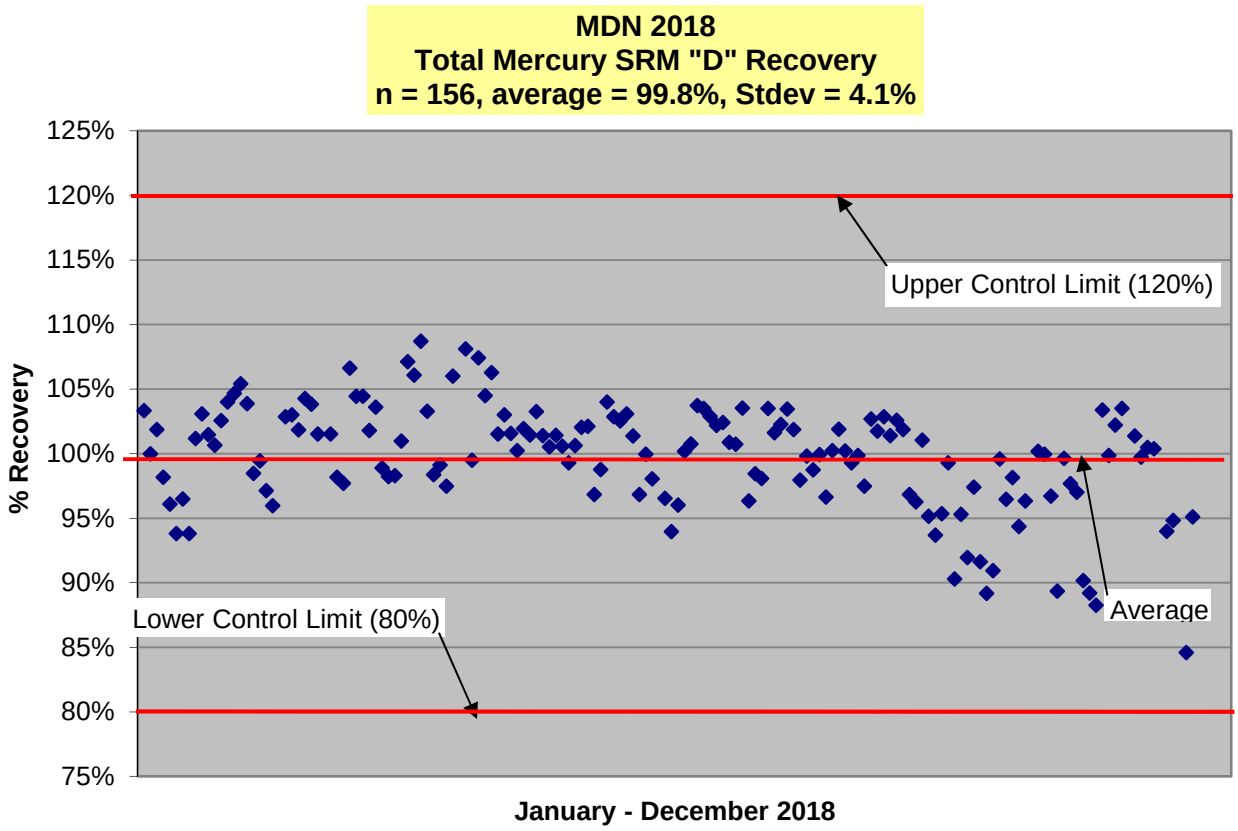
Certified Reference Materials are used to demonstrate HAL's ability to recover a target analyte from a specific matrix. For THg, the first CRM is analyzed immediately after the calibration standards to validate the analytical curve.

2.6.3 Discussion

For NIST reference material 1641d, the mean of 156 recoveries for THg was 99.8% with a standard deviation of 4.1% (figure 14). All CRM values were within the actual control limit of 80-120% used in the laboratory. The average RPD value for the CRM/CRM duplicate was 2.6% (n=72), with a standard deviation of 2.3%. All RPD values were below the 24% limit used in the laboratory, demonstrating good precision between the CRMs and CRM duplicates (figure 15).

For NIST reference material 1641e, the mean of 154 recoveries for THg was 99.8% with a standard deviation of 4.4% (figure 14). All CRM values were within the actual control limit of 80-120% used in the laboratory. The average RPD value for the CRM/CRM duplicate was 2.6% (n=77), with a standard deviation of 3.0%. All RPD values were below the 24% limit used in the laboratory, demonstrating good precision between the CRMs and CRM duplicates (figure 15).

The mean recovery of 20 blank spikes and blank spike duplicates (BS/BSD) for MMHg was 104.1% with a standard deviation of 10.4% (figure 16). All recovery values were within the 70-130% control limit used at HAL. The average RPD value for the BS/BSD was 8.1% (n=10) with a standard deviation of 5.1%. The method doesn't specify limits for BS/BSD RPD. All RPD values were within the 25% limit used in the laboratory (figure 17).



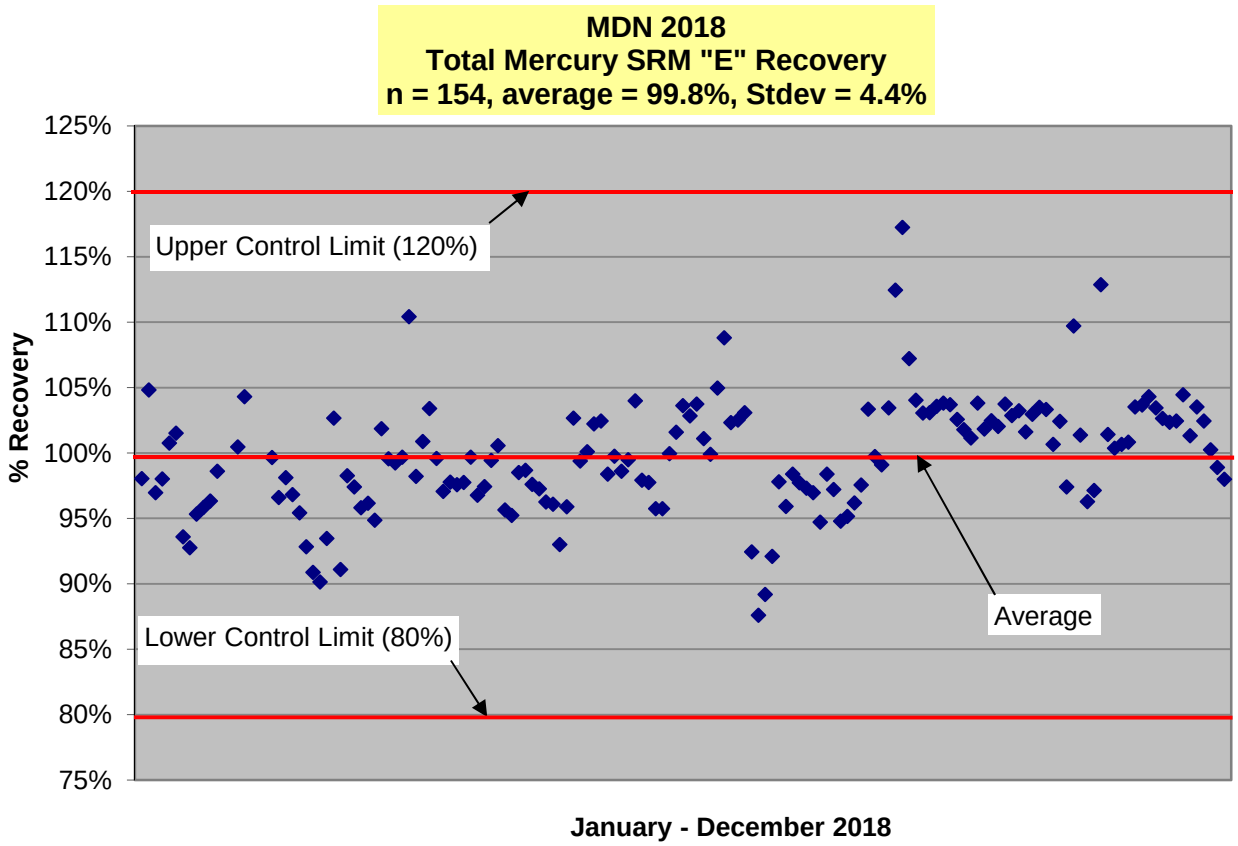
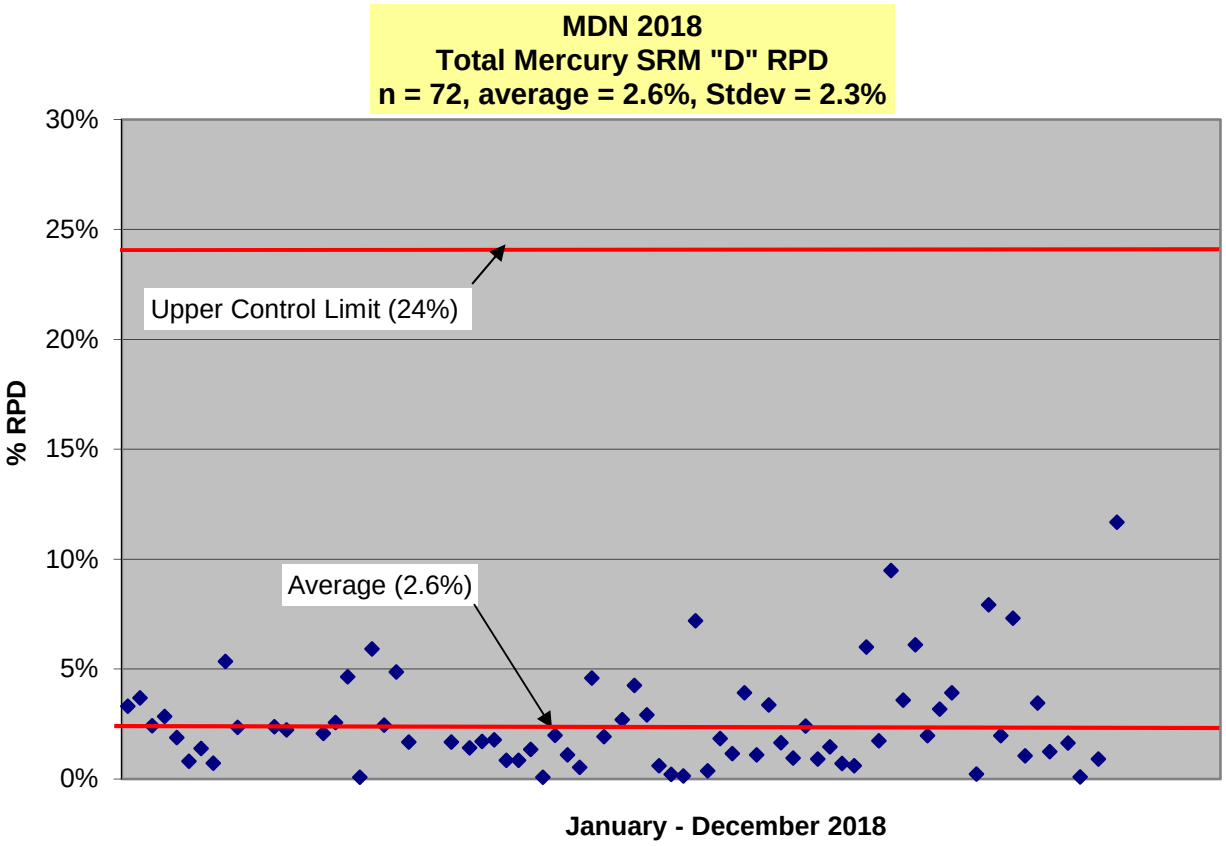


Figure 14 - Total Mercury Percent Recovery in Certified Reference Material Samples, 2018



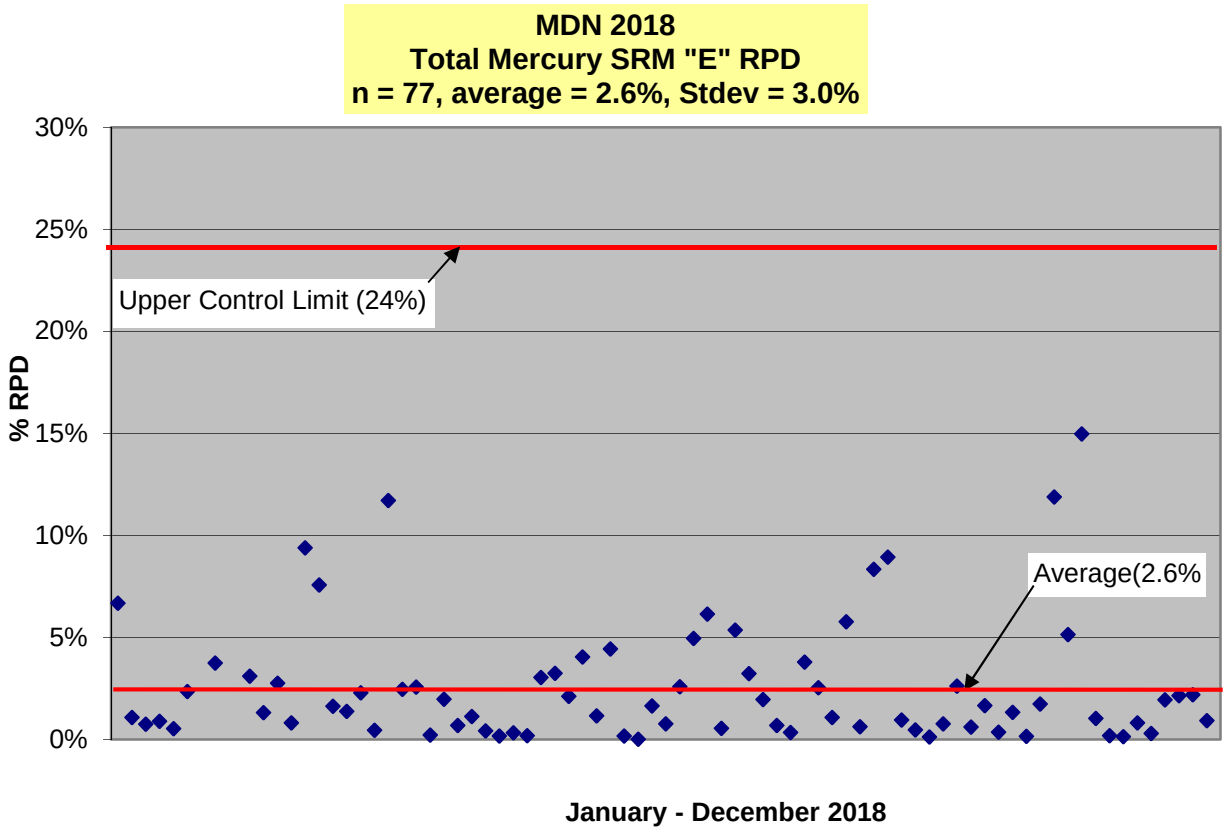


Figure 15 - Total Mercury Relative Percent Difference (RPD) between Certified Reference Materials (CRM) and CRM Duplicate Analyses, 2018

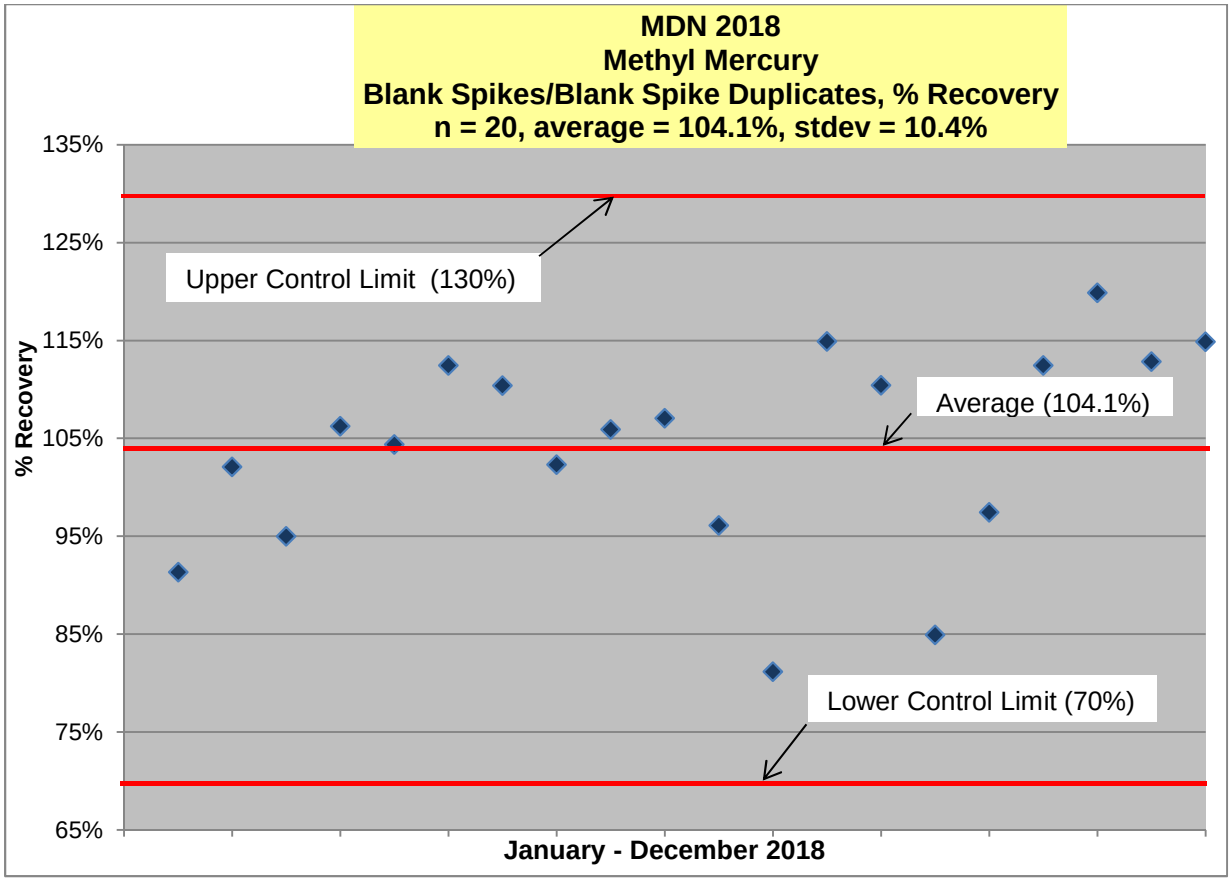


Figure 16 - Methyl Mercury Percent Recovery in Blank Spikes/Blank Spike Duplicate Samples, 2018

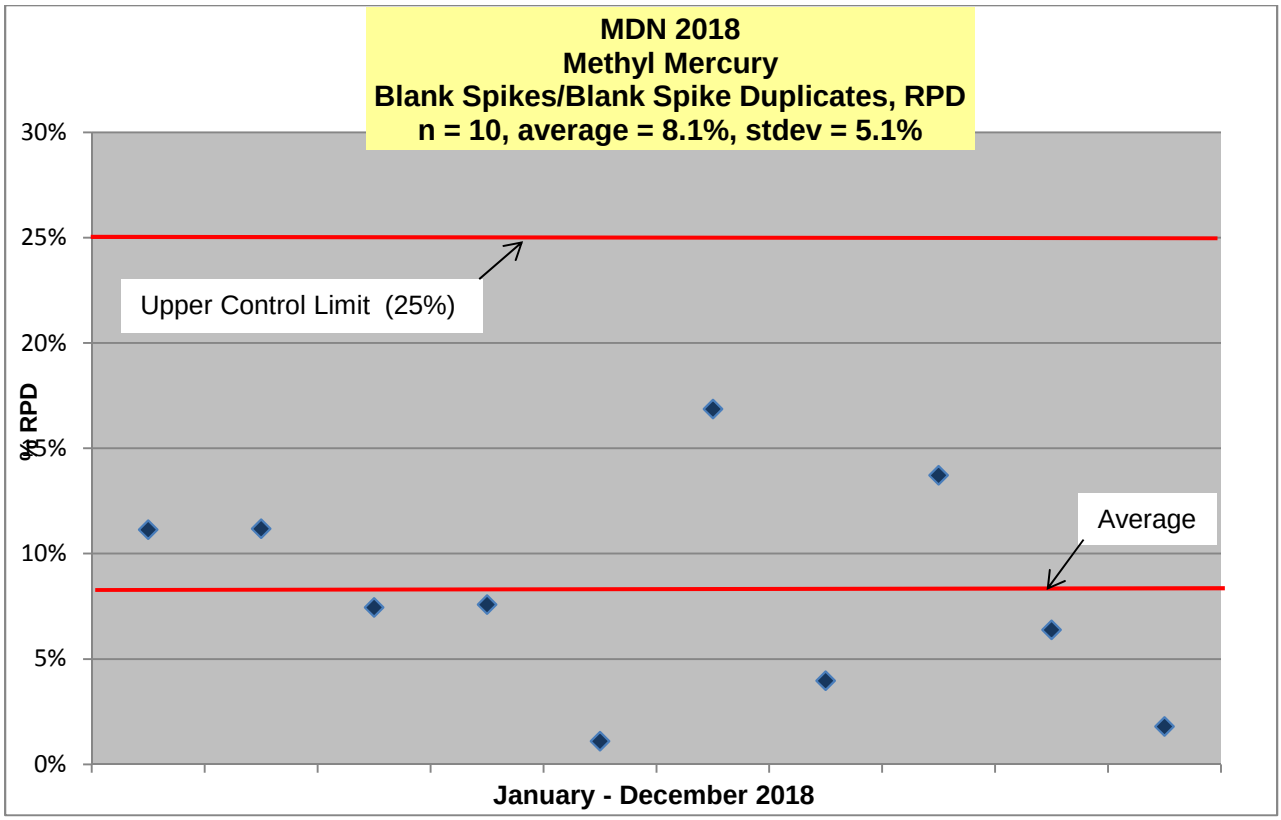


Figure 17 - Methyl Mercury Relative Percent Difference (RPD) in Blank Spikes/Blank Spike Duplicate Samples, 2018

3. Calculations

3.1 Calculation: Gross MDN Sample Concentration

{(Sample PA - Avg PB) / Slope} - {(Aliquot * BrCl RB) / 100} = ng Hg/aliquot (mL)

Sample PA = sample peak area (PA units)

Avg PB = average preparation blank (PA units)

Slope = slope (PA units/ng)

Aliquot = volume of sample analyzed (mL)

BrCl RB = BrCl reagent blank value (ng/mL of preservative)

1/100 = correction for 1% preservation concentration

3.2 Calculation: Net MDN Sample Concentration

ng Hg/aliquot (mL) * mL / Sample Bottle = ng Hg/Sample Bottle

ng Hg/Sample Bottle – ng Hg/Quarterly Bottle Blank = net ng Hg/Sample Bottle

net ng Hg/Sample Bottle * (Sample Bottle/mL) * 1000 = net ng Hg/L

3.3 Calculation: MDN Deposition

Deposition (ng/m^2) = Subppt x Concentration

Subppt: Substituted Precip, mm

If on the QA Data Package, "Do Not Use Rain Gage" is not selected, then Subppt is

= RainGauge (inch) x 25.4 (mm/inch)

If this is selected then Subppt is

=BottleCatch (ml) x 25.4 (mm/inch) x 0.003281 (inch/mL)

Note: 0.003281 (inch/mL) = comes from 1 inch of capture in sample bottle according to glass funnel opening area of 120 cm^2 x 2.54cm/inch = 304.8 cm^3 /inch = 304.8 mL/inch when the density of the rain water is assumed to be 1 g/cm^3 = 1 g/mL.

Concentration: Total Hg Concentration in Precipitation

Concentration THg = ((sampleHgMass – quarterly BottleBlank) / tmpVol) x 1000

Where:

tmpVol = FullMass – EmptyMass – 20 (20 mL preservative)

SampleHgMass = AliquotHg x (FullMass – EmptyMass) / AliquotVol

3.4 Calculation: Methyl Mercury

For both splits and composites samples, the samples are preserved on the day of receipt.

For MMHg sample splits, one sample produces one split. The split is accomplished using the procedures detailed in SOP EFMDN-T-MDN-SOP5696.

For MMHg sample composites, four weekly sub-samples are poured into one bottle to produce one MMHg sample composite representing that month's composite). The composite is prepared using the procedures detailed in SOP EFMDN-T-MDN-SOP5696.

Per EPA Method 1630, acid preserved samples that are kept chilled and in the dark are stable for at least six months.

Methyl Mercury Preservation

All MMHg samples are assessed for HCl preservation immediately after receipt.

If sample is > 100 g:

$$\left[\frac{(\text{total sample mass} - 100)}{100}\right] \times 0.3 = \text{mL HCl to add}$$

If sample is < 100 g: HCl preservation is not required.

Methyl Mercury Splits

A fraction of the total sample volume is set aside for MMHg analysis.

Total Volume	Split Volume (g)
< 25.5 g	NA (no split)
25.5-50.9 g	total / 10
51-150.9 g	total / 4
> 151 g	total / 2

Methyl Mercury Composites

Fractions of the total volume from each of four weekly samples are composited into a sample for the month.

Total Volume	Split Volume (g)
≤ 25 g	NA (no comp)
> 25 g	total / 10

4. Analytical Run Sequence

HAL includes the previously mentioned QC samples in all of its analyses for the MDN project. The following work sheet shows how these samples are arranged within a typical analysis day. For every set of ten samples analyzed, the sample set is preceded and followed with a Matrix Duplicate, a Matrix Spike, Continuing Calibration Verification (CCV), and a Continuing Calibration Blank (CCBs). In addition, after the twentieth sample an additional Reference Material sample is analyzed.

MDN Precipitation Sample Analysis Lab Sheet

Analysis Date:
Analyzer:
Analyst:

REVIEWER:

FGS DATA SET ID:
MDN LAB DATA SET CODE:
DATE:

Analytical Run
D=Duplicate Analysis

Trap Set:
S=Sample Spike @ 1.00ng

Run	Tp	Bub	HAL Code	Sample ID	PA	% BrCl	Aliquot Volume	THg per Aliquot	THg Conc (Net)	Remarks
1	1	1		4.00 ng						
2	2	2		2.00 ng						
3	3	3		1.00 ng						
4	4	4		0.50 ng						
5	5	1		0.05 ng						
6	6	2		BB-1						
7	7	3		BB-2						
8	8	4		BB-3						
9	9	1		NIST1641d		2				
10	10	2		BrCl-1						
11	1	3		BrCl-2						
12	2	4		BrCl-3						
13	3	1		BB-4						
14	4	2		Sample #1						
15	5	3		Sample #1 D						
16	6	4		Sample #1 S						
17	7	1		Sample #2						
18	8	2		Sample #3						
19	9	3		Sample #4						
20	10	4		Sample #5						
21	1	1		Sample #6						
22	2	2		Sample #7						
23	3	3		Sample #8						
24	4	4		Sample #9						
25	5	1		Sample #10						
26	6	2		1.00						
27	7	3		BB-5						
28	8	4		Sample #11						
29	9	3		Sample #12						
30	10	4		Sample #13						
31	1	1		Sample #14						
32	2	2		Sample #15						
33	3	3		Sample #16						
34	4	4		Sample #17						
35	5	1		Sample #18						
36	6	2		Sample #19						
37	7	3		Sample #20						
38	8	4		Sample #11 D						
39	9	3		Sample #11 S						
40	10	4		1.00						
41	1	1		BB-6						
42	2	2		NIST1641d						
43	3	3		Sample #21						
44	4	4		Sample #22						
45	5	1		Sample #23						
46	6	2		etc…						
47	7	3								
48	8	4								
49	9	1								
50	10	2								
51	1	3								
52	2	4								
53	3	1		Sample #21 D						
54	4	2		Sample #21 S						
55	5	3		1.00						
56	6	4		BB-7						

Key
Reference Materials
Preparation Blanks
Matrix Duplicates
Matrix Spikes
CCVs
CCBs

Figure 18 - Example of Sample Analysis Worksheet

5. Proficiency Tests and Laboratory Intercomparison Studies

Eurofins Frontier Global Sciences, Inc. (EFGS)/HAL participated in quarterly inter-laboratory comparison studies provided by USGS 2018. Samples are submitted for mercury analysis in both spiked and ultrapure deionized water.

EFGS also participated in two drinking water, five water pollution and four soil proficiency tests in 2018. One of the water pollution proficiency tests is used for the annual DMR-QA (Discharge Monitoring Report-Quality Assurance) study program, which is a requirement for laboratories that have clients with NPDES (National Pollutant Discharge Elimination System) permits. The Proficiency Test (PT) studies are either purchased from a licensed and approved commercial provider or supplied by a government agency. Results for each of these studies are submitted to all of Frontier's accreditation bodies and are available to any client upon request. While these studies are a requirement of accreditation, they are also a valuable tool for internal quality control.

5.1 Proficiency Tests

The proficiency tests listed in table 10 were completed by EFGS during 2018, in addition to the quarterly USGS samples that are not included in the table. Results for any tests are available upon request. A summary of the HAL's USGS inter-laboratory comparison results are provided in Appendix A.

Table 10 - Proficiency Tests

Proficiency Test	Organization	Open-close date	Scored Total Hg Results
MAPEP 39 water & soil	US DOE	9/5/2018 – 11/15/2018	Passed
HW0718	Phenova	7/30/2018 – 9/13/2018	Passed
WS0718	Phenova	7/16/2018 – 8/30/2018	Passed
WP0718	Phenova	7/9/2018 – 8/23/2018	Passed
Study 112	Canada ECCC	6/6/2018 – 7/30/2018	Passed
WP0417 (Make-up for (WP0117)	Phenova	4/5/2018 – 5/15/2018	Passed
MAPEP 38 water & soil	US DOE	3/5/2018 – 5/17/2018	Passed
HW0118	Phenova	1/29/2018 – 3/15/2018	Passed
WS0118	Phenova	1/17/2018 – 3/1/2018	Passed
WP0118	Phenova	1/8/2018 – 2/22/2018	Passed

6. Field Quality Control

The MDN network utilizes two different procedures to ensure that the sample train is not compromised. The two procedures are field blanks and system blanks.

6.1 Field Bottle Blanks

6.1.1 Description

A field bottle blank has the same contents as a laboratory bottle blank. However, this blank is left exposed at the sampling site for the entire collection period without the collector being opened at any time (no rain accumulation and no unexplained collector openings). All field bottle blanks that maintain enough of the initial 20 mL 1% hydrochloric acid (15-21.3 mL) pre-charge so that at least 15 mL can be measured out as aliquot size, are analyzed for THg. These samples are identified as field bottle blank samples and are "A" coded and receive "Q" as a sample type. Field blanks with a measured aliquot size less than 15 mL are analyzed and are "A" coded, but receive "D" (Dry week) as the sample type. The analysis is based on mass of sample analyzed and therefore no dilution is needed. There was 1 sample in 2018 that had no recorded precipitation with the event recorder indicating the collector did not open and that also had less than 15 mL of preservative in the sample bottle. This result is not tabulated. The HAL and the original Program Office were attempting to address sample evaporation through lab and field testing. Results from initial testing were submitted at the 2014 NADP Fall Meeting. The HAL has discontinued its evaporation studies until the new Program Office has an opportunity to review this topic and further discussions take place to determine a best practice approach that addresses this issue.

6.1.2 Purpose

Outside of the controlled laboratory environment, the ambient mercury levels increase and this is where the majority of the sample handling occurs. High field blanks can be a result of a problem with keeping the container closed due to malfunction of the lid seal pad. In dry and windy areas, there is a risk for dust contamination.

6.1.3 Discussion

The MDL for THg was converted to ng/bottle (using 20mL charge volume/bottle) in Table 3 to accommodate comparisons with the bottle blank data. In 2018, the mean of 40 Field Bottle Blanks was 0.026 ng/bottle with a standard deviation of 0.030 ng/bottle. As would be expected, the average for the field bottle blanks is greater than the average for the laboratory bottle blanks. Field bottle blanks generally exceeded the MDL all of the time. Figure 19 shows field bottle blanks KS3220180709, OK0520180116 and NS0120180529 with elevated mercury values of approximately 0.15, 0.09, and 0.08 ng, respectively.

KS32, OK05, and NS01 have NCON collectors. There were a total of 4 field blanks for OK05, but only 1 field blank for the other 2 sites. Two of the other three field blanks for OK05, collected on 2/6/18 and 3/13/18, contained about twice the calculated average for THg, while the third blank, collected on 1/2/18 contained about the average. Any windy conditions, even if not severe, would have a higher chance of blowing in dust/dirt particles into the sample, which could contribute to the high blanks.

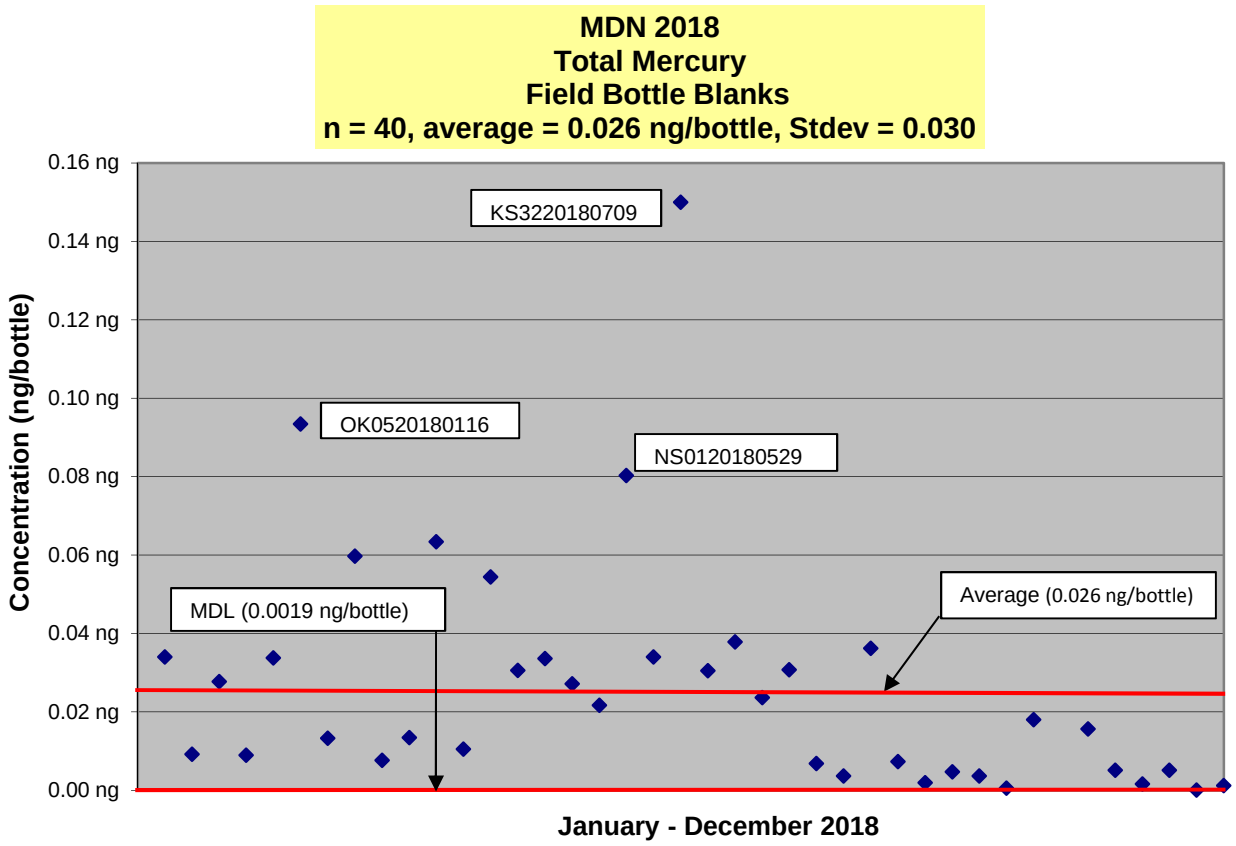


Figure 19 - Total Mercury Concentrations in Field Bottle Blanks, 2018

6.2 Field System Blanks

6.2.1 Description

A field system blank is essentially a field bottle blank in which a solution (RO-water) is poured through the wet side collection sample train that was installed in the field for an entire week with no precipitation. The system blank THg concentration is compared to the THg concentration of an aliquot of the same solution that was not poured through the sample train (i.e. control sample).

6.2.2 Purpose

This quality assurance program, conducted jointly by the U.S. Geological Survey and EFGS, is intended to measure the effects of field exposure, handling, and processing on the chemistry of MDN precipitation samples.

6.2.3 Discussion

Although the U.S. Geological Survey did not coordinate any field system blanks in 2018, there were seven field system blanks distributed to site operators in previous years that made their way to the HAL in 2018. When adjusted for 50mL blank volume, the MDL and PQL for THg convert to 0.005 ng/aliquot and 0.025 ng/aliquot, respectively. In 2018, the mean of 7 system blanks was 0.016 ng/aliquot with a standard deviation of 0.017 ng/aliquot compared to the control sample with a mean of 0.003 ng/aliquot and a standard deviation of 0.004 ng/aliquot. The mean for the field systems blanks is comparable to the mean for the laboratory bottle blanks (0.009 ng/bottle).

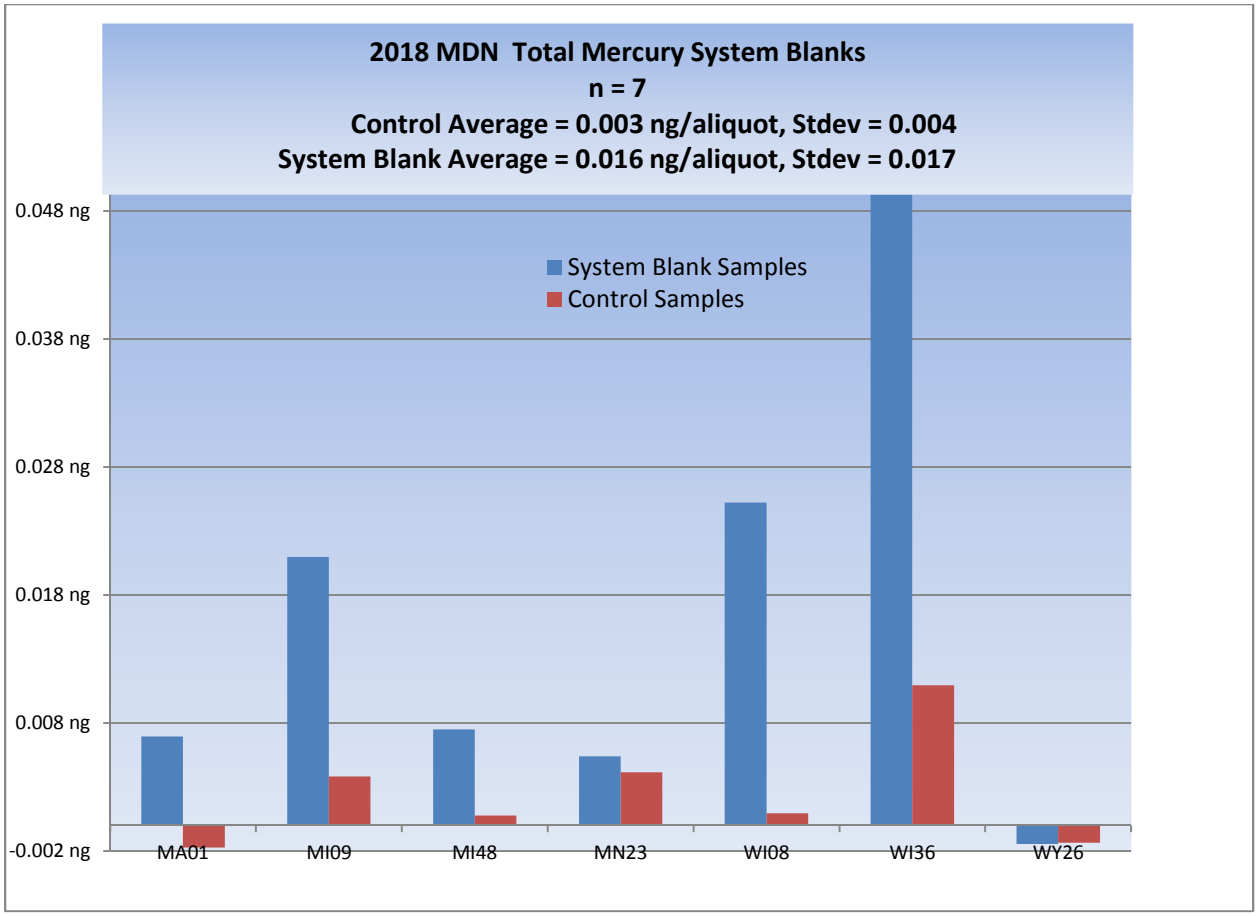


Figure 20 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2018

7. Quality Rating Codes

The Quality Rating (QR) code is designed as a user-friendly method to indicate the overall quality of each individual MDN data value. The MDN QR code criterion is modeled after the NADP AIRMoN QR code criterion. The QR code is an advisory flag for the general data user. QR codes are assigned by a computer program based on the results of the notes codes given to each MDN sample. A general description of each QR code follows.

A. Valid samples with no problems; contained only precipitation; all sampling and laboratory protocols were followed; all required equipment was installed and operating properly.

B. Valid samples with minor problems; may have visible contaminants (e.g., insects or other debris); there may be an exception to approved sampling or laboratory methods; required equipment may be lacking or not operating properly. The laboratory does not consider these problems sufficient to invalidate the data, but there is more uncertainty than for A-rated data. These data are used along with A-rated data to calculate mean annual concentrations and deposition.

C. Invalid samples; major problems occurred; the laboratory does not have confidence in the data.

The HAL processed 4,740 samples in 2018, which is 6% less than the 5059 samples that were processed during 2017. There were 941 samples that received a QR code of "A", while 3,454

samples received a "B" QR code and 345 samples received a "C" QR code (none of the 345 samples were disqualified due to laboratory issues/errors). This distribution is illustrated in figure 21. As noted in the previous annual report, the original Program Office discovered that note codes and QR values were not updated when a sample record was edited in the MS Access database by their Office. At the time, the Program Office indicated that they expected to resolve the problem in late 2017 or early 2018, but the HAL never received a confirmation that this action was completed.

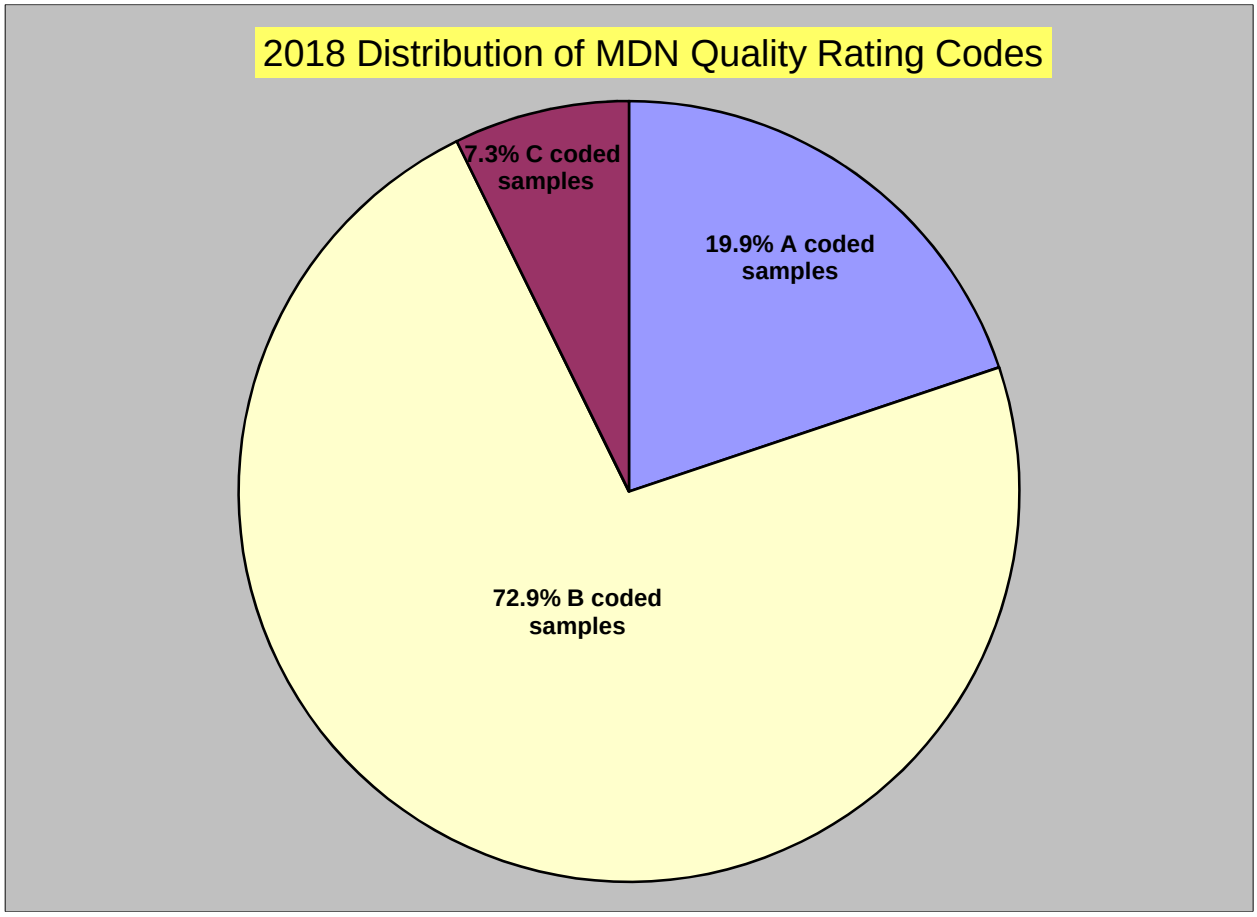


Figure 21 - Distribution of Quality Rating Codes for Samples Received in 2018

8. Summary and Conclusions

The HAL continued to maintain and demonstrate acceptable quality control in 2018. The five DQOs (precision, accuracy, representativeness, comparability, and completeness) were met. The MDL for total THg was 0.095 ng/L at a PQL of 0.50 ng/L, and the MDL for MMHg was 0.040 ng/L at a PQL of 0.05 ng/L. Average bottle blank Hg and MMHg content was quantified at 0.009 ng Hg/bottle and 0.0001 ng MMHg/bottle, respectively. Preparation and calibration blank total Hg and MHg contents were acceptable and within control limits. External proficiency testing by Phenova, ECCC, DOE and USGS yielded acceptable results. QC sample recoveries for ICVs, CCVs, MS/MSDs, BS/BSDs, and CRMs, as well as QC RPDs for MDs, MS/MSDs, BS/BSDs, were generally within control limits.

Field bottle blanks (n=40) and system blanks (n=7) generally indicated that field contamination levels continue to be low.

The HAL at Eurofins Frontier Global Sciences will process MDN samples for the first six months of 2019 only. By mid-2019, the responsibility for the HAL transfers to the University of Wisconsin.

9. Definitions of Abbreviations and Acronyms

APDC	Ammonium PyrrolidineDithioCarbamate
AS/ASD	Analytical Spike/ Analytical Spike Duplicate
BrCl	Bromine monochloride
BS/BSD	Blank Spike/ Blank Spike Duplicate
CCB	Continued Calibration Blank
CCV	Continued Calibration Verification
CFR	Code of Federal Regulations
CRM	Certified Reference Material
DEP	Department of Environmental Protection
DEQ	Department of Environmental Quality
DHHS	Department of Health and Human Services
DMR-QA	Discharge Monitoring Report-Quality Assurance
DOE	Department of Ecology (Washington) Department of Energy
DOH	Department of Health
DNR	Department of Natural Resources
DQO	Data Quality Objectives
ECCC	Environment and Climate Change Canada
EPA	Environmental Protection Agency
EFGS	Eurofins Frontier Global Sciences
ELAP	Environmental Laboratory Accreditation Program
HAL	Mercury (Hg) Analytical Laboratory
HCl	Hydrochloric acid
HW	Hazardous Waste
IAEA	International Atomic Energy Agency
ICB	Initial Calibration Blank
ICV	Initial Calibration Verification
ISO/IEC	International Organization for Standardization (ISO) / International Electrotechnical Commission (IEC)
MAPEP	Mixed Analyte Performance Evaluation Program
MD	Matrix Duplicate
MDL	Method Detection Limit

MDN	Mercury Deposition Network
mL	milliliters
mm	millimeters
MMHg	Methyl Mercury
MRL	Method Reporting Limit
MS/MSD	Matrix Spike/ Matrix Spike Duplicate
n	Number of samples
NADP	National Atmospheric Deposition Program
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
ng	Nanograms
ng/bot	Nanograms per bottle
ng/L	Nanograms per liter
ng/mL	Nanograms per milliliter
ng/m^2	Nanograms per square meter
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
NRCC	National Research Council Canada
PA	Peak area
PB	Preparation Blank
PO	Program Office
PQL	Practical Quantitation Limit
QA	Quality Assurance
QC	Quality Control
QR	Quality Rating
QCS	Quality Control Sample
RB	Rinse Blank
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
stdev	Standard deviation
subppt	Substituted precipitation
tmpVol	Total Minus Preservative Volume
TNI	The NELAC Institute
THg	Total Mercury (Hg)
TV	True Value
USGS	United States Geological Survey

WP	Water Pollution
WS	Water Supply
<	Less than
%	percent

10. Appendix A:

10.1 QC Criteria

Table 11 - QC Criteria for EPA 1631E and EPA 1630

QC Item	EPA Method 1631E Criteria THg	EPA Method 1630 Criteria MMHg
Calibration Factor RSD	≤15%	≤15%
Low Standard Recovery	75-125% recovery	65-135% recovery
QCS (Quality Control Sample)	The laboratory must obtain a Quality Control Sample (QCS) from a source different than used to produce the standards. The QCS should be analyzed as an independent check of instrument calibration in the middle of the analytical batch. The recovery criterion is the same as the Ongoing Precision and Recovery (OPR) (77-123%).	The laboratory must obtain a Quality Control Sample (QCS) from a source different than used to produce the standards. The QCS should be analyzed as an independent check of instrument calibration in the middle of the analytical batch. The recovery criterion is the same as the Ongoing Precision and Recovery (OPR) (77-123%).
ICV	OPR Standard at 5.0ng/L required at the beginning and end of each run, 77-123% recovery.	OPR Standard at 0.5ng/L required at the beginning and end of each run, 67-133% recovery.
CCV	No CCV required, see QCS.	No CCV required, see QCS.
MD	No MD required.	No MD required.
MS/MSD	Water: 71-125% Rec. RPD ≤ 24% Frequency of 1 MS/MSD per 10 samples. MS/MSD spiking level shall be 1-5 times the sample concentration.	65-135% recovery with RPD ≤ 35% Frequency of 1 MS/MSD per 10 samples. MS/MSD spiking level shall be 1-5 times the sample concentration.
Bubbler blanks	Individually <0.5ng/L, mean <0.25ng/L with a standard deviation <0.10ng/L. All bubbler blanks are analyzed before the calibration curve.	A single, or more, Ethylation Blanks are analyzed with each analytical run. The value is used to blank correct the standard curve.
ICB and CCB	No ICB, CCBs required.	No ICB, CCBs required.
Preparation Blanks	Minimum of 3, individually <0.50 ng/L.	Minimum of 3. Mean <0.045 ng/L Variability <0.015 ng/L

10.2 USGS Inter-Laboratory Comparison Results

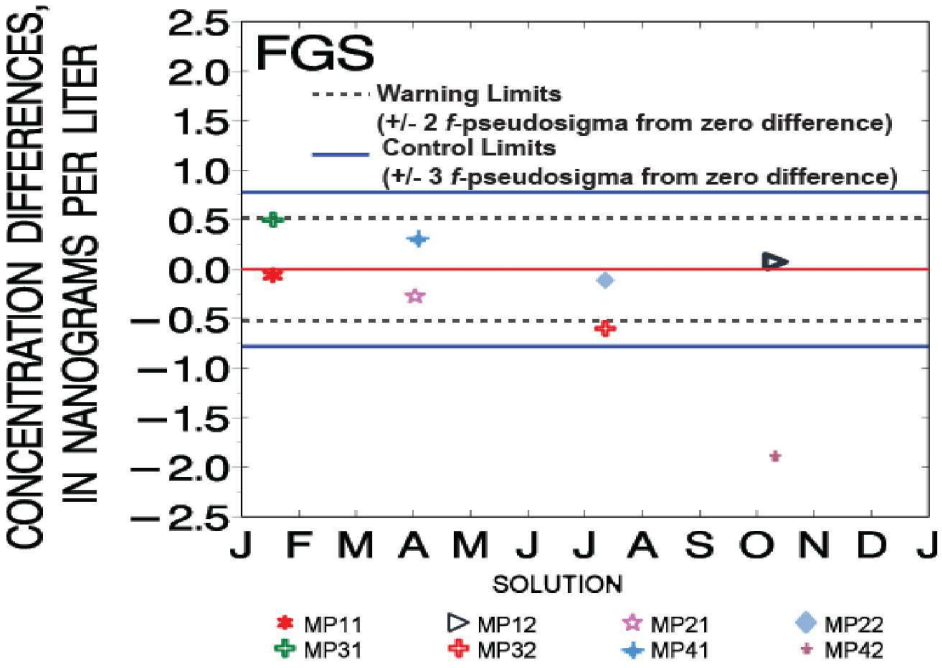


Figure 1. Control chart for 2018 results from Eurofins Frontier Global Sciences, Inc. for the U.S. Geological Survey Interlaboratory-Comparison Program for the National Atmospheric Deposition Program / Mercury Deposition Network.

2018 Blanks: Number of blanks (total N=3) with total Hg concentrations exceeding the reported analytical detection limits.

Lab				
A	**FGS**	C	D	E
1	**0**	2	3	3

10.3 MDL Studies

eurofins | Frontier Global Sciences	**MDL Study: Total Mercury in Water (EPA 1631E, EFAFS-T-AFS-SOP2992)**

Analyzed by: Blake Cassidy 3/22/19
Reviewed by: Don Moran, Phayvanh Lameny 3/22/19 3/22/19
Report Prepared by: Dave Wunderlich 3/22/19
Report Reviewed by: Matthew Prolo 3/25/2019

MDL Study Data for Total Mercury in Precipitation Samples
Data Sets: THg26002-180725-1, THg26002-180726-1, THg26002-180730-1
Sequences: 8G25014, 8G26006, 8G31006
Batches: F807565, F807577, F807609
Dates: 07/25/18, 7/26/18, 7/31/18

Objective

This study serves as the annual MDN MDL for total mercury (2018). The MDL study was performed using the preservation method EFSR-P-SP-SOP2796 and analysis method EPA 1631 E (EFAFS-T-AFS-SOP2992), and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for Total Mercury in water was determined to be **0.0954 ng/L**.

Analytical Method

A calibration was performed according to EPA 1631 E (EFAFS-T-AFS-SOP2992). Briefly, this method incorporates oxidation with the addition of BrCl, reduction of Mercury in the sample aliquot with $SnCl_2$ and analysis by purge and trap and dual amalgamation CV-AFS.

A solution of reagent water was spiked with a 0.09 mL aliquot of a 1 ng/mL Hg standard (LIMS #1803728) and preserved with BrCl. The MDL study consisted of ten replicates of this solution, divide into three groups, that were prepared and analyzed on three different days, with each replicate having a final spike level of 0.3012 ng/L of THg oxidized to 1% with BrCl. This solution was also used for the PQL study.

The results of these measurements are found in the table on pages 2, as well as the raw data sheets. All results are reported **corrected** for both instrument blanks and preparation blanks.

MDL Calculation

Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked samples, with n = 10 replicates (9 degrees of freedom). In this case, the t value of 2.821 was used at a 99% Confidence Level. In the following equation, σ is the standard deviation of the results obtained on replicates.

$$MDL = t*\sigma$$

The MDL calculated for the 0.3012 ng/L spike was (2.821)*(0.033826), or **0.0954 ng/L**.

MDL Validation

The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, R-value, etc.) passed. An existing MDL is verified, if a newly calculated MDL is less than 2X the existing value and the ratio of the spike level (true value or TV) to the calculated MDL does not exceed 10. Since the newly-calculated MDL is less than 0.16 ng/L and the TV/MDL ratio for this study was 3.16, the existing MDL of 0.08 ng/L was verified.

The current PQL is 0.50 ng/L. In order to verify a PQL, the percent recoveries for all MDL replicates must fall within the acceptance range for the low calibration point. All ten replicates spiked at 0.3012 ng/L recovered with these limits (75-125%). The current PQL is verified.

Overall, the studies demonstrate that the existing MDL and PQL for the analysis of THg in water can be applied to data generated by CV AFS 2600-2.

MDL/PQL Study

Dates: 7/25/18, 7/26/18, 7/31/2018
THg26002-180725-1, -180726-1, -180730-1
Sequences: 8G25014, 8G26006, 8G31006
Batches: F807565, F807577, F807609

Eurofins Frontier Global Sciences
11720 North Creek Pkwy North, Suite 400
Bothell, WA 98011

Sample	[THg], ng/L
F807565-BLK1	ND (<0.08)
F807565-BLK2	ND (<0.08)
F807565-BLK3	ND (<0.08)
F807577-BLK1	0.09J
F807577-BLK2	ND (<0.08)
F807577-BLK3	ND (<0.08)
F807609-BLK1	ND (<0.08)
F807609-BLK2	ND (<0.08)
F807609-BLK3	ND (<0.08)
Mean	NA
SD	NA

Limits:
75-125%

	[THg], ng/L	[TV], ng/L	[%Rec]
F807565-BS1	0.312	0.3012	104%
F807565-BS2	0.328	0.3012	109%
F807565-BS3	0.318	0.3012	106%
F807577-BS1	0.301	0.3012	100%
F807577-BS2	0.261	0.3012	87%
F807577-BS3	0.267	0.3012	89%
F807609-BS1	0.277	0.3012	92%
F807609-BS2	0.254	0.3012	84%
F807609-BS3	0.238	0.3012	79%
F807609-BS4	0.234	0.3012	78%
Mean	0.279	0.3012	93%
SD	0.033826	0.000	12.2%

MDL	0.0954
TV/MDL	3.156
FMDL in LIMS	0.08
2x LIMS FMDL	0.16
FPQL in LIMS	0.50

eurofins | Frontier Global Sciences	**MDL Study: Total Mercury in Water (EPA 1631E, EFAFS-T-AFS-SOP2992)**

Analyzed by: Blake Cassidy 3/22/19
Reviewed by: Don Moran, Phayvanh Lameny 3/22/19 3/22/19
Report Prepared by: Dave Wunderlich 3/22/19
Report Reviewed by: Matthew Prolo 3/25/2019

MDL Study Data for Total Mercury in Precipitation Samples
Data Sets: THg26003-180725-1, THg26003-180726-1, THg26003-180730-1
Sequences: 8G25016, 8G27006, 8G31011
Batches: F807566, F807578, F807610
Dates: 07/25/18, 7/26/18, 7/31/18

Objective

This study serves as the annual MDN MDL for total mercury (2018). The MDL study was performed using the preservation method EFSR-P-SP-SOP2796 and analysis method EPA 1631 E (EFAFS-T-AFS-SOP2992), and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for Total Mercury in water was determined to be **0.0726 ng/L**.

Analytical Method

A calibration was performed according to EPA 1631 E (EFAFS-T-AFS-SOP2992). Briefly, this method incorporates oxidation with the addition of BrCl, reduction of Mercury in the sample aliquot with $SnCl_2$ and analysis by purge and trap and dual amalgamation CV-AFS.

A solution of reagent water was spiked with a 0.09 mL aliquot of a 1 ng/mL Hg standard (LIMS #1803728) and preserved with BrCl. The MDL study consisted of ten replicates of this solution, divide into three groups, that were prepared and analyzed on three different days, with each replicate having a final spike level of 0.3012 ng/L of THg oxidized to 1% with BrCl. This solution was also used for the PQL study.

The results of these measurements are found in the table on pages 2, as well as the raw data sheets. All results are reported **corrected** for both instrument blanks and preparation blanks.

MDL Calculation

Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked samples, with n = 10 replicates (9 degrees of freedom). In this case, the t value of 2.821 was used at a 99% Confidence Level. In the following equation, σ is the standard deviation of the results obtained on replicates.

$$\mathbf{MDL = t^{*}\sigma}$$

The MDL calculated for the 0.3012 ng/L spike was (2.821)*(0.025744), or **0.0726 ng/L**.

MDL Validation

The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, R-value, etc.) passed. An existing MDL is verified, if a newly calculated MDL is less than 2X the existing value and the ratio of the spike level (true value or TV) to the calculated MDL does not exceed 10. Since the newly-calculated MDL is less than 0.16 ng/L and the TV/MDL ratio for this study was 4.15, the existing MDL of 0.08 ng/L was verified.

The current PQL is 0.50 ng/L. In order to verify a PQL, the percent recoveries for all MDL replicates must fall within the acceptance range for the low calibration point. All ten replicates spiked at 0.3012 ng/L recovered with these limits (75-125%). The current PQL is verified.

Overall, the studies demonstrate that the existing MDL and PQL for the analysis of THg in water can be applied to data generated by CV AFS 2600-3.

MDL/PQL Study

Dates: 7/25/18, 7/26/18, 7/31/2018
THg26003-180725-1, -180726-1, -180730-1
Sequences: 8G25016, 8G27006, 8G31011
Batches: F807566, F807578, F807610

Eurofins Frontier Global Sciences
11720 North Creek Pkwy North, Suite 400
Bothell, WA 98011

Sample	[THg], ng/L
F807566-BLK1	ND (<0.08)
F807566-BLK2	ND (<0.08)
F807566-BLK3	ND (<0.08)
F807578-BLK1	ND (<0.08)
F807578-BLK2	ND (<0.08)
F807578-BLK3	ND (<0.08)
F807610-BLK1	ND (<0.08)
F807610-BLK2	ND (<0.08)
F807610-BLK3	ND (<0.08)
Mean	NA
SD	NA

Limits: 75-125%

	[THg], ng/L	[TV], ng/L	[%Rec]
F807566-BS1	0.310	0.3012	103%
F807566-BS2	0.321	0.3012	107%
F807566-BS3	0.287	0.3012	95%
F807578-BS1	0.291	0.3012	97%
F807578-BS2	0.287	0.3012	95%
F807578-BS3	0.276	0.3012	92%
F807610-BS1	0.244	0.3012	81%
F807610-BS2	0.265	0.3012	88%
F807610-BS3	0.242	0.3012	80%
F807610-BS4	0.266	0.3012	88%
Mean	0.279	0.3012	93%
SD	0.025744	0.000	9.23%

MDL	0.0726
TV/MDL	4.149
FMDL in LIMS	0.08
2x LIMS FMDL	0.16
FPQL in LIMS	0.50

eurofins | Frontier Global Sciences	**MDL Study:** **Methyl Mercury in Water** **(EPA 1630, EFAFS-T-AFS-SOP2808)**

Analyzed by: Blake Cassidy, Don Moran 3/22/19
Reviewed by: Don Moran, Phayvanh Lameny 3/22/19 3/22/19
Report Prepared by: Dave Wunderlich 3/22/19
Report Reviewed by: Matthew Prolo 3/21/2019

MDL Study Data for Methyl Mercury in Precipitation Samples
Data Sets: MHg27001-180223-1, MHg27001-180309-1,MHg27001-180320-1,
Sequences: 8B26008, 8C12013, 8C21010
Batches: F802347, F803241, F803375
Dates: 2/23/18, 3/9/18, 3/20/18

Objective

This study serves as the annual MDN MDL for methyl mercury (2018). This MDL study applies to Methyl Mercury in precipitation samples as prepared by EFAFS-T-AFS-SOP2797 and analyzed by EFAFS-T-AFS-SOP2808 (EPA 1630) and follows the protocols outlined in 40 CFR 136. As detailed below, the MDL for Methyl Mercury in water was determined to be **0.040 ng/L**.

Analytical Method

Before analysis, the MHg in an aliquot of sample is co-distilled into pure water. The distillates are then analyzed for MHg by aqueous phase ethylation and Cold Vapor – Gas Chromatography – Atomic Fluorescence Spectroscopy (CV-GC-AFS).

For this dataset, an efficiency factor of 0.869 was used and the calibration was performed according to EFAFS-T-AFS-SOP2808.

The MDL study consisted of a 0.077856 ng/L solution of MHg divided into nine replicates. The nine replicates were divided three groups of three replicates. The groups were distilled on three different days and then analyzed on three different days. This solution was also used for the PQL study.

The results of these measurements are found in the table on pages 2, as well as the raw data sheets. All peak heights were **corrected** for the instrument blanks and all final concetrations were **corrected** for the preparation blanks.

MDL Calculation

Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked samples, with n = 9 replicates (8 degrees of freedom). In this case, the t value of 2.896 was used at a 99% Confidence Level. In the following equation, σ is the standard deviation of the results obtained on replicates.

$$MDL = t*\sigma$$

The MDL calculated for the 0.077856 ng/L spike was (2.896)*(0.0138), or **0.040 ng/L**.

MDL Validation

The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, R-value, etc.) passed. An existing MDL is verified if a newly-calculated MDL is less than 2X the exisiting value and the ratio of spike level (true value or TV) to the calculated MDL does not exceed 10. Since the newly-calculated MDL is less than 0.052 ng/L and the TV/MDL ratio for this study was 1.946, the existing MDL of 0.026 ng/L was verified.

The current PQL is 0.050 ng/L. In order to verify a PQL, the percent recoveries for all MDL replicates must fall within the acceptance range for the low calibration point. Only eight of nine replicates recovered with these limits (65-135%). The current PQL is not verified.

Overall, the studies demonstrate that the existing MDL for the analysis of MHg in water can be applied to data generated by Tekran 2700-1, but the existing PQL is suspect. The PQL will be evaluated in subsequent studies.

MDL/PQL Study

Dates: 2/23/18, 3/9/18, 3/20/18
MHg27001-180223-1, -180309-1, -180320-1
Sequences: 8B26008, 8C12013, 8C21010
Batches: F802347, F803241, F803375

Eurofins Frontier Global Sciences
11720 North Creek Pkwy North, Suite 400
Bothell, WA 98011

Sample	[MHg], ng/L
F802347-BLK1	ND (<0.026)
F802347-BLK2	ND (<0.026)
F802347-BLK3	ND (<0.026)
F803241-BLK1	ND (<0.026)
F803241-BLK2	ND (<0.026)
F803241-BLK3	ND (<0.026)
F803375-BLK1	ND (<0.026)
F803375-BLK2	ND (<0.026)
F803375-BLK3	ND (<0.026)
Mean	NA
SD	NA

Limits:
65-135%

	[MHg], ng/L	[TV], ng/L	[%Rec]
F802347-BS1	0.0582	0.077856	75%
F802347-BS2	0.0783	0.077856	101%
F802347-BS3	0.0376	0.077856	48%
F803241-BS1	0.0777	0.077856	100%
F803241-BS2	0.0794	0.077856	102%
F803241-BS3	0.0705	0.077856	91%
F803375-BS1	0.0658	0.077856	85%
F803375-BS2	0.0807	0.077856	104%
F803375-BS3	0.0667	0.077856	86%
Mean	0.0683	0.077856	88%
SD	0.0138	0.000	20.2%

MDL	0.040
TV/MDL	1.946
FMDL in LIMS	0.026
2x LIMS FMDL	0.052
FPQL in LIMS	0.050