National Atmospheric Deposition Program

Mercury Analytical Laboratory

2016 Annual Quality Assurance Report

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Table of Contents

List of Figures

List of Tables

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 103 active sites in the United States and Canada at the end of 2016. In 2016, 9 sites were closed, 1 new site was 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 12 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 2016. 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 2016:

- The laboratory reorganized. MDN Receiving (Connor Foote and Mark Delgado) was melded into EFGS S&R; EFGS S&R staff now report to the EFGS Client Services Manager (Amy Goodall).
- Lou Ann McKown (MDN analyst) resigned in February.
- Mark Delgado (MDN equipment cleaning) resigned in April.
- Lars Mittet (EFGS-S&R) was cross trained on MDN receiving procedures.
- Biniam Woldhaimanot and Jason Lindstrom were hired for MDN equipment cleaning in June
- Dani Litwin was hired for MDN equipment cleaning in July
- Anne Willey was hired for MDN equipment cleaning in August
- Dani Litwin's and Chae Park's positions (MDN equipment cleaning) were terminated in August
- Jeanne Harrel (MDN analyst) began transitioning out of MDN and into Project Management in August; transition was completed in mid-September
- Anne Willey (MDN equipment cleaning) resigned 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 ten 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 2016. 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 and 2600-3 (datasets THg26002-160520-2 and THg26003-160518-1), were performed at 0.50 and 0.40 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, 0.079 ng/L, will be used to evaluate data.

A MDL study was performed for MMHg on instrument #15 in datasets MMHg15-170105-1 and MMHg15170106-1 at a PQL of 0.05 ng/L. The TV/MDL ratio was less than 10. Since the TV/MDL ratio was in control, the study is valid and 0.019 ng/L will be used to evaluate data.

Table 1 - MDL Studies for 2016 Summary

Instrument	Dataset	MDL (ng/L)	PQL (ng/L)	True Value TV (ng/L)	TV/MDL
FI-AFS 2600-2	THg26002-160520-2	0.062	0.50	0.40	6.46
FI-AFS 2600-3	THg26003-160518-1	0.079	0.50	0.50	6.36
CV-GC-AFS #15	MMHg15-170105-1 MMHg15-170106-1	0.019	0.050	0.050	2.58

1.3 Accreditations

In 2016 Eurofins Frontier Global Sciences was accredited in ten states and maintained ISO/IEC 17025:2005 and DOD ELAP accreditations:

Table 2 – Accreditation Summary for 2016

Accrediting Agency	Accreditation Type	Accreditation or Certificate Number
Perry Johnson Lab Accreditation	ISO/IEC 17025:2005	L16-341
Perry Johnson Lab Accreditation	DOD ELAP	L16-340
U.S. Department of Energy	DOECAP	audits, but doesn't accredit *
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
Maine DHHS	State	2016021 (105)
Nevada DEP	State	WA012732017-1
Washington DOE	State	C788-17
Wisconsin DNR	State	998348230

* Frontier is subjected to routine Department of Energy Consolidated Audit Program (DOECAP) site assessments for the work it performs to support cleanup and monitoring projects at various DOE facilities.

1.4 Laboratory Bottle Blanks

1.4.1 Description

Following cleaning, HAL bottles are charged with 20 mL of 1% hydrochloric acid. One sample bottle is randomly selected from each cleaning event and is analyzed for THg. On average, 2-3 laboratory bottle blanks are 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 is collected per month and analyzed for MMHg.

1.4.2 Purpose

Even in an ultra-clean laboratory, mercury exposure is inherent to the handling of MDN 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.

1.4.3 Discussion

MDLs and PQLs for THg and MMHg were converted to ng/bottle (using 20mL charge volume/bottle) in Table 3 to accommodate comparisons with the bottle blank data. Laboratory bottle blanks for THg exceeded the PQL about 50% of the time and generally exceeded the MDL all of the time (figure 1).

There were eight laboratory bottle blanks that exceeded the MDL for MMHg and eight of those also exceeded the PQL (figure 2). Laboratory bottle blanks are expected to be at, or near, the MDL (0.00038 ng/bottle, Table 3). High bottle blanks for MMHg are difficult to investigate, since there is only enough volume for one analysis and the bottles associated with that batch have already been sent into the field. Possible contamination sources are researched, but in this case, the sources weren't identified. Methyl mercury results are not bottle blank corrected.

Table 3 - Laboratory Bottle Blank Summary

2016 Laboratory Bottle Blanks	n	Average (ng/bottle)	Standard Deviation	MDL (ng/bottle)	PQL (ng/bottle)
Total Mercury	86	0.013	0.007	0.0016	0.010
Methyl Mercury	11	0.003	0.009	0.00038	0.001

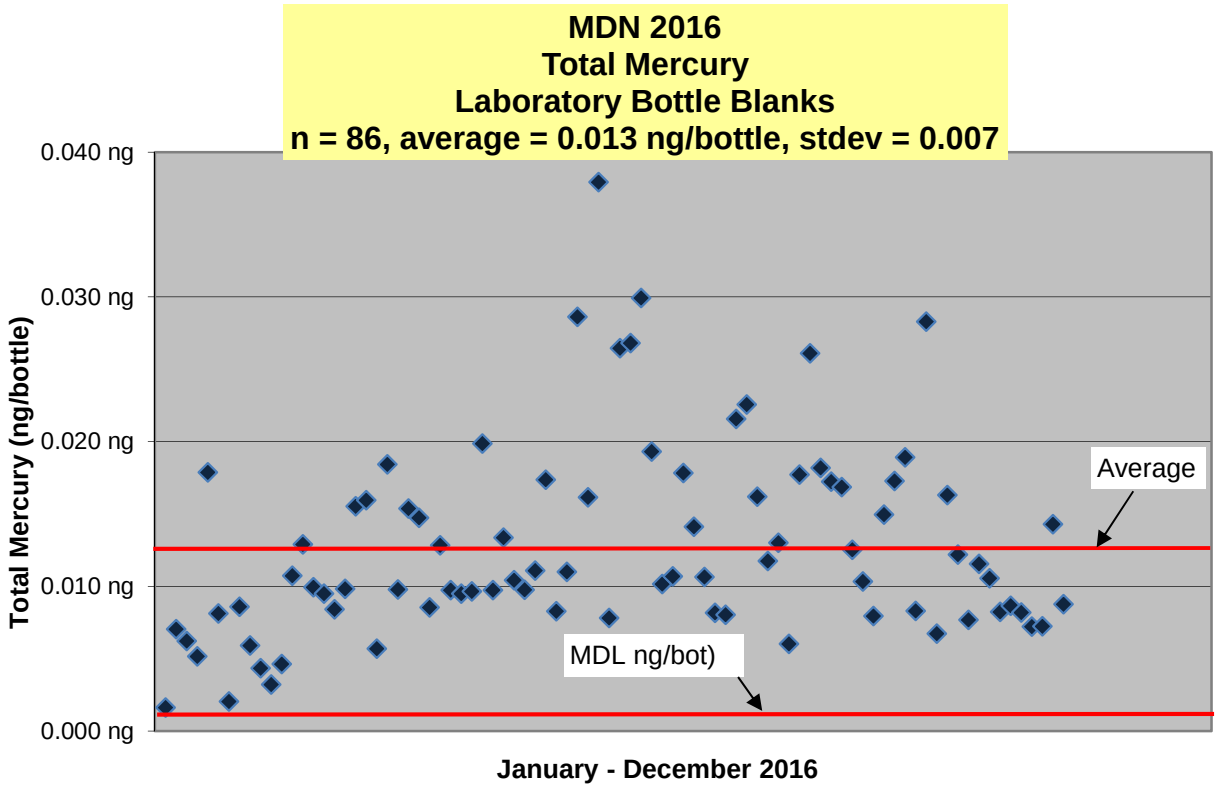

Figure 1 - Total Mercury Mass in Laboratory Bottle Blanks for 86 Samples, 2016

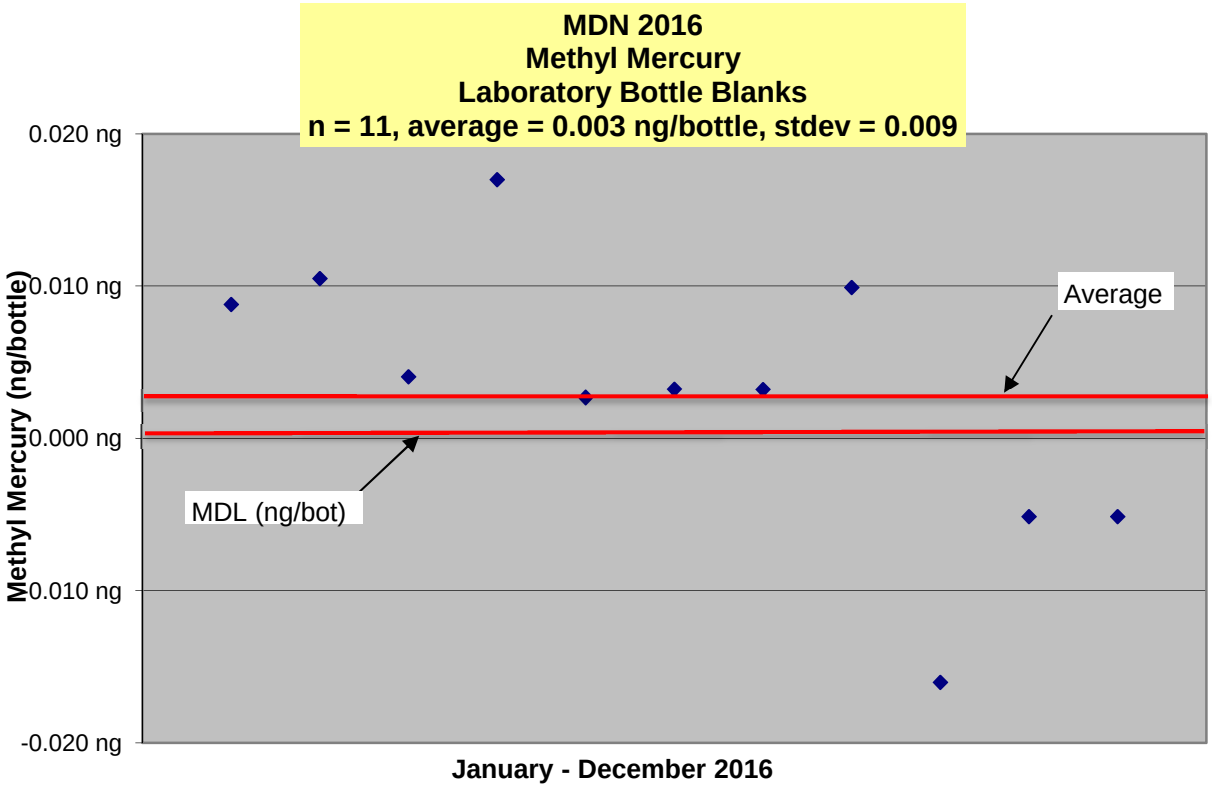

Figure 2 - Methyl Mercury Mass in Laboratory Bottle Blanks for 11 Samples, 2016

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 2016 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 2016 were less than the EFGS control limit of 0.045 ng/L (table 4 and figure 4).

Table 4 - Preparation Blanks Summary

2016 Preparation Blanks	n	Average (ng/L)	Std Dev (ng/L)	MDL (ng/L)	HAL Control Limit (ng/L)	EPA 1631E/1630 Requirements
Total Mercury	583	0.038	0.053	0.079	0.25	< 0.50
Methyl Mercury	65	0.007	0.008	0.019	0.045	Mean <0.045 σ<0.015

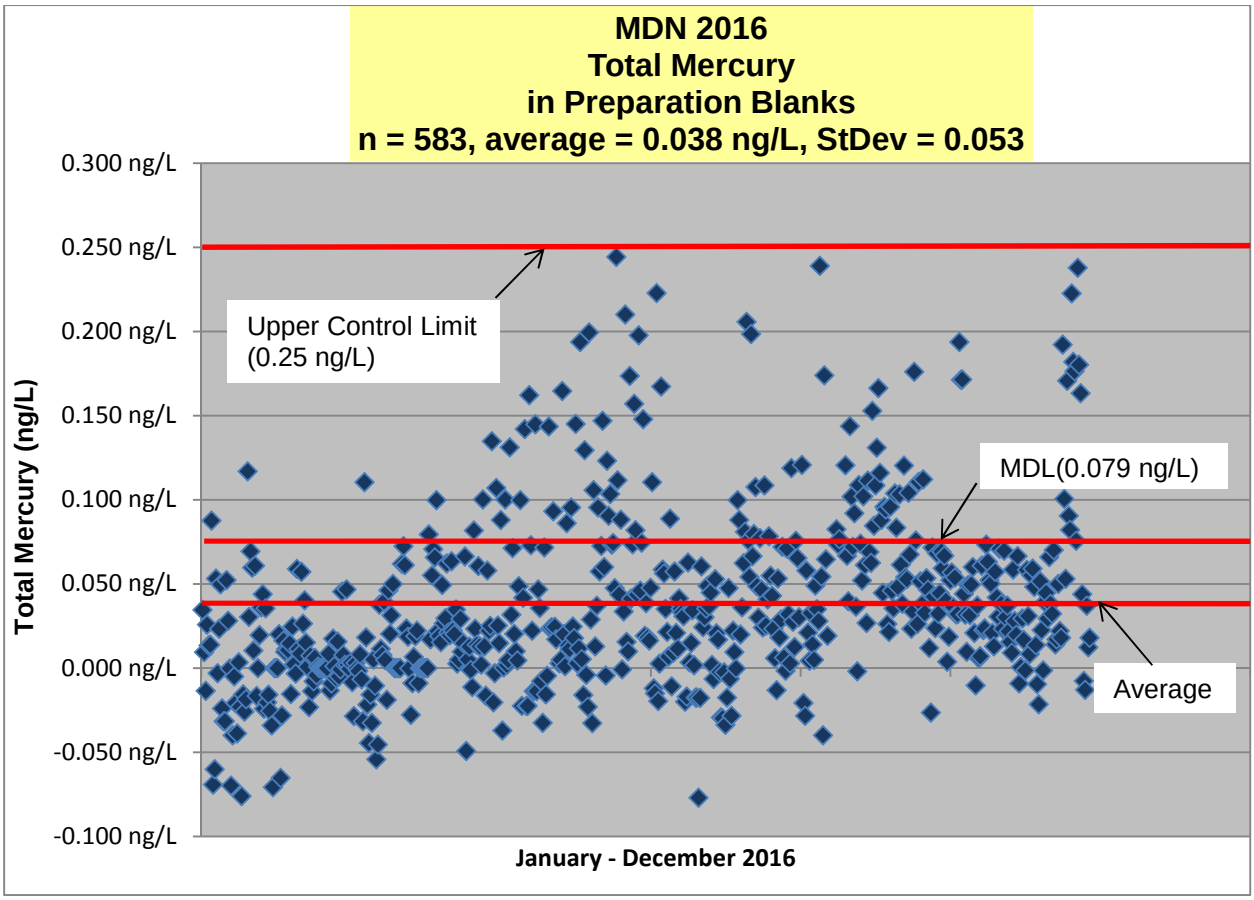

Figure 3 - Total Mercury Concentrations in Reagent Preparation Blanks, 2016

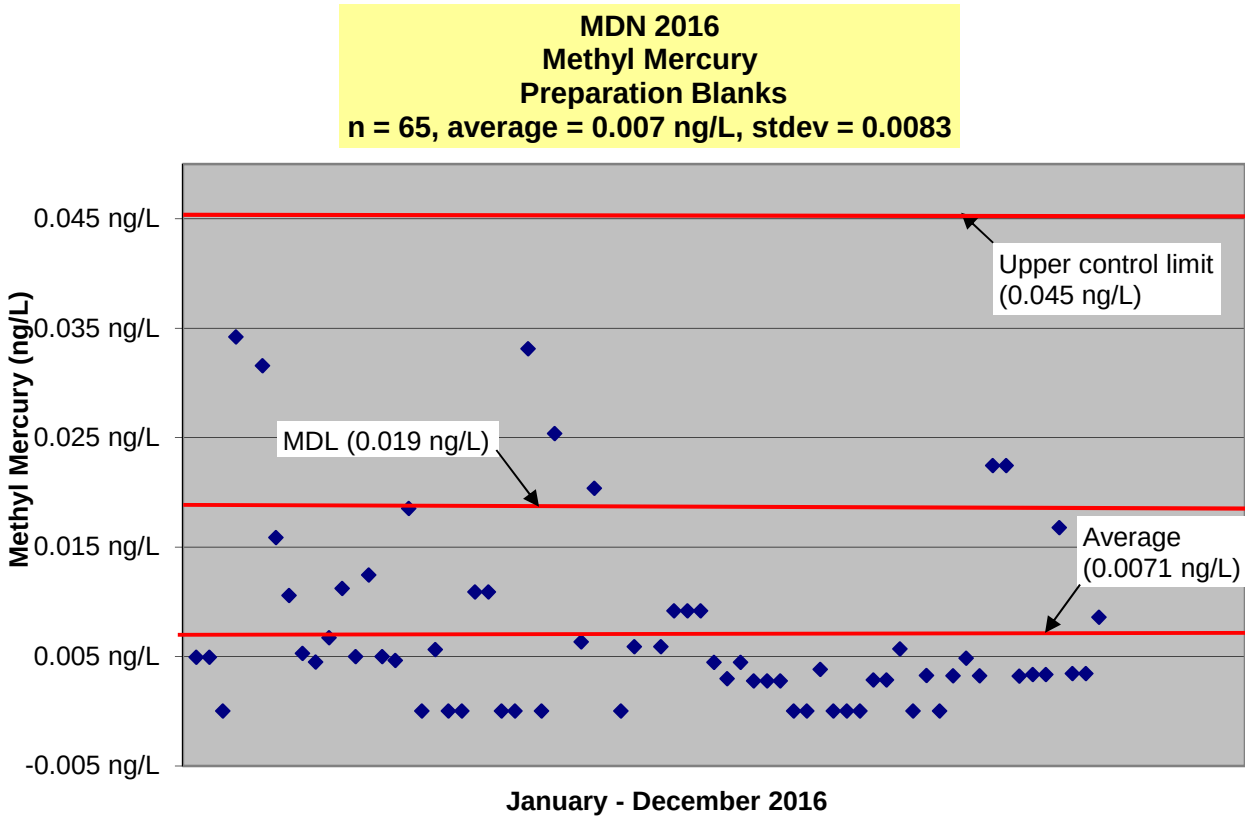

Figure 4 - Methyl Mercury Concentrations in Reagent Preparation Blanks, 2016

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 is the secondary source analyzed after the calibration curve and also after the second set of matrix spikes, and is 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

2016 Continuing Calibration Standard	n	Average recovery (%)	Std dev of recovery (%)	Control Limit (%)	EPA 1631E/1630 Control Limits (%)
Total Mercury	642	100.8	4.1	77-123	77-123
Methyl Mercury	152	97.7	13.4	67-133	67-133

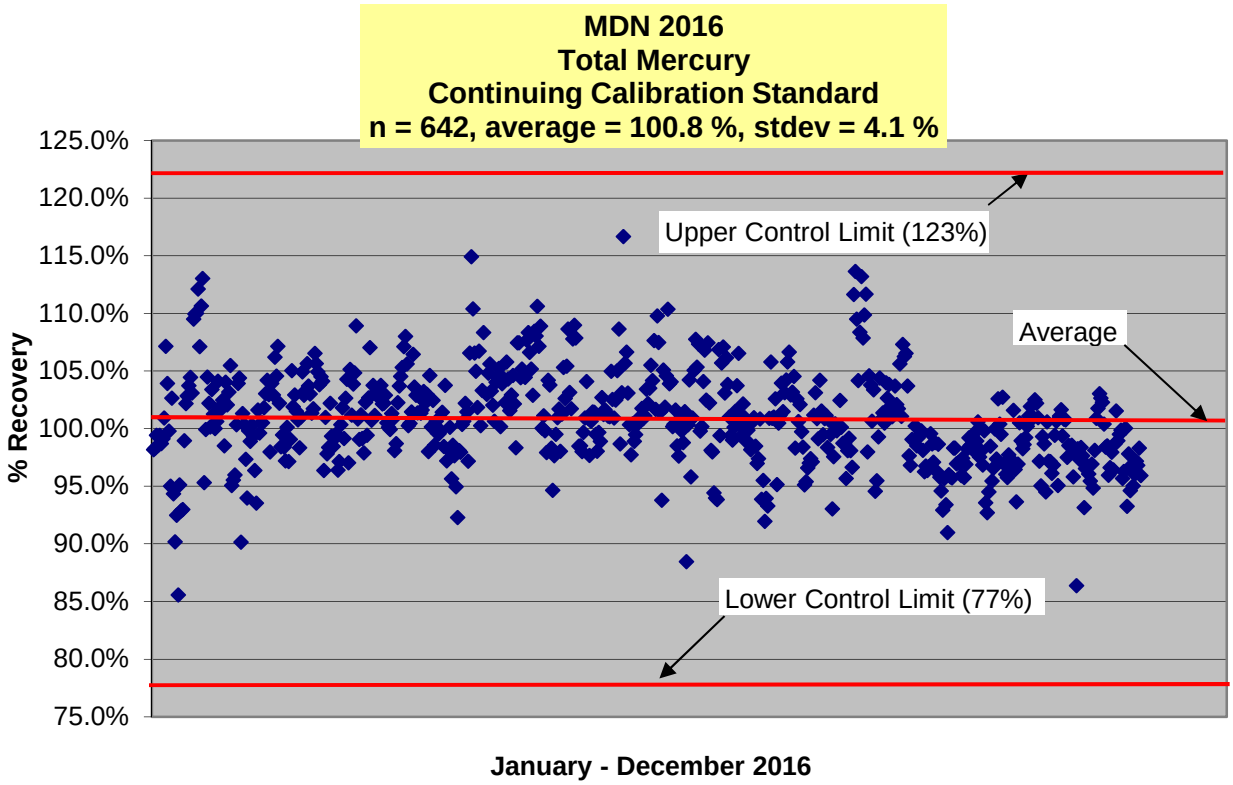

Figure 5 - Total Mercury Continuing Calibration Standard Percent Recovery, 2016

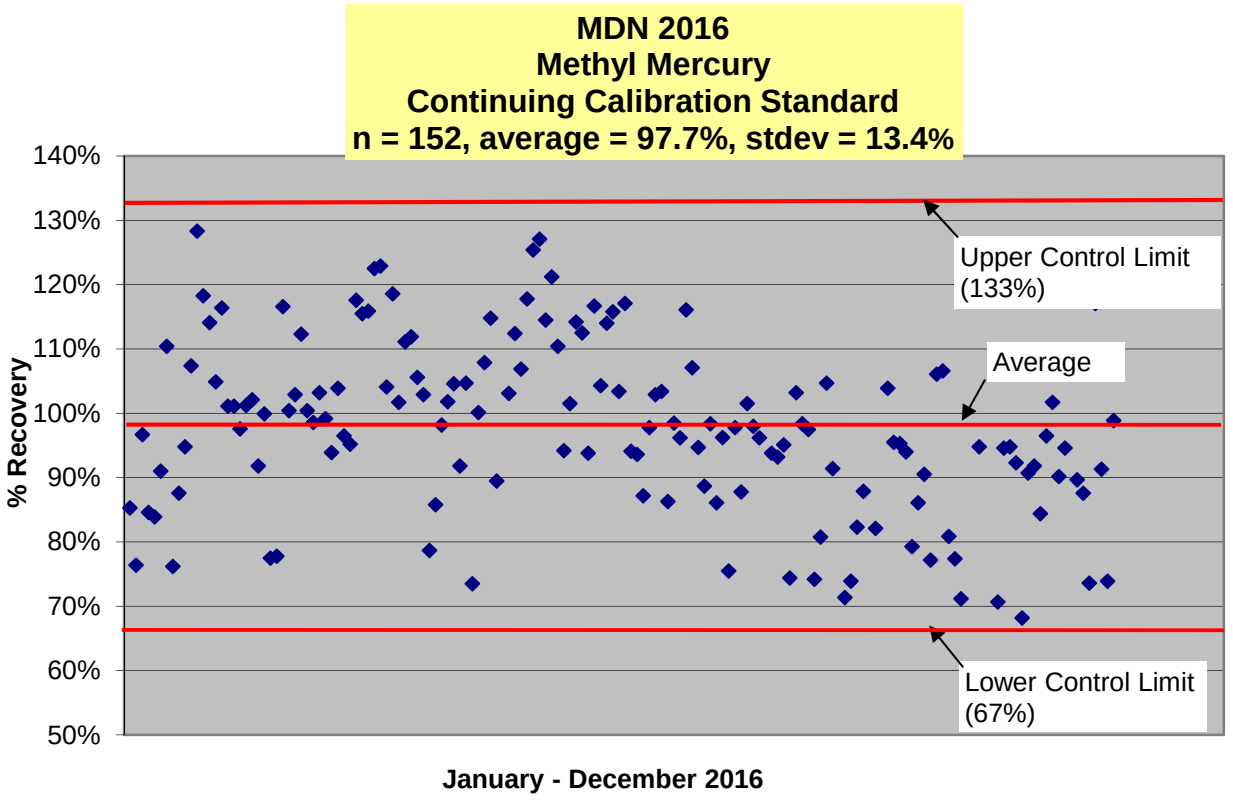

Figure 6 - Methyl Mercury Continuing Calibration Standard Percent Recovery, 2016

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

All of the ongoing CCBs for THg were less than the control limit of 0.25 ng/L used for MDN analysis at HAL (table 6 and figure 7).

One of the 102 ongoing CCBs for MMHg were greater than 0.025 ng/L, which is the control limit used for MDN analysis at HAL (table 6 and figure 8). The CCB was used to evaluate sample data for IL(SB)20160419, WA18COMP0503 and WACOMP0531. The concentration of MMHg in IL(SB)20160419 was less than 0.025 ng/L, thereby indicating this sample was not affected. Sample volume for WA18COMP0503 and WACOMP0531 was exhausted during the original preparation, so re-analyses of these samples was not feasible.

Table 6 - Continuing Calibration Blanks Summary

2016 Continuing Calibration Blanks	n	Average (ng/L)	Std Dev (ng/L)	MDL (ng/L)	HAL Control Limits
Total Mercury	633	0.0761	0.060	0.079	Individually <0.50 ng/L, mean <0.25 ng/L with a standard deviation <0.10 ng/L
Methyl Mercury	102	0.003	0.004	0.019	0.025 ng/L

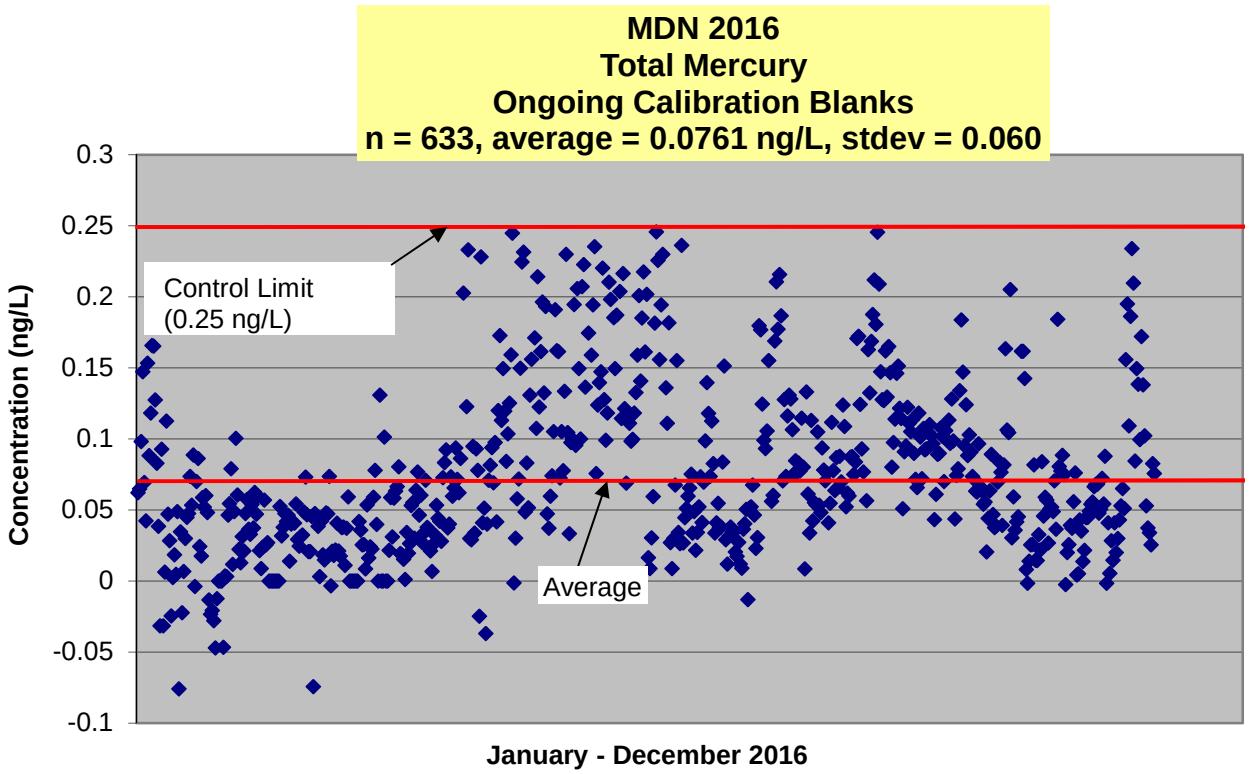

Figure 7 - Total Mercury Continuing Calibration Blanks, 2016

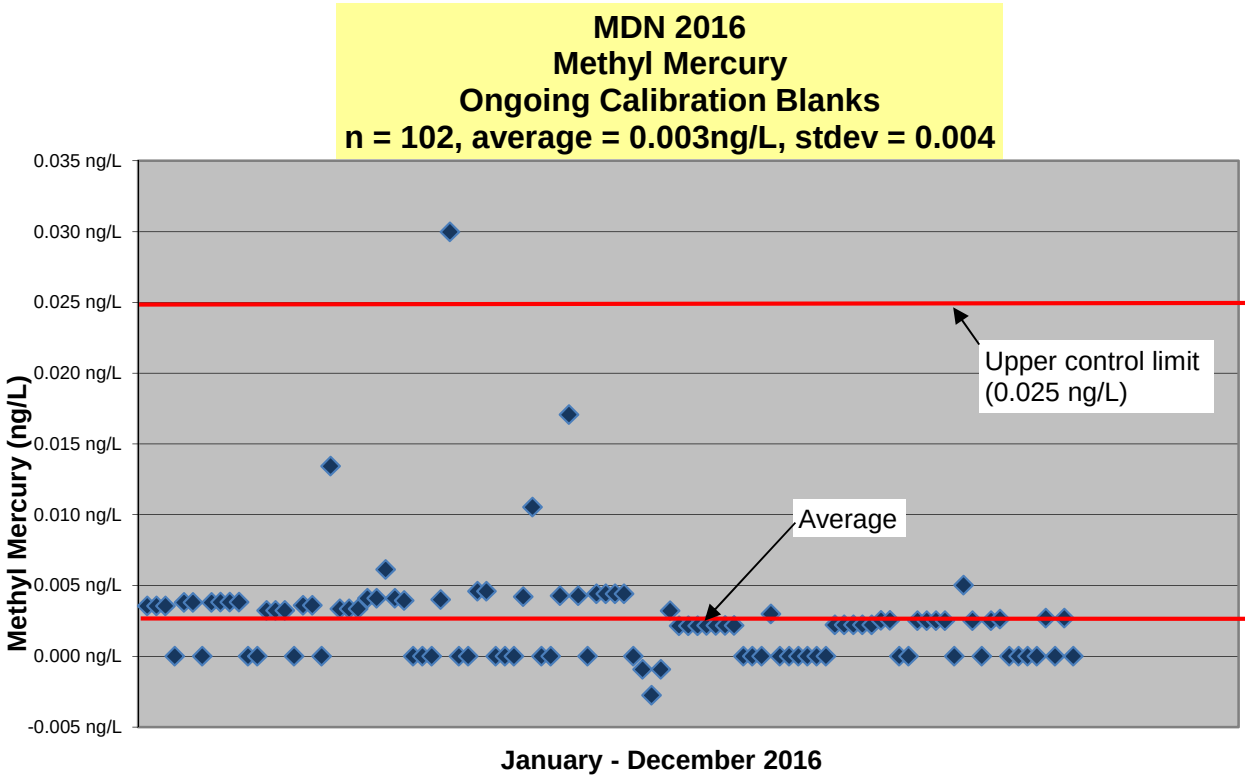

Figure 8 - Methyl Mercury Continuing Calibration Blanks, 2016

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. 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, one of the RPDs calculated for duplicate pairs was not within the control limit of 25% RPD used at HAL (table 7 and figure 9).

For MMHg, one of the RPDs calculated for duplicate pairs was not within the control limit of 25% RPD used at HAL (table 7 and figure 10). For many of the samples, the MMHg concentration is lower than, or equal to, the reporting limit of 0.050 ng/L and can result in high RPD. Also, the recovery criteria for the calibration point at the PQL (0.050 ng/L) level is 70-130%, and analytical values of 0.035 ng/L and 0.065 ng/L, which are within the control criteria for the low calibration point, would be above the acceptance limit of 25% and give a RPD of 60.0%, if these values were produced from duplicate samples. 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

2016 Matrix Duplicates	n	Average RPD (%)	Std Dev (%)	HAL control Limit (%)	EPA 1631E/1630 Control Limits
Total Mercury	565	2.39	2.8	25	NA
Methyl Mercury	13	14.1	7.1	25	NA

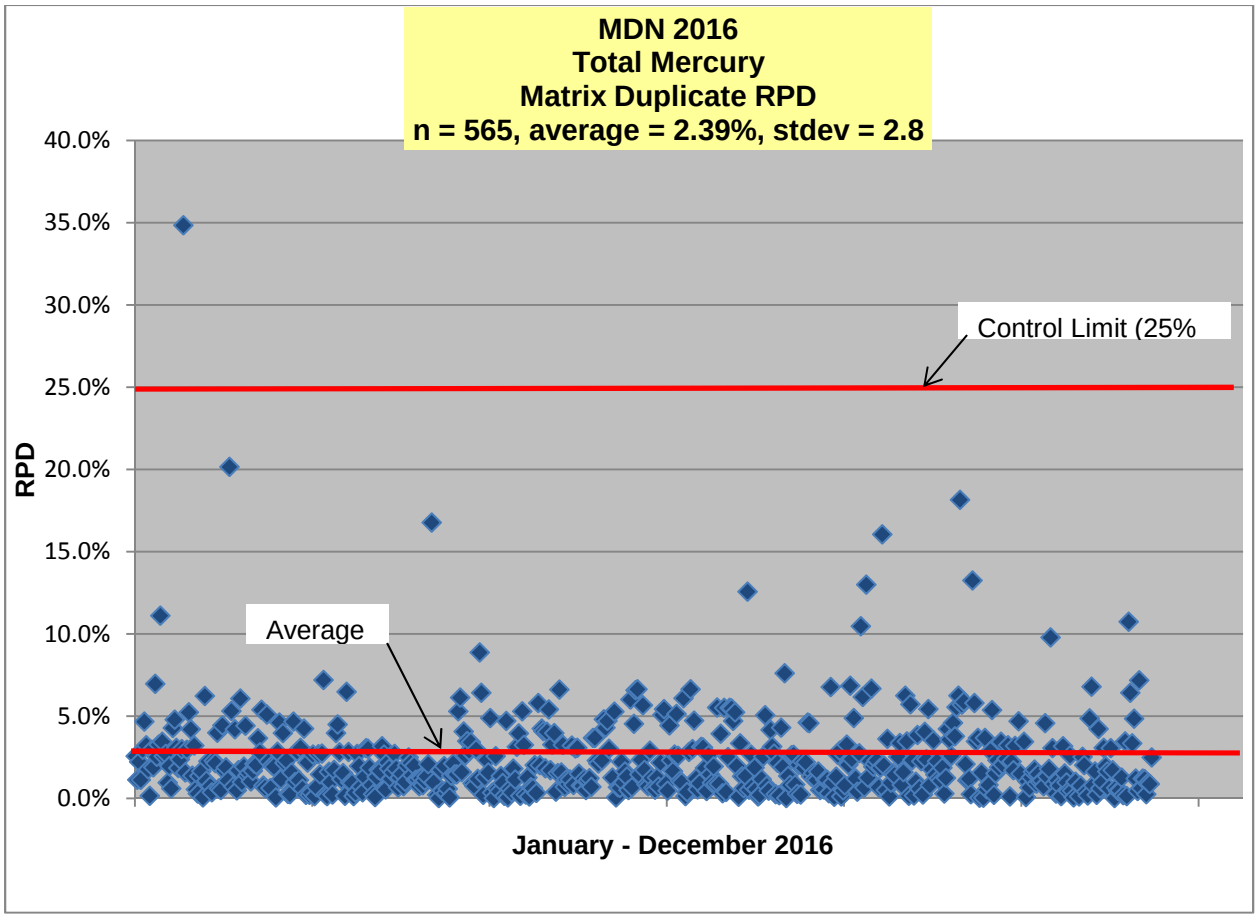

Figure 9 - Relative Percent Differences for Total Mercury Concentrations in Matrix Duplicates, 2016

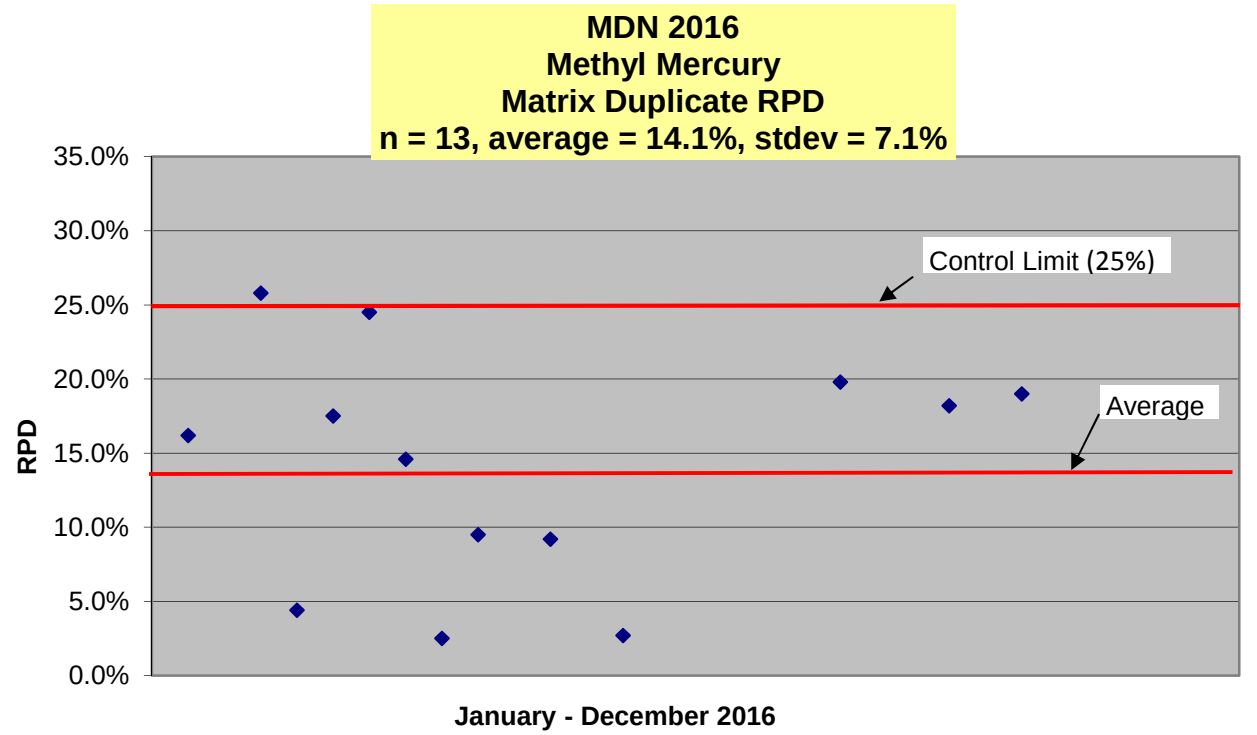

Figure 10 - Relative Percent Differences for Methyl Mercury Concentrations in Matrix Duplicates, 2016

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 0.06 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 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 are 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 2016 Samples

2016 Matrix Spikes	n	Average Recovery (%)	Std Dev of Recovery (%)	HAL Control Limits	EPA 1631E/1630 Control Limits (%)
Total Mercury	567	100.7	6.0	75-125	71-125
Methyl Mercury	84	101.5	12.2	65-135	65-135

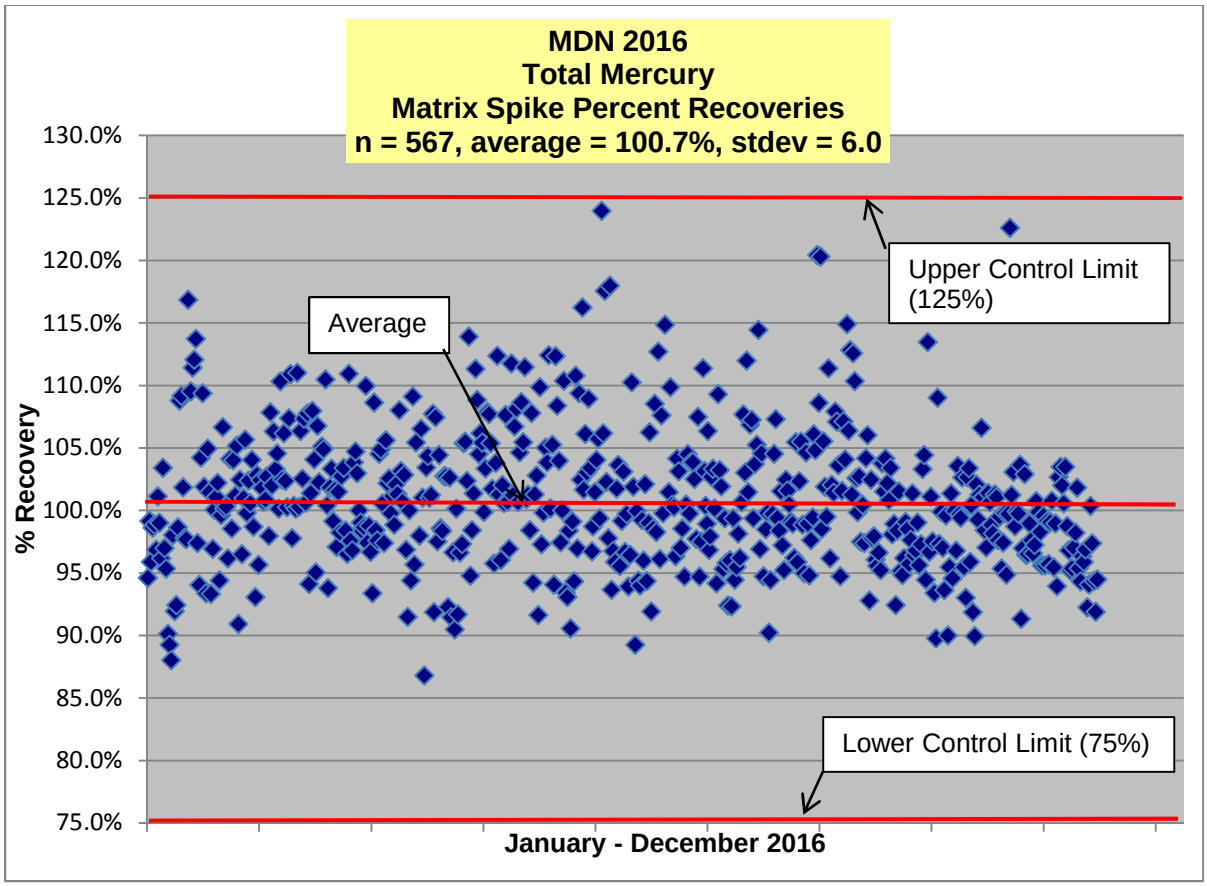

Figure 11 - Total Mercury Percent Recovery in Matrix Spikes, 2016

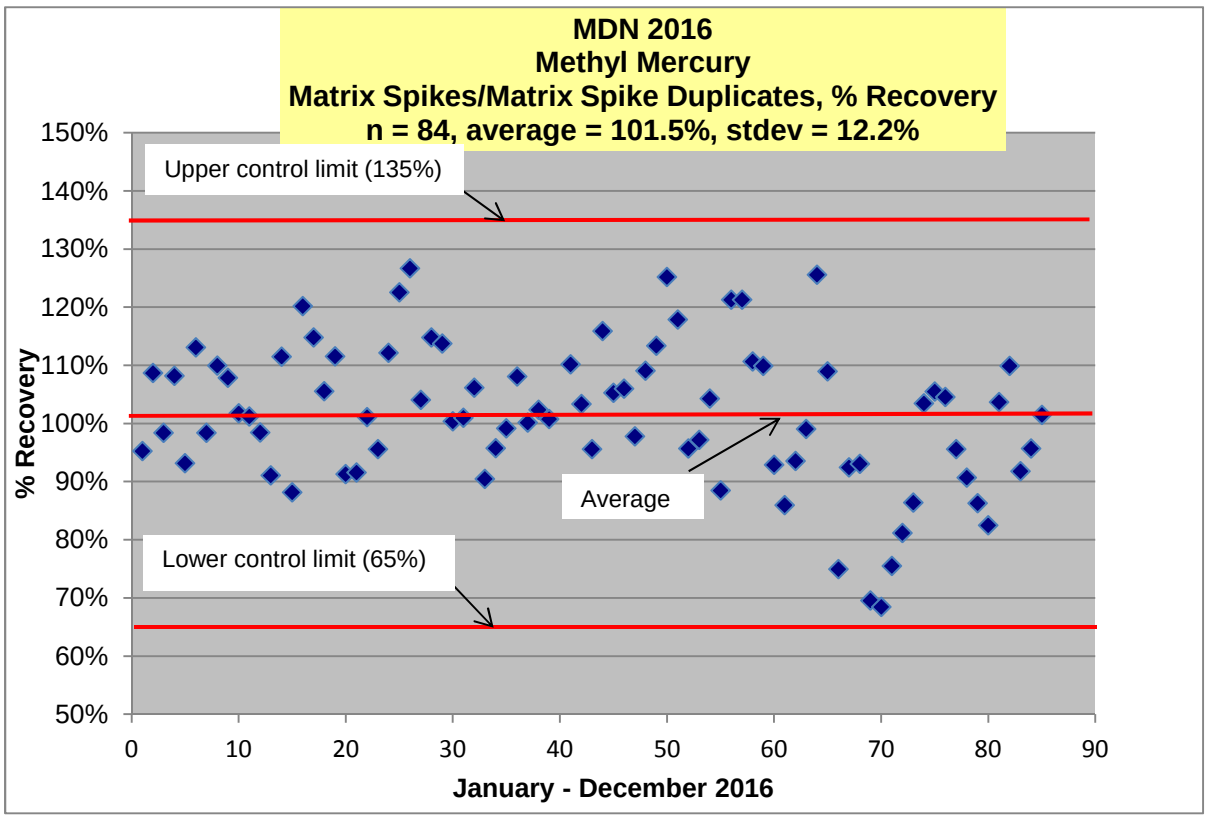

Figure 12 - Methyl Mercury Percent Recovery in Matrix Spikes, 2016

There were no RPD values for MMHg that exceeded the 25% control limit used at HAL (table 9 and figure 13).

Table 9 - Matrix Spike/Matrix Spike Relative Percent Differences (RPD) for 2016 Samples

2016 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	36	7.8	6.6	<25	<35

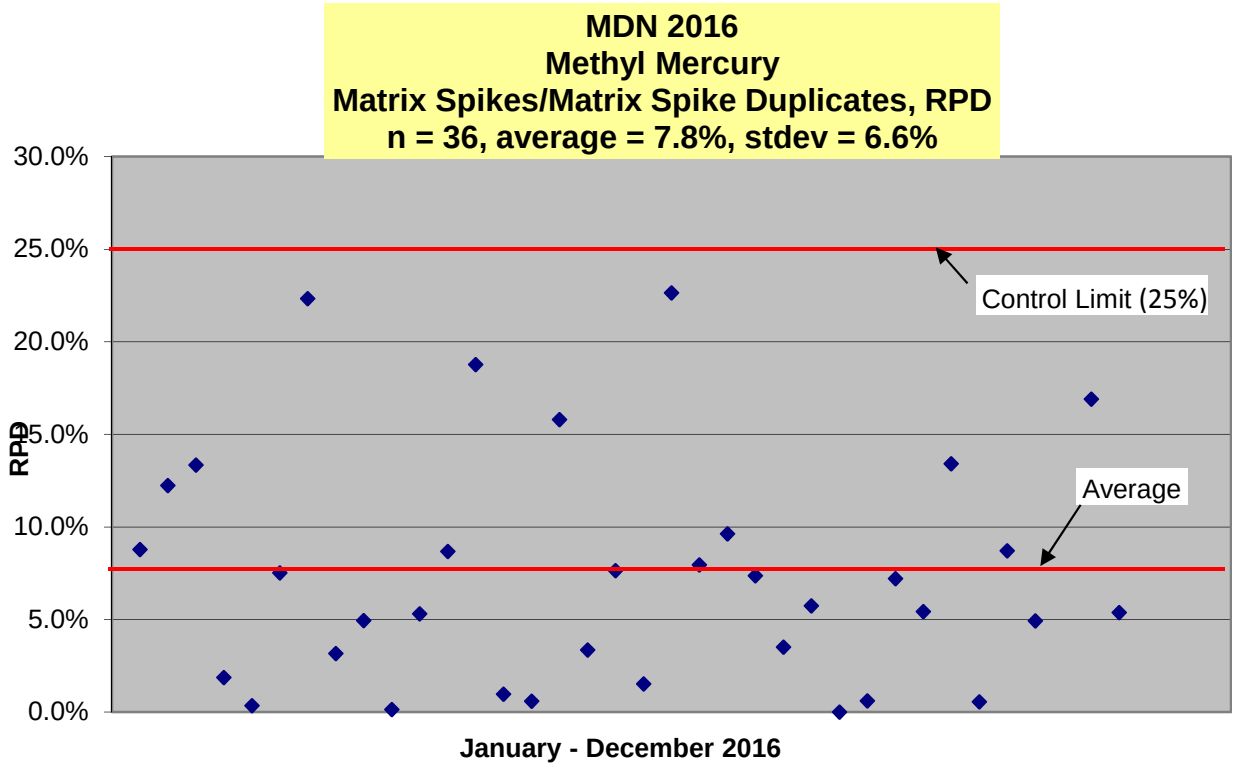

Figure 13 - Relative Percent Differences (RPD) for Methyl Mercury Matrix Spike/Matrix Spike Duplicate Pairs, 2016.

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." The percent recovery control limits for THg 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

The mean of 387 certified reference material recoveries for THg was 98.3% with a standard deviation of 3.7% (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 2.7% (n=190), with a standard deviation of 2.0%. 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 46 blank spikes and blank spike duplicates (BS/BSD) for MMHg was 97.1% with a standard deviation of 10.8% (figure 16). All recovery values were within the 70-130% control limit used at HAL. The average RPD value for the BS/BSD was 7.0% (n=23) with a standard deviation of 7.0%. The method doesn't specify limits for BS/BSD RPD. All RPD values were within the 25% limit used in the laboratory (figure 17).

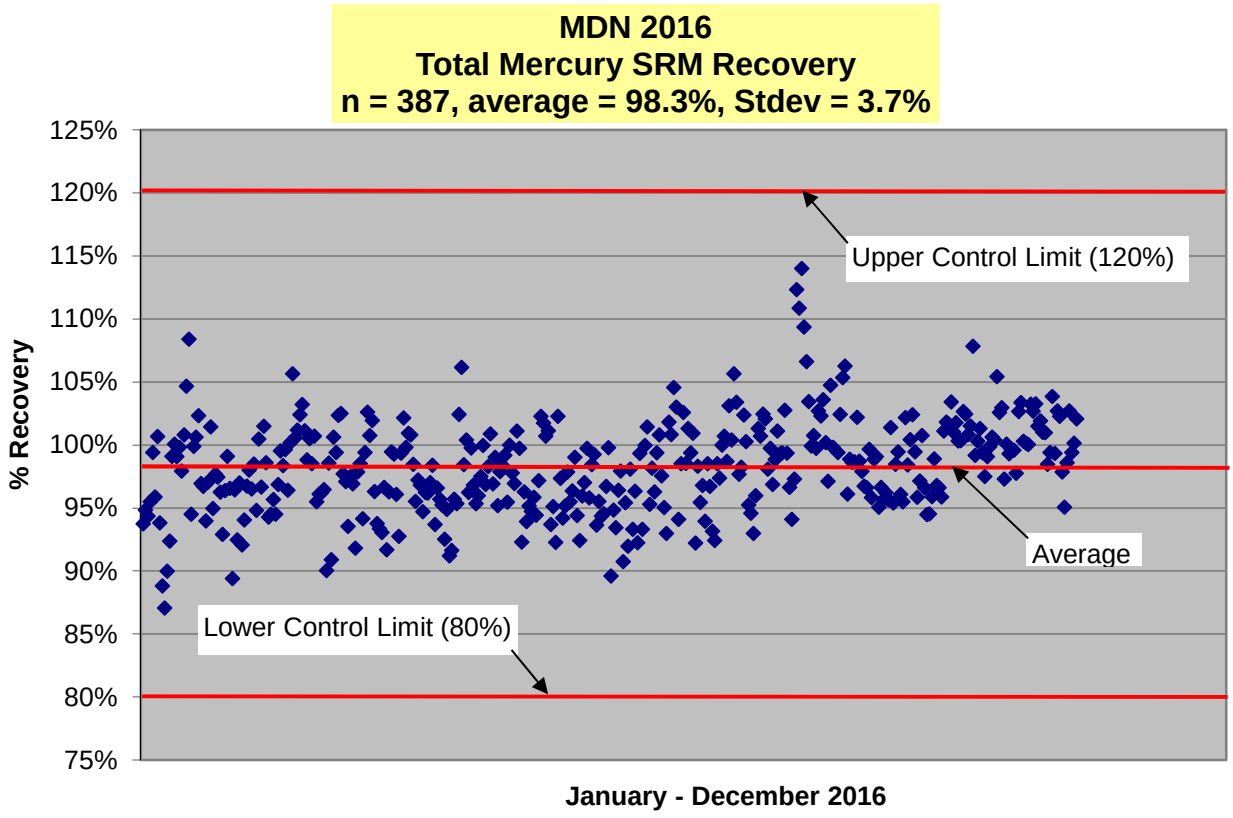

Figure 14 - Total Mercury Percent Recovery in Certified Reference Material Samples, 2016

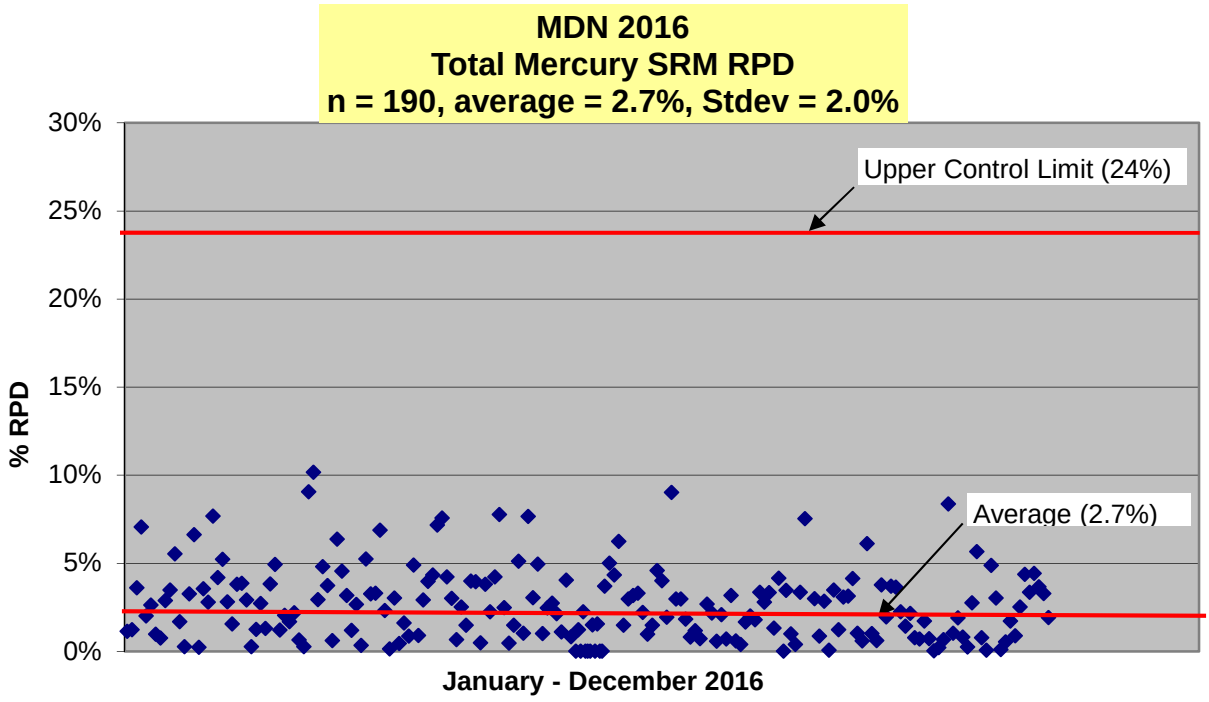

Figure 15 - Total Mercury Relative Percent Difference (RPD) between Certified Reference Materials (CRM) and CRM Duplicate Analyses, 2016

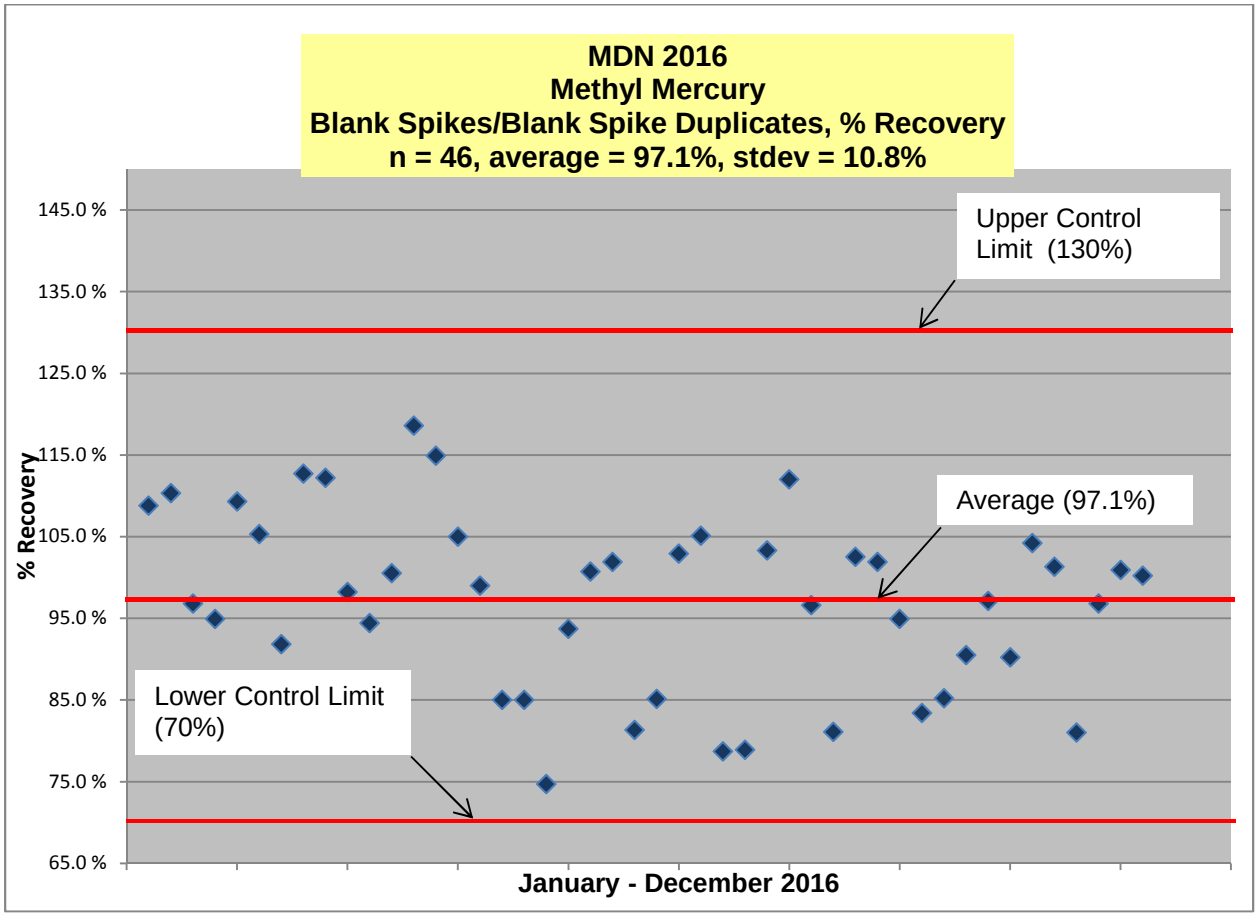

Figure16 - Methyl Mercury Percent Recovery in Blank Spikes/Blank Spike Duplicate Samples, 2016

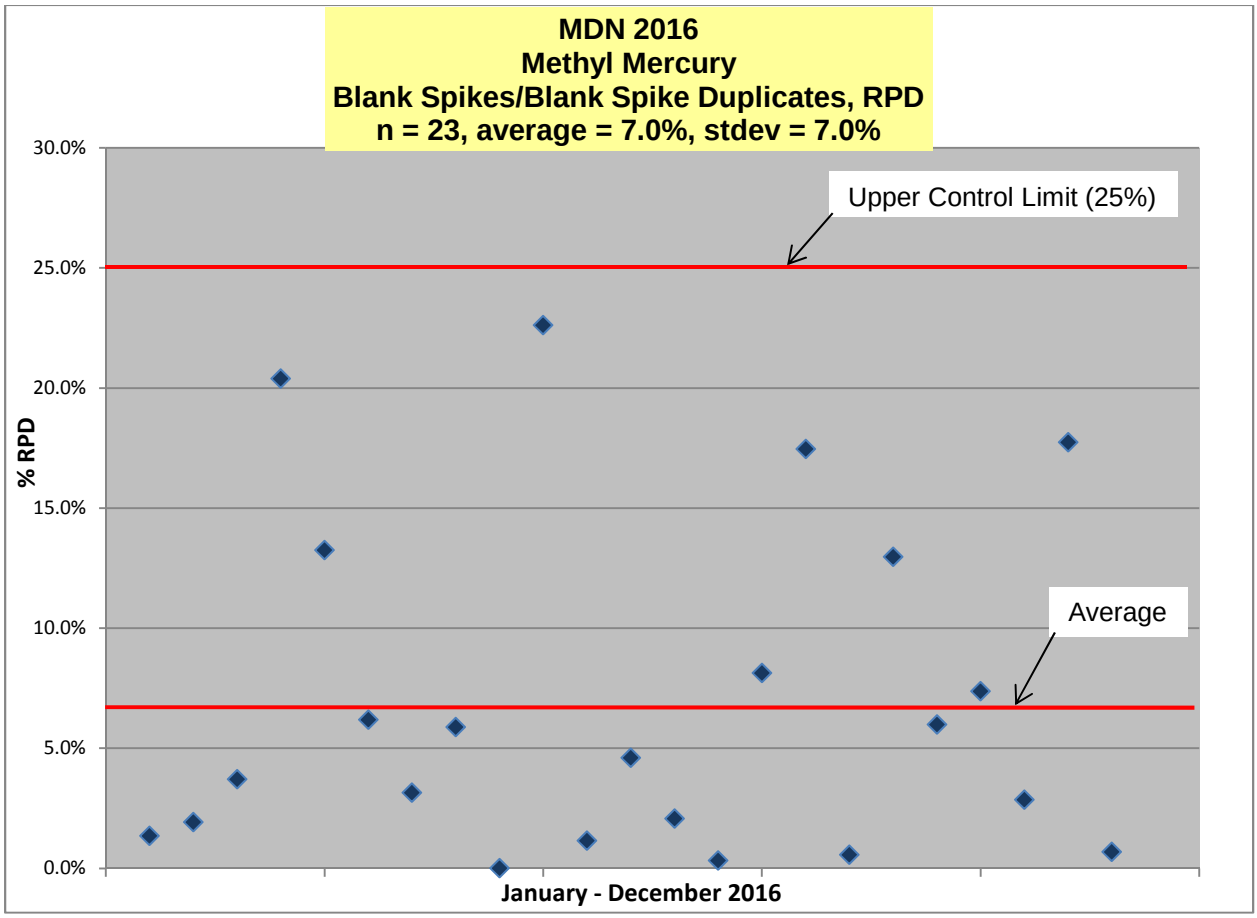

Figure 17 - Methyl Mercury Relative Percent Difference (RPD) in Blank Spikes/Blank Spike Duplicate Samples, 2016

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:

FGS DATA SET ID:
MDN LAB DATA SET CODE:
REVIEWER:
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 inter-laboratory comparison studies provided by USGS on a monthly basis during 2016. Samples are submitted for mercury analysis in both spiked and ultrapure deionized water.

EFGS also participated in one drinking water, five water pollution and four soil proficiency tests in 2016. 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 2016, in addition to the monthly USGS samples that are not included in the table. Results for any tests are available upon request. Control charts for the USGS samples may be viewed at https://bqs.usgs.gov.

Table 10 - Proficiency Tests

Proficiency Test	Organization	Open-close date	Scored Total Hg Results
MAPEP 35 water & soil	US DOE	9/8/2016 – 11/16/2016	Passed
HW0716	Phenova	7/25/2016 – 9/8/2016	Passed
WS0716	Phenova	7/11/2016 – 8/25/2016	Passed
WP0716	Phenova	7/5/2016 – 8/19/2016	Passed
Study 108	Canada ECCC	6/6/2016 – 8/1/2016	Passed
MAPEP 34 water & soil	US DOE	3/10/2016 – 5/18/2016	Passed
HW0116	Phenova	1/25/2016 – 3/10/2016	Passed
WP0116	Phenova	1/11/2016 – 2/25/2016	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 added to the bubbler and therefore no dilution is needed. There were 27 samples in 2016 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. These results are not tabulated. The HAL and the Program Office are attempting to address sample evaporation through lab and field testing. Results from initial testing were submitted at the 2014 NADP Fall Meeting. The HAL will continue its evaporation studies 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 2016, the mean of 68 Field Bottle Blanks was 0.041 ng/bottle with a standard deviation of 0.041 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 AL1920160414 and MD0820160419 and with elevated mercury values of approximately 0.26 and 0.23 ng, respectively.

AL19 has a NCON collector, while MD08 has an ACM collector. For both there was only 1 field blank. Any windy condition, 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.

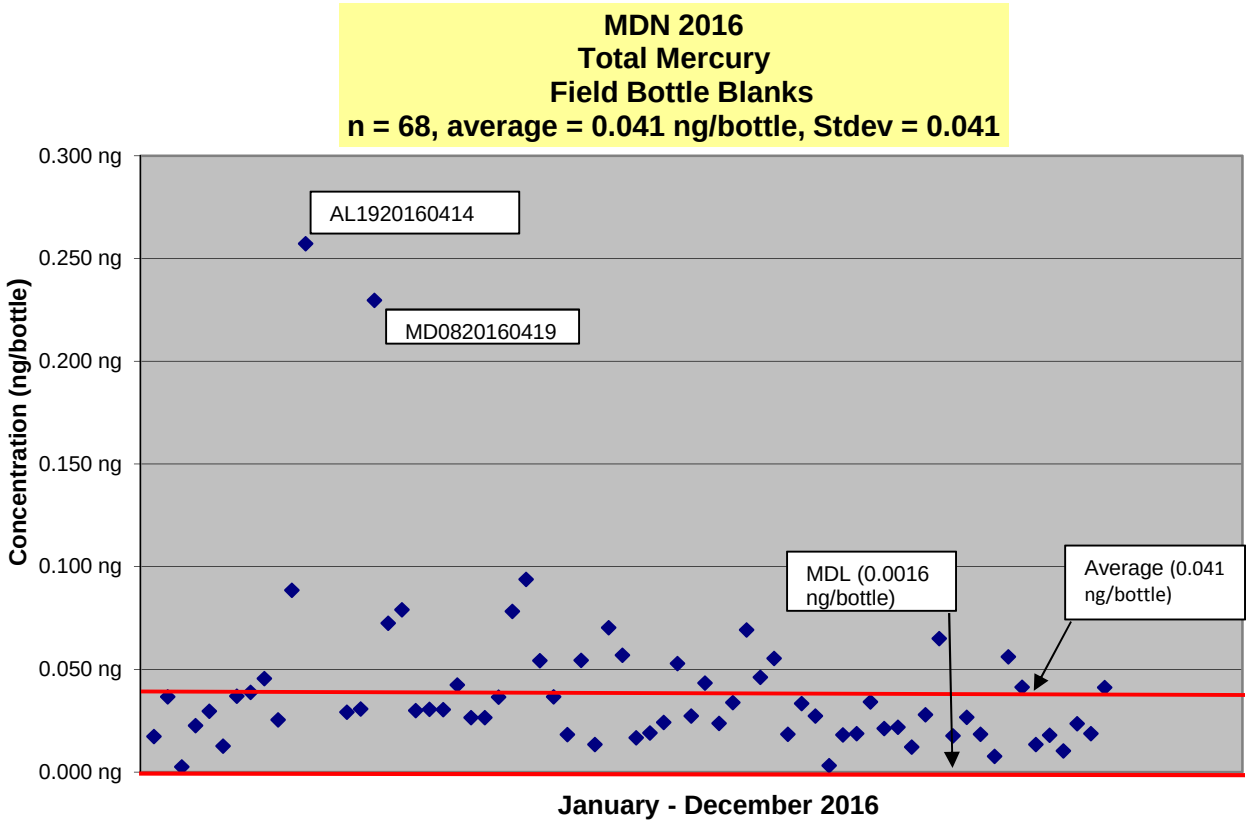

Figure 19 - Total Mercury Concentrations in Field Bottle Blanks, 2016

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

When adjusted for 50mL blank volume, the MDL and PQL for THg convert to 0.004 ng/aliquot and 0.025 ng/aliquot, respectively. In 2016, the mean of 43 system blanks was 0.019 ng/aliquot with a standard deviation of 0.016 ng/aliquot compared to the control sample with a mean of 0.005 ng/aliquot and a standard deviation of 0.009 ng/aliquot. The mean for the field systems blanks is comparable to the mean for the laboratory bottle blanks (0.013 ng/bottle). Several locations (NC08, NC26, SC03 and SC19) had a higher level of mercury in their control sample compared to their system blank.

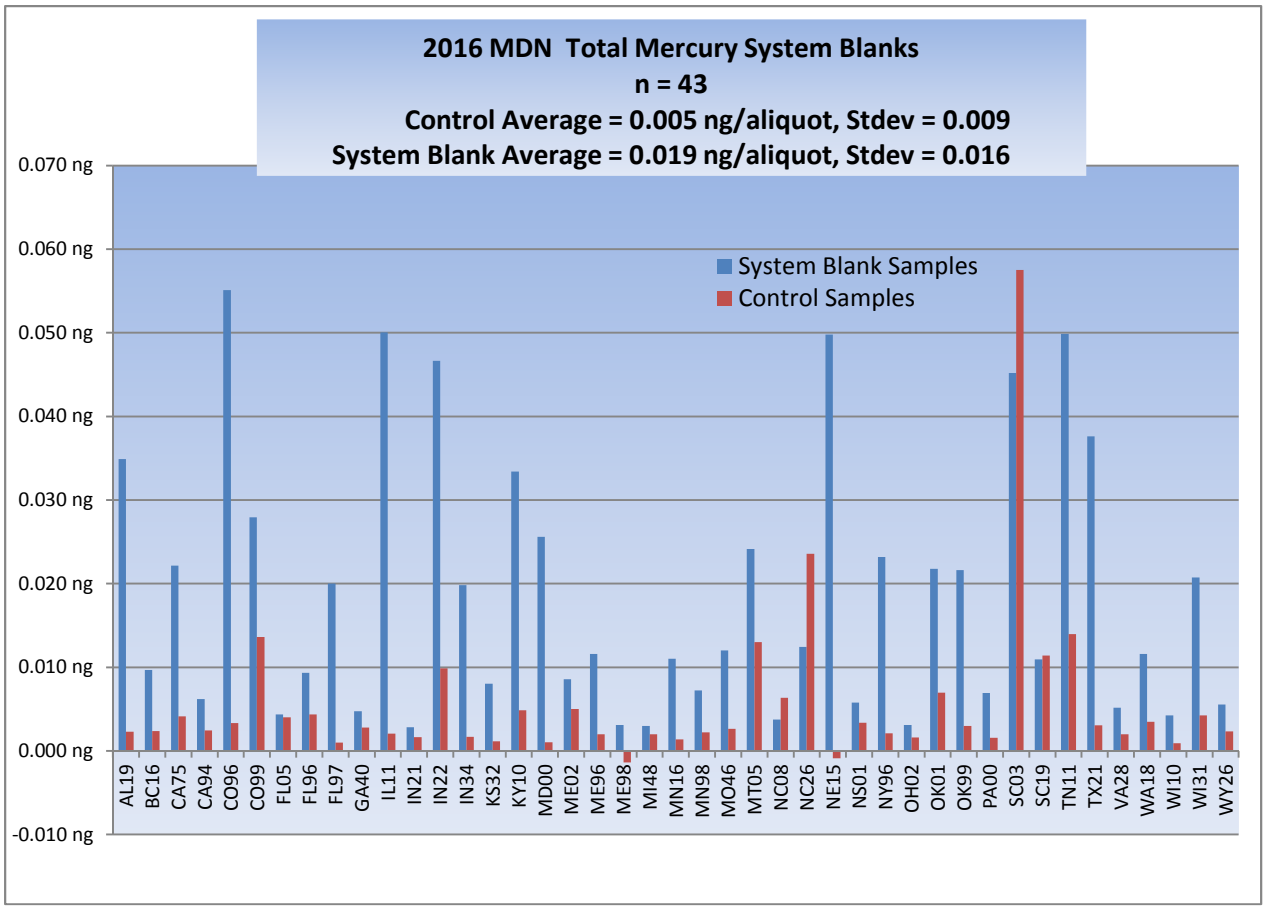

Figure 20 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2016

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. Notes codes are defined on the NADP web site at http://nadp.isws.illinois.edu/MDN/mdndata.aspx. 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 5,617 samples in 2016, which is comparable to the 5,974 samples that were processed during 2015. As it currently stands, there were 586 samples that received a QR code of "A", while 4,558 samples received a "B" QR code and 473 samples received a "C" QR code (none of the 473 samples were disqualified due to laboratory issues/errors). This distribution is illustrated in figure 21. However, during the end of year data review, a problem was discovered with the assignment of note codes and QR values in the MS Access database. It was discovered that note codes and QR values were not updated when a sample record was edited. The problem is being addressed. Resolution is expected in late 2017 or early 2018.

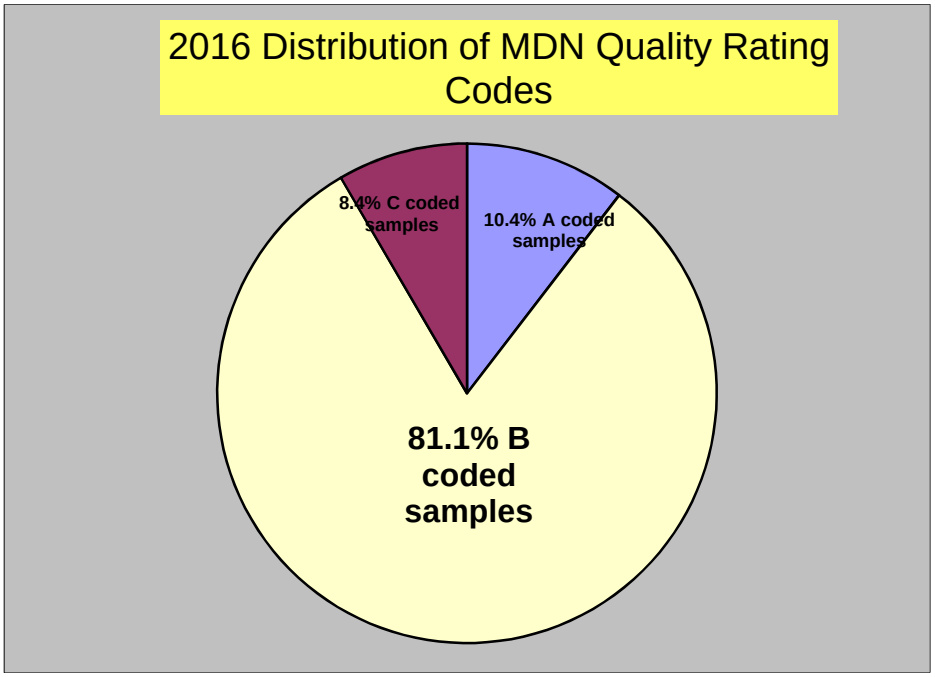

Figure 21 - Distribution of Quality Rating Codes for Samples Received in 2016

8. Summary and Conclusions

The HAL continued to maintain and demonstrate acceptable quality control in 2016. The five DQOs (precision, accuracy, representativeness, comparability, and completeness) were met. The MDL for total THg was 0.079 ng/L at a PQL of 0.50 ng/L, and the MDL for MMHg was 0.019 ng/L at a PQL of 0.05 ng/L. Average bottle blank Hg and MMHg content was quantified at 0.013 ng Hg/bottle and 0.003 ng MMHg/bottle, respectively. Preparation and calibration blank total Hg and MHg contents were acceptable and within control limits. External proficiency testing by Phenova 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=68) and system blanks (n=43) generally indicated that field contamination levels continue to be low.

The HAL will continue to look for ways to improve the program both in the laboratory and field to ensure the highest quality data for the MDN.

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 MDL Studies

Matrix Specific MDL Study: Total Mercury in Water According to EPA 1631 E, EFAFS-T-AFS-SOP2992

Hg-CVAFS Analyzed by Blake Cassidy: 9/6/16
Report Prepared by Allison Kazlauskas: 9/6/2016
Mercury Supervisor; Ryan Nelson: 9/6/16
Report Reviewed by Dave Wunderlich: 9/6/2016

MDL Study Data for Total Mercury in Waters
Sequence: 6E20016 (ID#THg26002-160520-2)
Batch:F605255
Date: 05/20/16

Objective

Verify the method detection limit (MDL) for total mercury in water, using the preservation method EFSR-P-SP-SOP2796 and analysis method 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 **0.062ng/L THg**.

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 $SnCl_2$, analysis by purge and trap and dual amalgamation CV-AFS.

A solution of reagent water spiked with a 20ml aliquot of a 10 ng/mL Hg standard (LIMS # 1601450) and preserved with BrCl was prepared. The MDL study consisted of ten aliquots (replicates) of this solution, with each replicate having a final spike level of 0.400 ng/L of THg oxidized to 1% with BrCl.
The results of these measurements are found in the table on the page 2, as well in the raw data sheets (ID#THg26002-160520-2). All results are reported corrected for the instrument blanks and the method 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 leel. In the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$MDL = t^*\sigma = (2.821)^*(0.022) = \mathbf{0.062\ ng/L}.$$

MDL and PQL Validation. The dataset was peer reviewed and all qualifiying parameters (ICV,CCV,CCB,LCS, R-value, etc) passed.

To verify or establish a new MDL, the ratio of the spike level (true value or TV) to the calculated MDL must be ≤10. The TV/MDL ratio for this study was valid at **6.42**. Additionally, the MDL verification requires that the newly calculated MDL be within 2x the exsisting MDL. Twice the existing MDL is 0.16 ng/L. The calculated MDL of **0.062ng/L** meets the verification criteria.

In order to verify or establish a new PQL, the percent recoveries for all MDL replicates must fall within the acceptance range for the low calibration point. All ten replicates recovered with these limits (75-125%).

Matrix Specific MDL Study: Total Mercury in Water According to EPA 1631 E, EFAFS-T-AFS-SOP2992

MDL Summary Table
Total Mercury for Waters
MDL Study Data for THg26002
Eurofins North Creek Pkwy North, Suite 400
Bothell, WA 98011

Date: 5/20/16
Dataset ID:THg26002-160520-1
Sequence: 6E20016
Batch: F605255

Sample	[THg], ng/L
F605255-BLK1	-0.009
F605255-BLK2	-0.01
F605255-BLK3	0.01
Mean	**-0.003**
SD	**0.011**

	Final Result, ng/L	Spike Level, [TV], ng/L	[%Rec]
F605255-BS2	0.439	0.40	109.5%
F605255-BS3	0.414	0.40	103.2%
F605255-BS4	0.455	0.40	113.5%
F605255-BS5	0.380	0.40	94.7%
F605255-BS6	0.400	0.40	99.9%
F605255-BS7	0.400	0.40	99.8%
F605255-BS8	0.406	0.40	101.2%
F605255-BS9	0.398	0.40	99%
F605255-BSA	0.407	0.40	101.7%
F605255-BSB	0.428	0.40	106.8%
Mean	**0.413**	**0.40**	**102.5%**
SD	**0.022**	**0.000**	**5.2%**

	[THg], ng/L	Certified Value	[%Rec]	
NIST 1641d (F605255-BS1)	**16.42**	**15.68**	**104.7%**	**%RPD**
NIST 1641d DUP(F605255-BSD1)	**16.5**	**15.68**	**105.2%**	**0.486%**

MDL:	**0.062**
TV/MDL	**6.42**
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: Don Moran Don Moran 2/23/17
Report Prepared by: Allison Kazlauskas Allison Kazlauskas 2/23/17
Report Reviewed by: Dave Wunderlich Dave Wunderlich 2/23/17

Sequence: 5F04013 (THg26003-160518-1)
Batch: F605210
Date: 05/18/16

Objective

To verify the method detection limit (MDL) and practical quantitation limit (PQL) for Total Mercury in water on instrument CV-AFS 2600-3 after instrument re-location. This study will also serve as the annual MDN MDL for total mercury (2016). 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 **0.0787 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 25 uL aliquot of a 1 ng/mL Hg standard (LIMS #1601451) and preserved with BrCl. The MDL study consisted of ten aliquots (replicates) of this solution, with each replicate having a final spike level of 0.5010 ng/L of THg oxidized to 1% with BrCl. The PQL study replicates were prepared similarly using a 1 ng/mL Hg standard (LIMS #1601451) for a final spike concentration of 0.5010 ng/mL.

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 0.500 ng/L spike was (2.821)*(0.028), or **0.0787 ng/L**.

MDL Validation

The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, R-value, etc.) passed.

To verify an MDL, the ratio of the spike level (true value or TV) to the calculated MDL must be ≤10. The TV/MDL ratio for this study was valid at 6.363. Additionally, MDL verification requires that the newly-calculated MDL be within 2x the existing MDL. Twice the existing MDL is 0.16 ng/L. The calculated MDL of 0.0787 ng/L meets the verification criteria.

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 recovered with these limits (75-125%) for both spike levels, but the 0.5010 ng/L spike level approximates that current PQL of 0.50 ng/L.

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 in its new location.

MDL/PQL Study

5/18/2016
THg26003-160518-1
Sequence:6E18014
Batch: F605210

Eurofins Frontier Global Sciences
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Bothell, WA 98011

Sample	[THg], ng/L		
F605210-BLK1	0.325		
F605210-BLK2	0.125		
F605210-BLK3	0.135		
Mean	0.225		Limits:
SD	0.141		75-125%
	[THg], ng/L	[TV], ng/L	[%Rec]
F605210-BS2	0.500	0.5010	100%
F605210-BS3	0.462	0.5010	92%
F605210-BS4	0.485	0.5010	97%
F605210-BS5	0.495	0.5010	99%
F605210-BS6	0.433	0.5010	86%
F605210-BS7	0.413	0.5010	82%
F605210-BS8	0.456	0.5010	91%
F605210-BS9	0.457	0.5010	91%
F605210-BSA	0.436	0.5010	87%
F605210-BSB	0.455	0.5010	91%
Mean	0.459	0.501	92%
SD	0.028	0.000	5.57%

MDL	0.0787
TV/MDL	6.363
FMDL in LIMS	0.08
2x LIMS FMDL	0.16

eurofins | Frontier Global Sciences	Matrix Specific MDL Study: Methyl Mercury in Precipitation Samples by CV-GC-AFS

Analyzed by: Ryan Nelson Ryan N 11/7/17
Mercury Supervisor: Ryan Nelson Ryan N 11/7/17
Report Prepared by: Sandra Mead 10/26/17
Report Reviewed by: Dave Wunderlich 11/2/17

MDL Study Data for Methyl Mercury in Precipitation Samples
Preparation Method: EFAFS-T-AFS-SOP2797
Analysis Method: EFAFS-T-AFS-SOP2808
Dataset: MMHg15-170105-1 and MMHg15-170106-1

Objective To verify the existing Method Detection Limit (MDL). This MDL verification study applies to Methyl Mercury in precipitation samples as prepared by method SOP2797 and analyzed by method SOP 2808. The MDL verification was calculated and evaluated in accordance with 40 CFR 136. As detailed below, the MDL for Methyl Mercury in Water was determined to be **0.01939 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 0.8690 was used and the calibration was performed according to SOP 2808.

The MDL study consisted of a 0.050 ng/L MHg solution divided into eleven replicates, which were distilled and then analyzed. The results of these measurements are found in the table on the next page, as well in the raw data sheets. All peak heights would have been corrected for the instrument blanks, but neither instrument blank produced a peak. All final concentrations were **corrected** for the preparation blanks (0.003 and 0.004 ng/L).

MDL Calculation Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked samples, with n = 11 replicates (10 degrees of freedom). In this case, the t value of 2.764 was used in the following equation, where σ is the standard deviation of the results obtained on the replicates.

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

The MDL calculated from these data is (2.764)*(0.007), or **0.01939 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 new study yields a true value (TV) to ratio which does not exceed 10. The TV/MDL ratio for this study was acceptable at **2.579** and the calculated MDL was less than twice the current MDL of **0.026** ng/L.

Percent recoveries for the studies are evaluated only when a new PQL needs to be established. The criteria for the percent recoveries are the acceptance limits for the low calibration point (65-135%). All 11 replicates were spiked at the current PQL (0.050 ng/L) and recovered within the control limits.

01/5/17 and 1/6/17
MMHg15-170105-1
MMHg15-170106-1
MDN MDL Study

Eurofins Frontier Global Sciences
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Bothell, WA 98011

Sample	[MHg], ng/L		
F701258-BLK1	0.003		
F701258-BLK2	0.005		
F701258-BLK3	0.003		
F701277-BLK1	0.003		
F701277-BLK2	0.003		
F701277-BLK3	0.003		
Mean	0.003		
SD	0.0008		65-135%
	[MHg], ng/L	[TV], ng/L	[%Rec]
F701258-BS1	0.048	0.050	96%
F701258-BS2	0.056	0.050	112%
F701258-BS3	0.037	0.050	74.0%
F701258-BS4	0.053	0.050	106%
F701258-BS5	0.045	0.050	90%
F701258-BS6	0.048	0.050	96%
F701258-BS8	0.038	0.050	76%
F701258-BS9	0.051	0.050	102%
F701258-BSA	0.035	0.050	70%
F701277-BS1	0.040	0.050	80%
F7071277-BSD1	0.041	0.050	82%
Mean	0.045	0.050	89%
SD	0.007	0.000	14.0%

MDL	0.01939
TV/MDL	2.579
Current MDL	0.026
2x Current MDL	0.052
PQL	0.050