National Atmospheric Deposition Program

Mercury Analytical Laboratory

2015 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 113 active sites in the United States and Canada at the end of 2015. In 2015, 7 sites were shut down, 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 13 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 2015. 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 2015:

- Lou Anne McKown, Don Moran and Blake Cassidy began analyzing MDN samples in January-February after completing new analyst training.
- Jeanne Harrel was promoted from AFS analyst to AFS Lead Analyst in June.
- Jason Karlstrom, MDN site liaison and project manager, resigned in July.
- Gerard became acting MDN project manager in July.
- Mark Delgado was hired in July to perform MDN equipment cleaning.
- The lab was audited by the NADP Program Office (NADP PO) in July.
- Doug Disney was promoted to MDN site liaison and Connor Foote was promoted to MDN Receiving in August.
- A new in-vial sparging system was installed on instrument 2600-1 and was validated in September, but it didn't impact MDN in 2015.
- Allison Kazlauskas was hired in September as a QA Specialist
- Mark Delgado began preserving, splitting and composting MDN samples in October.
- A major renovation affecting the entire building began at the end of October
- Gerard resigned in November.
- Kristine Teffeau (QA Specialist) resigned in November.
- Sandra Mead was hired as the Health & Safety Officer/Waste Disposal Manager in November
- MDN Receiving moved to the new location at the front of the building, co-located with EFGS S&R.

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 and methyl mercury 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. Ten replicates (t-1, 9 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 previous 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 (2003 NELAC regulation 5.5.5.2.2.1.h.3 and TNI Standard EL V1M4-2009 section 1.7.1.1.h.iii). 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 total and methyl mercury collected during 2015. All MDL and PQL studies are on file with the Quality Assurance department and are available upon request.

The MDL studies for total mercury for instruments 2600-1, 2600-2 and 2600-3 (datasets THg26001-151102-1, THg26002-151215-1 and THg26003-150604-2), were performed at 0.503 ng/L (the PQL is 0.50 ng/L). The TV/MDL ratios for all three instruments were less than 10. Since the TV/MDL ratios were in control for all three sets of MDLs, all three studies are valid and the highest MDL value, 0.129 ng/L, will be used to evaluate data.

A MDL study was performed for methyl mercury on instrument #15 in dataset MMHg15-151217-1 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 0.021 ng/L will be used to evaluate data.

Table 1 - MDL Studies for 2015 Summary Table

Instrument	Dataset	MDL (ng/L)	PQL (ng/L)	True Value TV (ng/L)	TV/MDL
FI-AFS 2600-1	THg26001-151102-1	0.129	0.50	0.50	3.89
FI-AFS 2600-2	THg26002-151215-1	0.064	0.50	0.50	7.84
FI-AFS 2600-3	THg26003-150604-2	0.056	0.50	0.40	7.18
CV-GC-AFS #15	MMHg15-151217-1	0.021	0.050	0.050	2.39

1.3 Accreditations

Eurofins Frontier Global Sciences is currently accredited in ten states and maintains ISO/IEC 17025:2005 and DOD ELAP accreditations:

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	E87575-18
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	WA012732015-2
Washington DOE	State	C788-15
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 total mercury. On average, 2-3 laboratory bottle blanks are analyzed each week for total mercury. 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 methyl mercury.

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 total mercury and methyl mercury were converted to ng/bottle (using 20mL charge volume/bottle) in Table 2 to accommodate comparisons with the bottle blank data. Laboratory bottle blanks for total mercury exceeded the PQL about 50% of the time and generally exceeded the MDL all of the time (figure 1). However, sample and laboratory bottle blank results are not corrected for BrCl and method blanks.

There were five laboratory bottle blanks that exceeded the MDL for methyl mercury and four of those also exceeded the PQL (figure 2). Laboratory bottle blanks are expected to be at, or near, the MDL (0.00044 ng/bottle, Table 2). High bottle blanks for methyl mercury 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 2 - Laboratory Bottle Blank Summary Table

2015 Laboratory Bottle Blanks	n	Average (ng/bottle)	Standard Deviation	MDL (ng/bottle)	PQL (ng/bottle)
Total Mercury	92	0.008	0.005	0.0026	0.010
Methyl Mercury	12	-0.007	0.017	0.00044	0.001

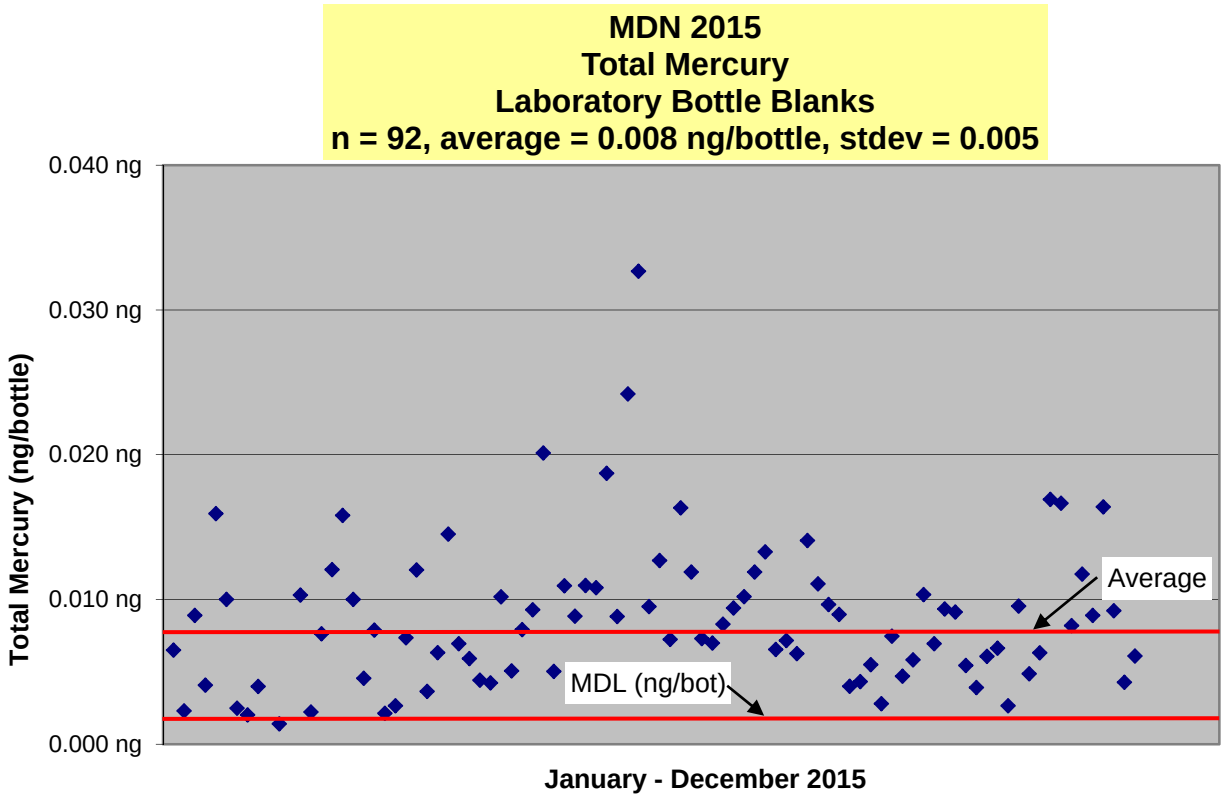

Figure 1 - 2015 Plot of Total Mercury Mass in Laboratory Bottle Blanks for 92 Samples

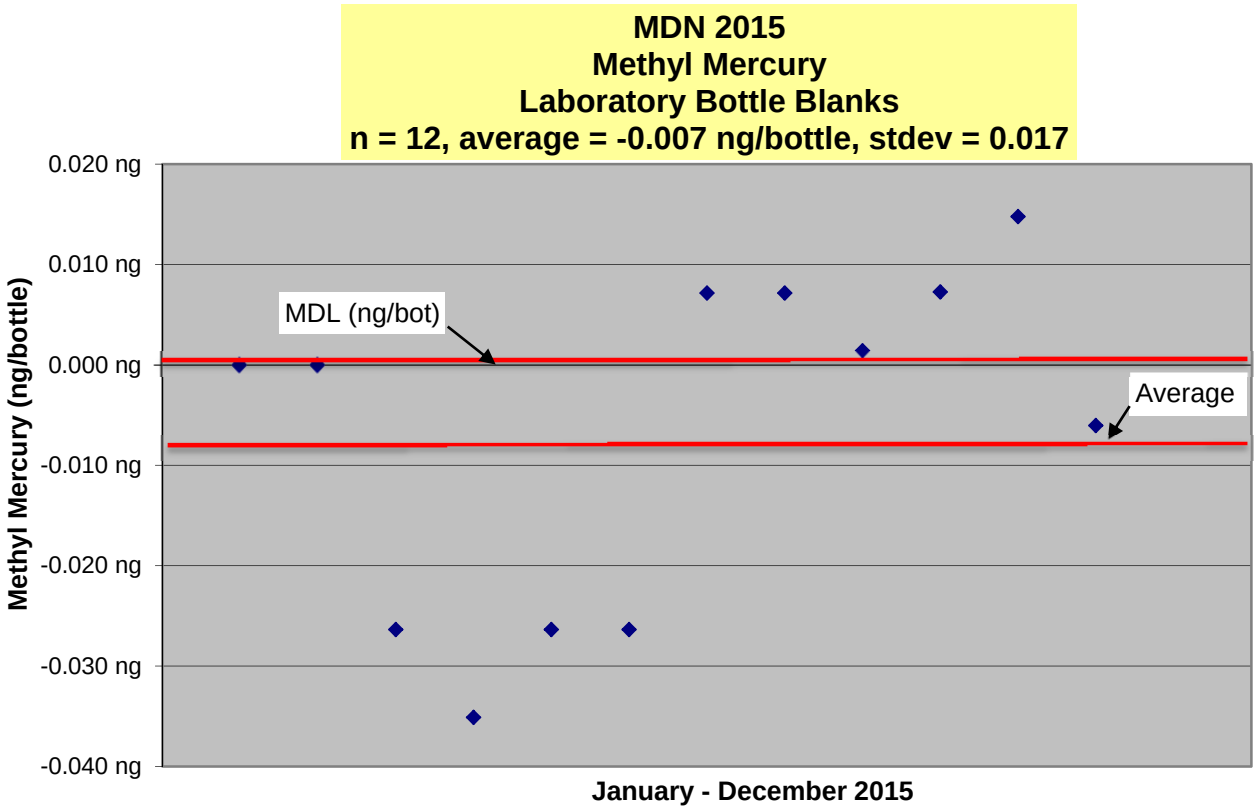

Figure 2 - 2015 Plot of Methyl Mercury Mass in Laboratory Bottle Blanks for 12 Samples

2. Quality Control

QC samples have expected target values that can be used to objectively assess performance of preparation and analytical methods. If performance on these known samples is acceptable, client sample results and other unknowns are assumed to be acceptable, as well. 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 methyl mercury)
- field blanks
- system blanks

2.1 Preparation Blanks

2.1.1 Description

Preparation blanks for total mercury consist of bromine monochloride (1% BrCl), hydroxylamine hydrochloride (0.200 mL), and stannous chloride (0.300 mL) in 50 mL of reagent water. The HAL control limit for total mercury 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 methyl mercury consist of 45 mL reagent water, hydrochloric acid (0.5%), ammonium pyrrolidine dithiocarbamate (0.200 mL of APDC) solution, ethylating agent (38.5 µL) and acetate buffer (0.300 mL). The HAL control limit for methyl mercury 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 blanks are a measure of how much of each sample result can be attributed to these necessary reagents. Preparation blanks also help when investigating possible sources of contamination.

2.1.3 Discussion

All but two of the preparation blanks analyzed for total mercury during 2015 were less than the control limit of <0.25 ng/L used at the laboratory; both of these blanks were however less than the EPA criteria of 0.50 ng/L (table 3 and figure 3). The two preparation blanks that exceeded the control limit were re-analyzed in their respective analytical sequences. The results for both reanalyzed preparation blanks were <0.25 ng/L. The contamination found in the preparation blanks was attributed to carryover and gold trap contamination from the previous day.

All of the preparation blanks analyzed for methyl mercury during 2015 were less than the EFGS control limit of 0.045 ng/L (table 3 and figure 4). There is a distinct increase in variability and high bias beginning mid-year. This doesn't correspond to a change in procedure, instrumentation or supplies, but it could have been caused by the integration of new analysts into this process.

Table 3 - Preparation Blanks Summary Table

2015 Preparation Blanks	n	Average (ng/L)	Std Dev (ng/L)	MDL (ng/L)	HAL Control Limit (ng/L)	EPA 1631E/1630
Total Mercury	621	0.009	0.059	0.129	0.25	< 0.50
Methyl Mercury	105	0.007	0.010	0.021	0.045	Mean <0.045 σ<0.015

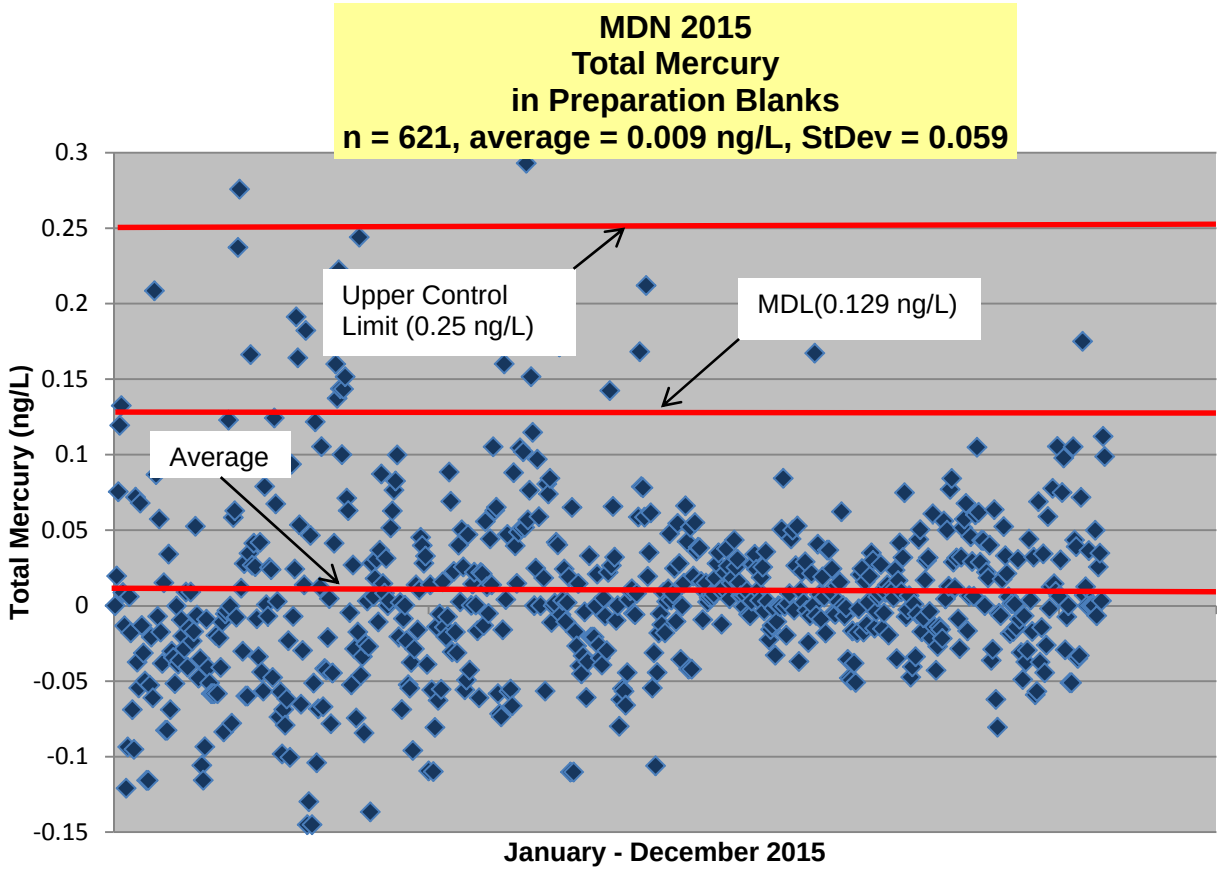

Figure 3 - 2015 Control Chart for Total Mercury Concentration in Reagent Preparation Blanks

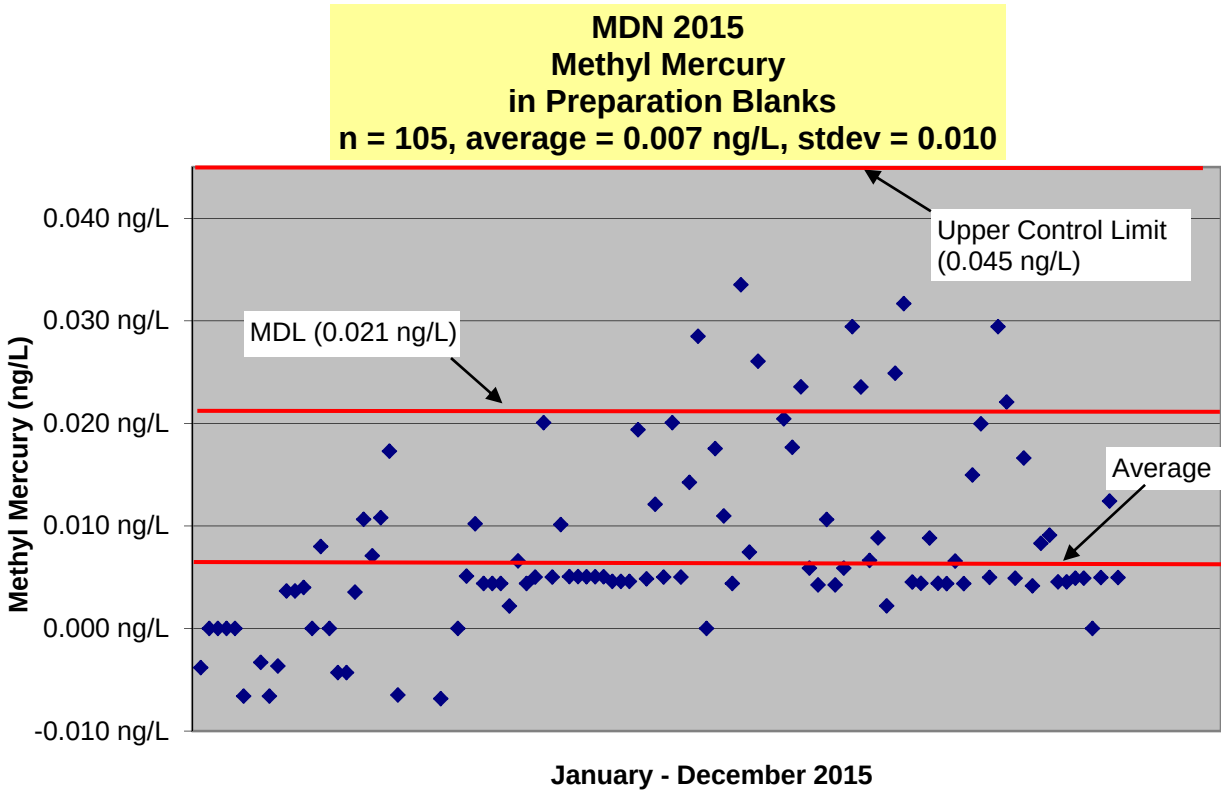

Figure 4 - 2015 Control Chart for Methyl Mercury Concentration in Reagent Preparation Blanks

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 92-102%. For the MDN total mercury 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 total mercury and a 0.5 ng/L standard for methyl mercury are analyzed as ongoing calibration standards. The MDN control limits for ICVs are set to 80-120% for total mercury, while the CCV limits are set to 77-123%; the control limits for methyl mercury ICVs are set to 80-120%, while the limits for CCVs are set to 67-133%.

2.2.2 Purpose

An ICV is analyzed following each calibration curve 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 or 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 total mercury (table 4 and figure 5).

No reportable CCV recoveries were outside the control limit of 67-133% for methyl mercury (table 4 and figure 6).

Table 4 - Continuing Calibration Standard Summary Table

2015 Continuing Calibration Standard	n	Average recovery (%)	Std dev of recovery (%)	Control Limit (%)	EPA 1631E/1630 Control Limits (%)
Total Mercury	677	100.7	5.0	77-123	77-123
Methyl Mercury	232	87.0	14.2	67-133	67-133

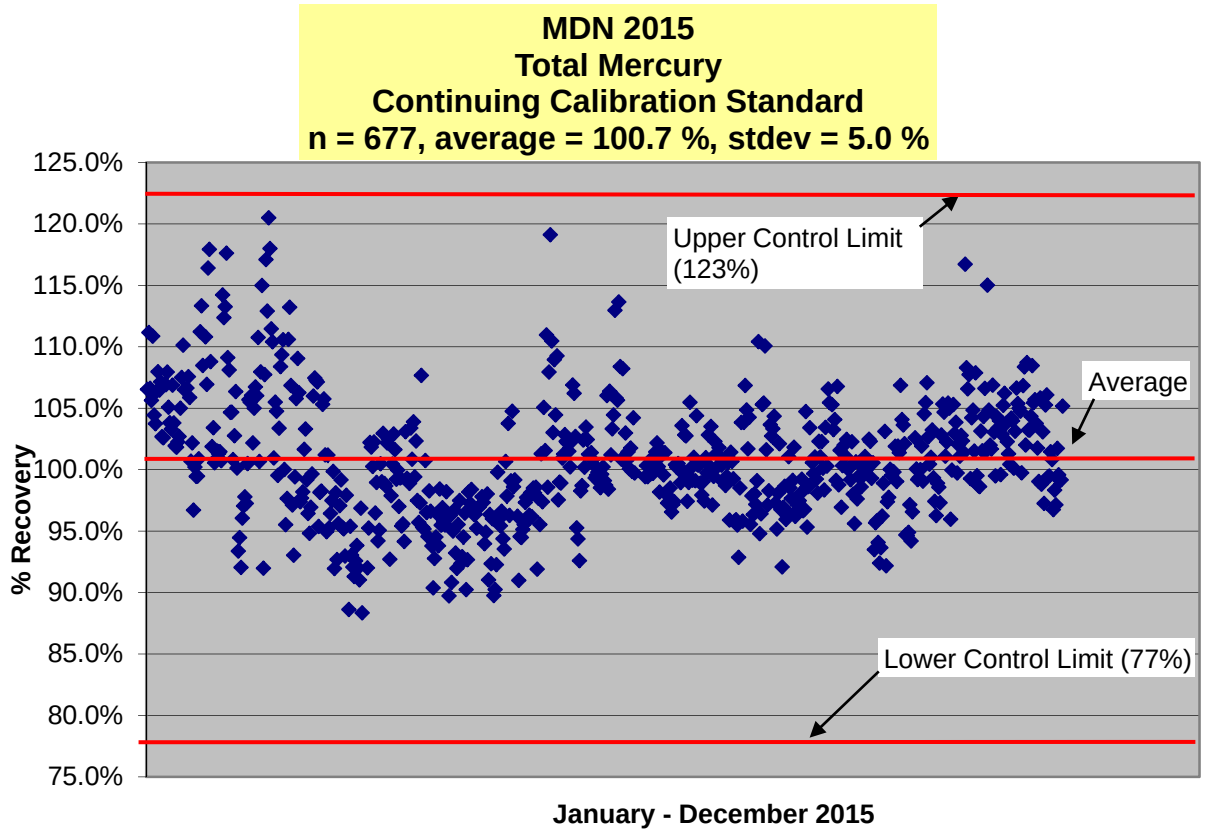

Figure 5 - 2015 Control Chart for Total Mercury Continuing Calibration Standard Percent Recovery

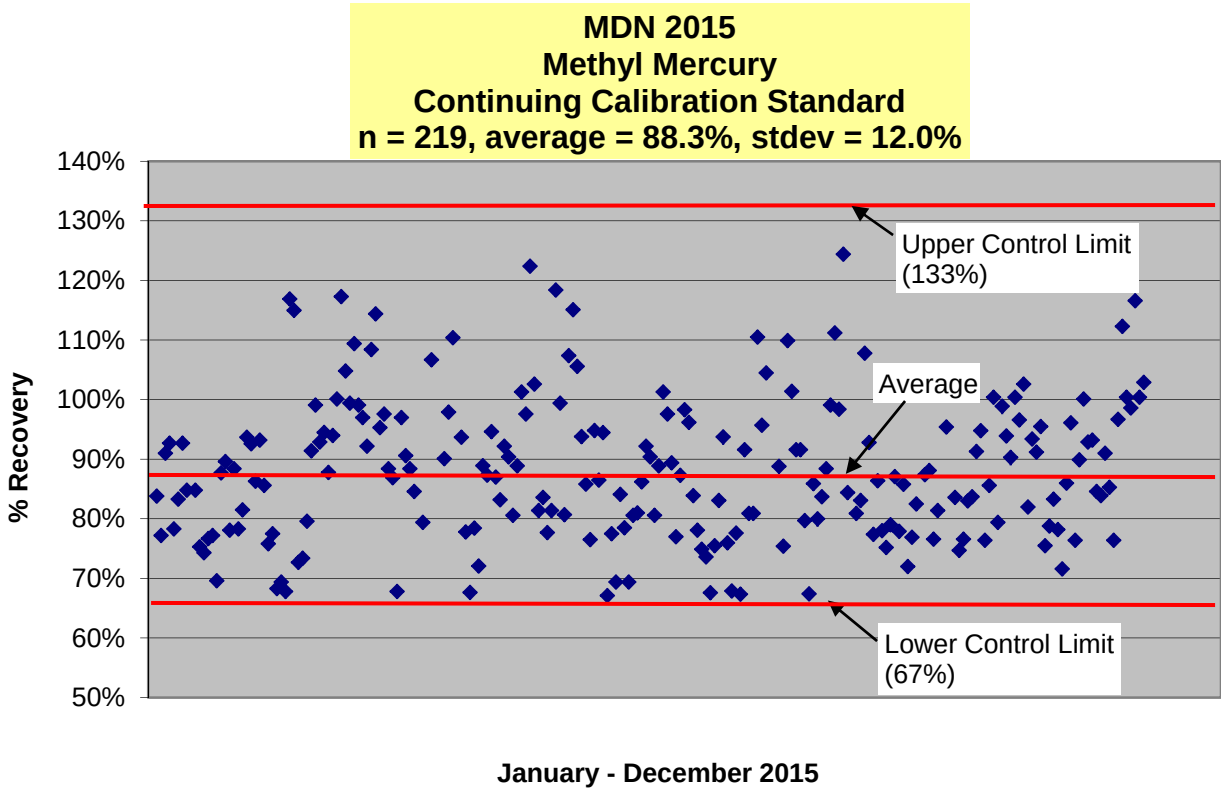

Figure 6 - 2015 Control Chart for Methyl Mercury Continuing Calibration Standard Percent Recovery

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. Individually, the initial calibration blank (ICB) and each CCB shall be less than 0.25 ng/L in order to be within control limits for total mercury. For MMHg, the mean of the ICB and CCB shall be less than 0.025 ng/L.

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 total mercury were less than the control limit of 0.25 ng/L used for MDN analysis at HAL (table 5 and figure 7).

Two of the 186 ongoing CCBs for methyl mercury were greater than 0.025 ng/L, which is the control limit used for MDN analysis at HAL (table 5 and figure 8). One of the CCBs was not used to evaluate sample data. The other CCB was affected by a loss of instrument sensitivity and the limitations imposed by processing data generated from a strip chart recorder.

Table 5 - Continuing Calibration Blanks Summary Table

2015 Continuing Calibration Blanks	n	Average (ng/L)	Std Dev (ng/L)	MDL (ng/L)	HAL Control Limits
Total Mercury	677	0.0589	0.054	0.129	Individually <0.50 ng/L, mean <0.25 ng/L with a standard deviation <0.10 ng/L
Methyl Mercury	186	0.002	0.006	0.021	0.025

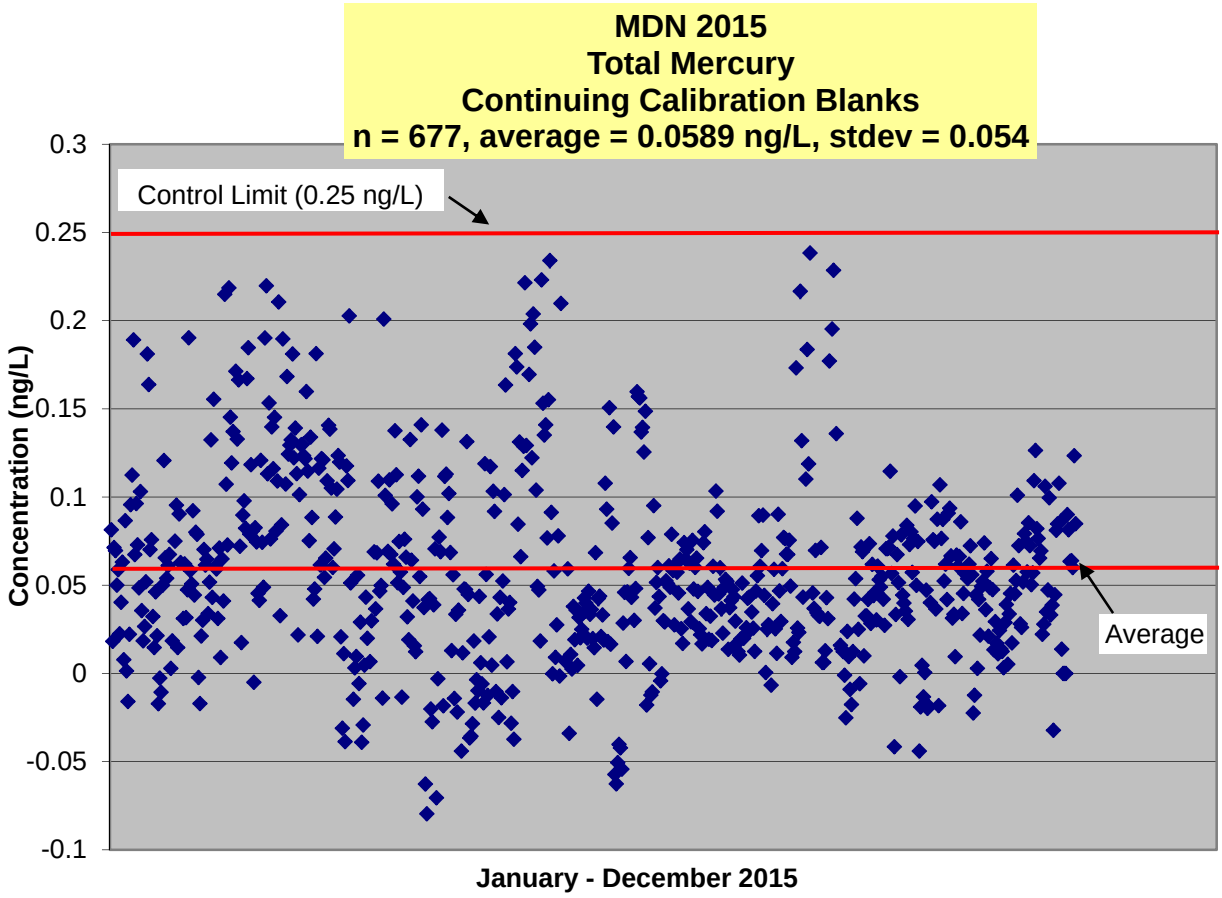

Figure 7 - 2015 Control Chart for Total Mercury Continuing Calibration Blanks

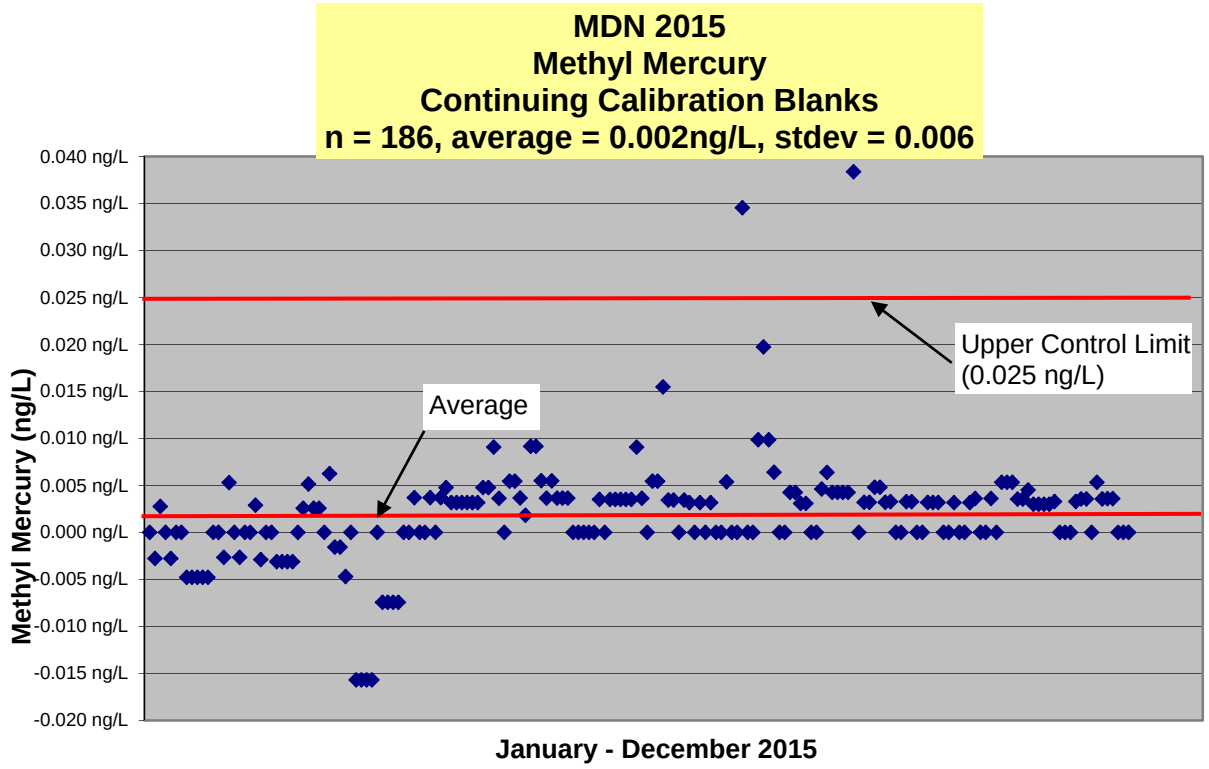

Figure 8 - 2015 Control Chart for Methyl Mercury Continuing Calibration Blanks

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 total mercury. 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 total mercury 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 total mercury, all of the RPDs calculated for duplicate pairs were within the control limit of 25% RPD used at HAL (table 6 and figure 9).

For methyl mercury, all of the RPDs calculated for duplicate pairs were within the control limit of 25% RPD used at HAL (table 6 and figure 10). For many of the samples, the methyl mercury 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. 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 one time the reporting limits.

Table 6 - Matrix Duplicates Summary Table 2015

2015 Matrix Duplicates	n	Average RPD (%)	Std Dev (%)	HAL control Limit (%)	EPA 1631E/1630 Control Limits
Total Mercury	604	2.45	2.5	25	NA
Methyl Mercury	20	10.9	6.3	25	NA

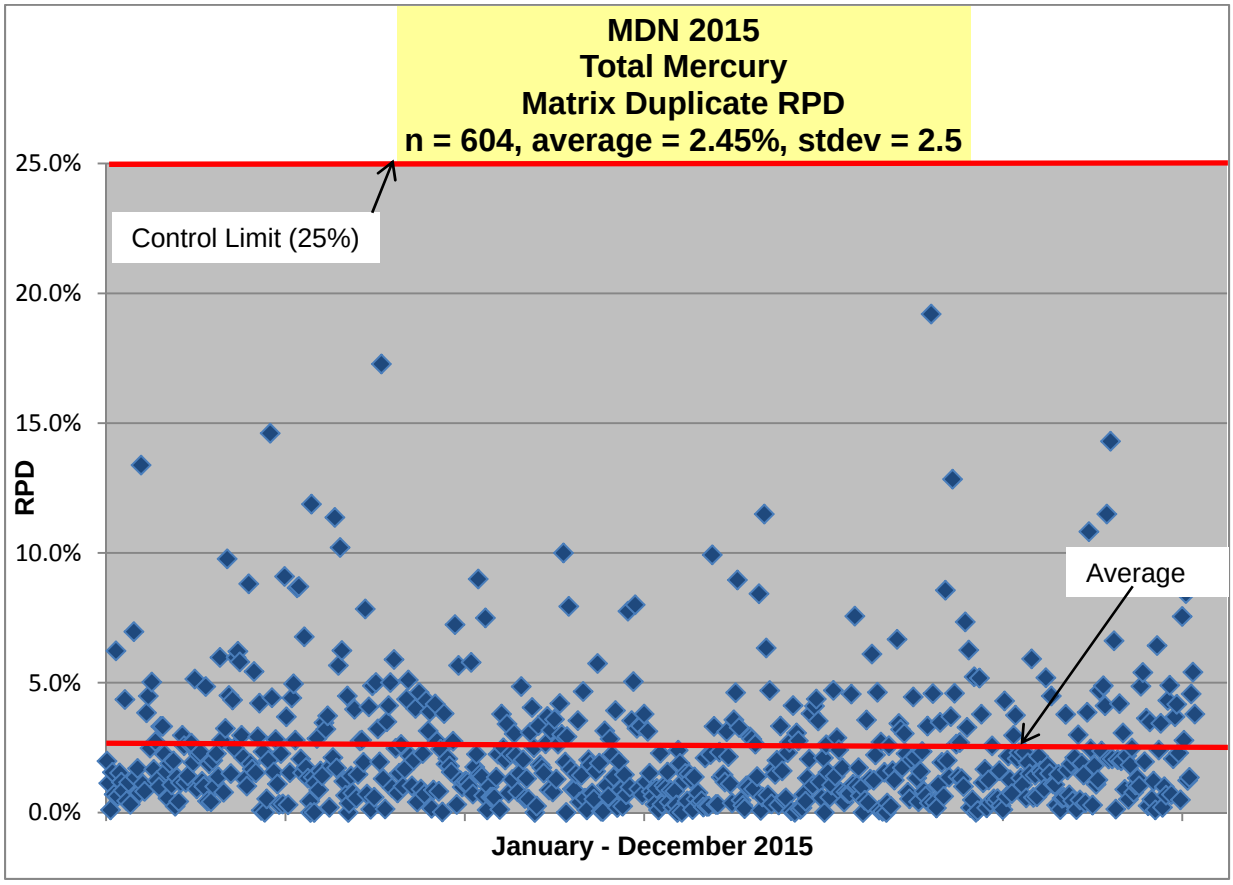

Figure 9 - 2015 Control Chart of the Relative Percent Differences for Total Mercury Concentrations in Matrix Duplicates

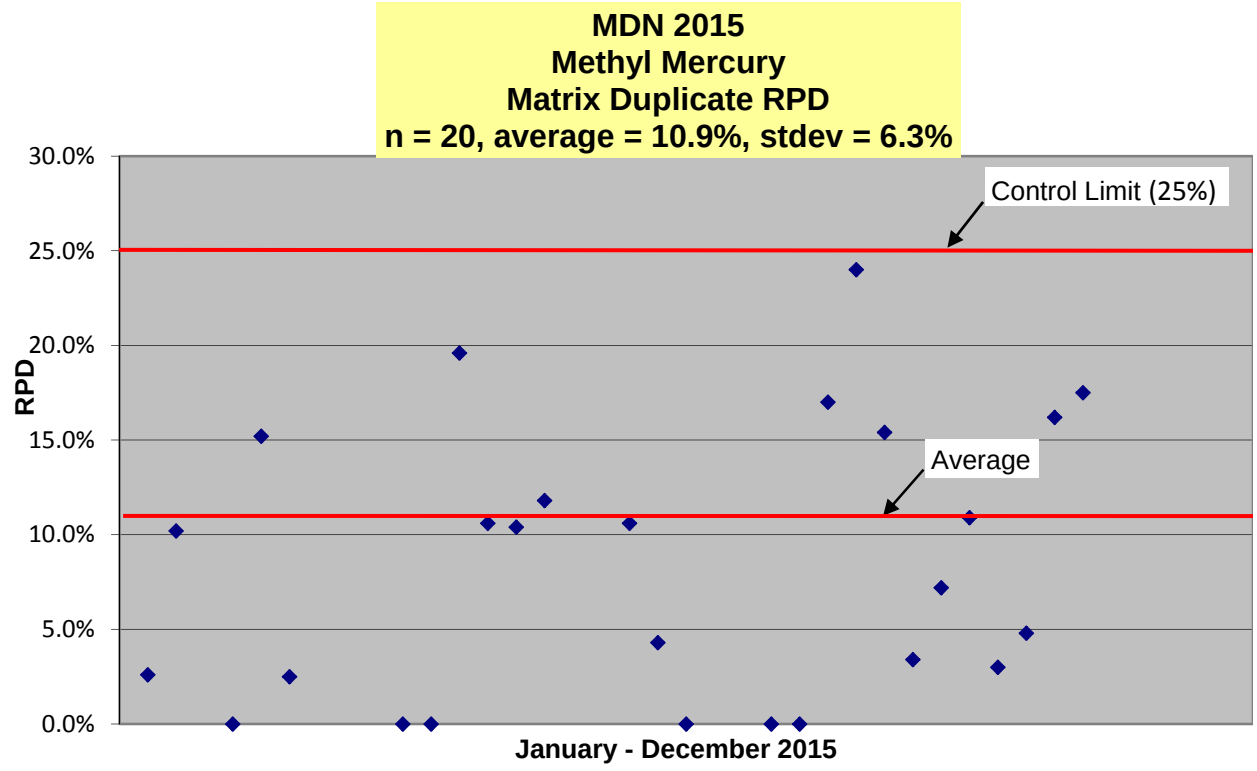

Figure 10 - 2015 Control Chart of the Relative Percent Differences for Methyl Mercury Concentrations in Matrix Duplicates

2.5 Matrix Spikes

2.5.1 Description

A Matrix Spike (MS) for total mercury 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 total mercury, since only a MS is analyzed. A MS/MSD is performed for methyl mercury 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 total mercury and preservation with HCl and distillation for methyl mercury analysis. *Because of the limited volume of sample that's usually available for methyl mercury quality control samples, the laboratory changed its approach to aliquoting for that QC. Beginning in 2015, the laboratory attempted to use the same volumes for the duplicate and matrix spike as it did for the source sample. This usually means less volume was available for the matrix spike duplicate*. 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 total mercury, all recovery values are within the 75-125% control limit used at HAL (table 7 and figure 11).

For methyl mercury, all recovery values are within the 65-135% control limit used at HAL (table 7 and figure 12).

Table 7 - Matrix Spike Recoveries for 2015 Samples

2015 Matrix Spikes	n	Average Recovery (%)	Std Dev of Recovery (%)	HAL Control Limits	EPA 1631E/1630 Control Limits (%)
Total Mercury	598	100.2	5.6	75-125	71-125
Methyl Mercury	130	106.7	11.2	65-135	65-135

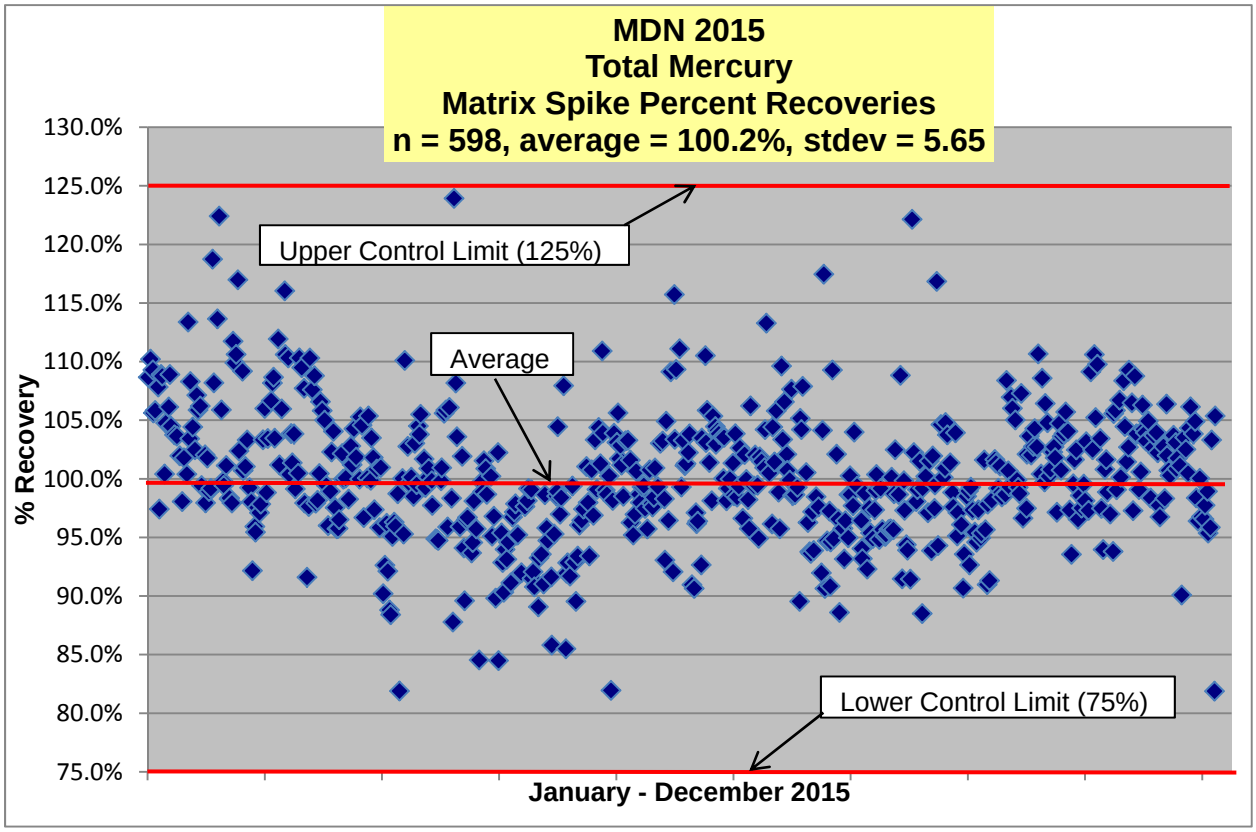

Figure 11 - Control Chart for Total Mercury Percent Recovery in Matrix Spikes During 2015

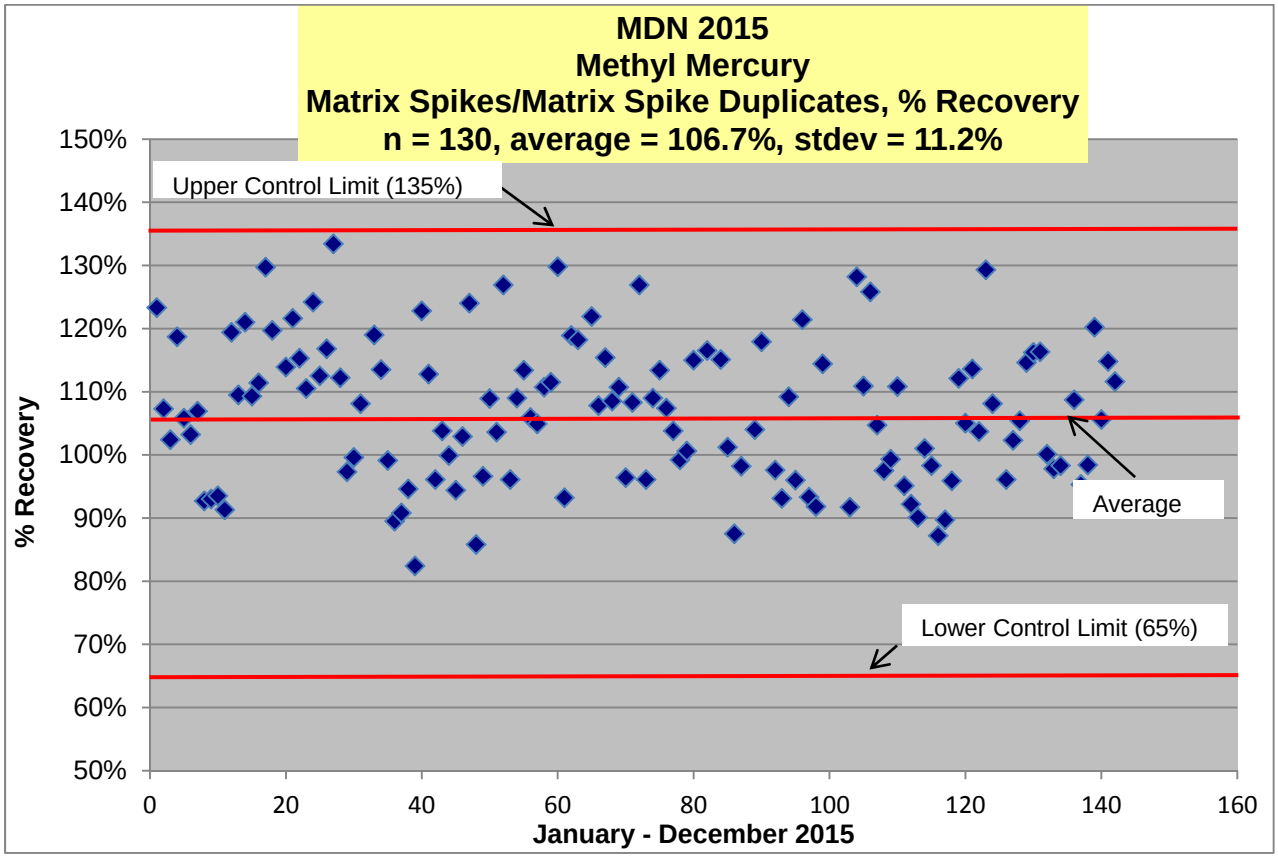

Figure 12 - Control Chart for Methyl Mercury Percent Recovery in Matrix Spikes During 2015

Because of the changes noted above regarding the allocating of sample for methyl mercury QC, it seemed appropriate to change the calculation for RPD from concentration-based to percent recovery-based. Four RPD values for methyl mercury exceeded the 25% control limit used at HAL (table 8 and figure 13). However, all RPDs were within the method control limit of 35%.

Table 8 - Matrix Spike/Matrix Spike RPD for 2015 Samples

2015 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	66	10.1	8.2	<25	<35

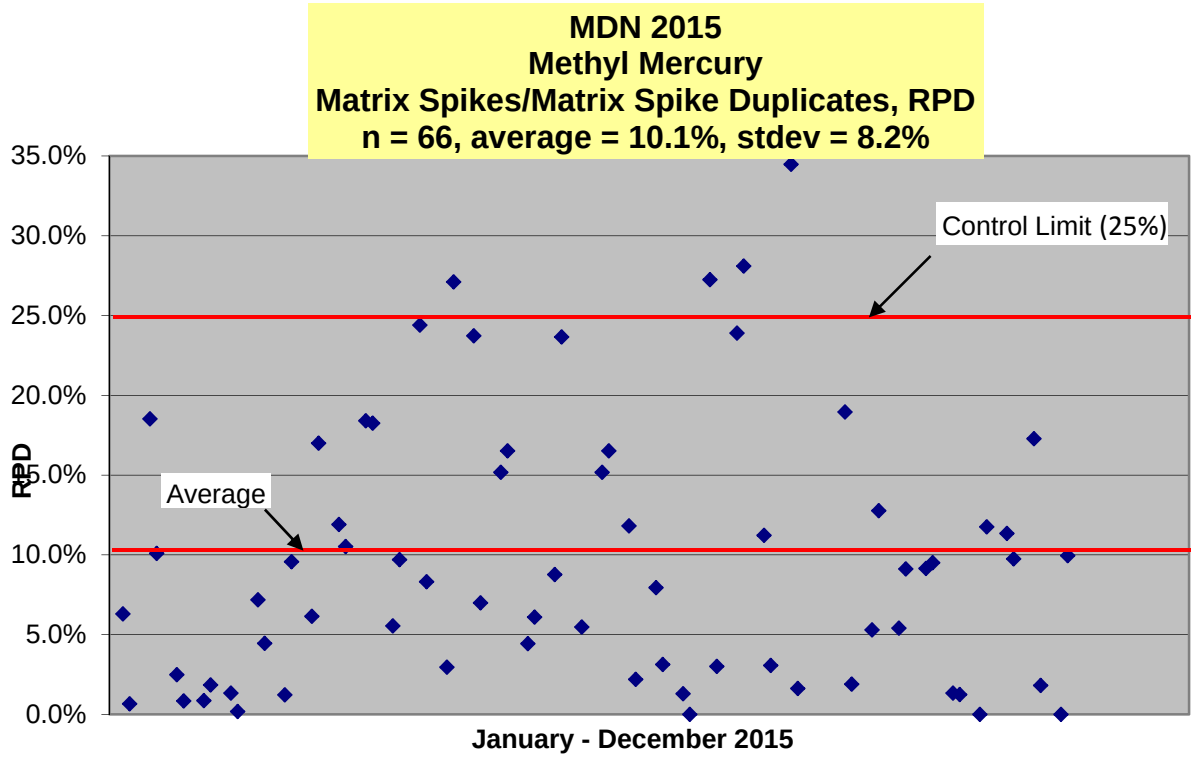

Figure 13 - Control Chart of the Relative Percent Differences for Methyl Mercury Matrix Spike/Matrix Spike Duplicate Pairs during 2015.

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.

Currently, there is no available CRM matching the MDN rainwater matrix. Therefore, HAL uses National Institute of Standards and Technology (NIST) reference material 1641d "Mercury in

Water." The percent recovery control limits for total mercury are currently set at 80-120% with a RPD of 24%. There is no CRM available for methyl mercury. Therefore, a Blank Spike and a Blank Spike Duplicate (BS/BSD) are analyzed for methyl mercury 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 total mercury, the first CRM is analyzed immediately after the calibration standards to validate the analytical curve.

2.6.3 Discussion

The mean of 409 certified reference material recoveries for total mercury was 98.4% with a standard deviation of 5.0% (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 2.8% (n=202), 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).

The mean recovery of 71 blank spikes and blank spike duplicates (BS/BSD) for methyl mercury was 107.0% with a standard deviation of 16.0% (figure 16). Three recovery values were above the 70-130% control limit used at HAL. Sample results associated with these blank spikes were reported if they were less than the RL or the sample volume was depleted. The average RPD value for the BS/BSD was 9.7% (n=33) with a standard deviation of 8.2%. The method doesn't specify limits for BS/BSD RPD. Two RPD values were above the 25% limit used in the laboratory (figure 17).

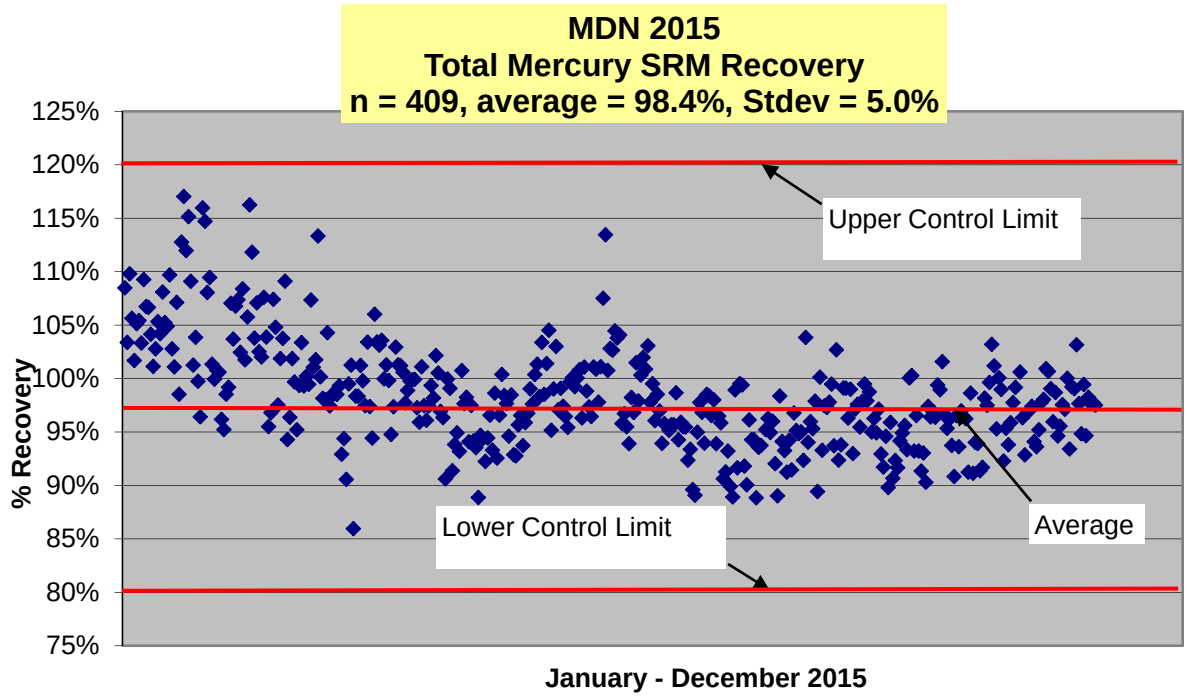

Figure 14 - Control Chart for Total Mercury Percent Recovery in Certified Reference Material Samples During 2015

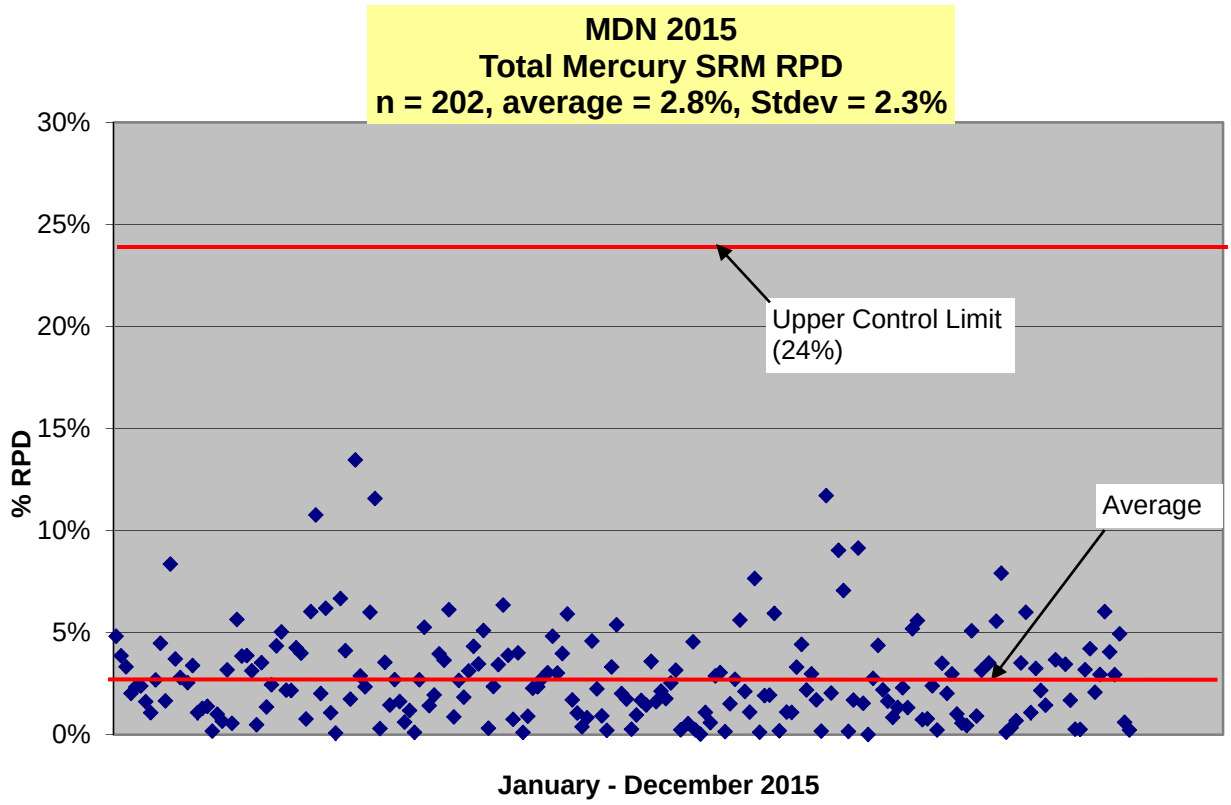

Figure 15 - Control Chart for Total Mercury Relative Percent Difference (%RPD) in CRM /CRM Duplicates Samples During 2015

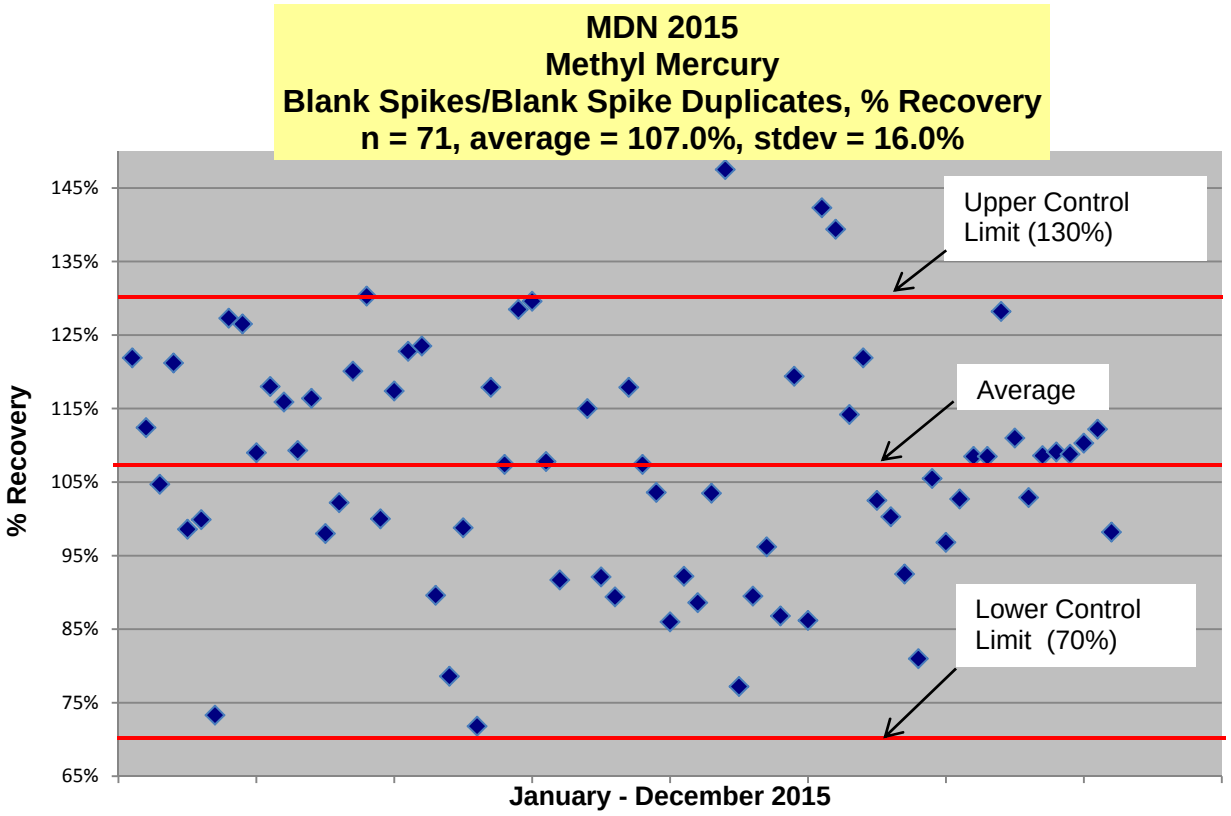

Figure16 - Control Chart for Methyl Mercury Percent Recovery in Blank Spikes/Blank Spikes Duplicates Samples During 2015

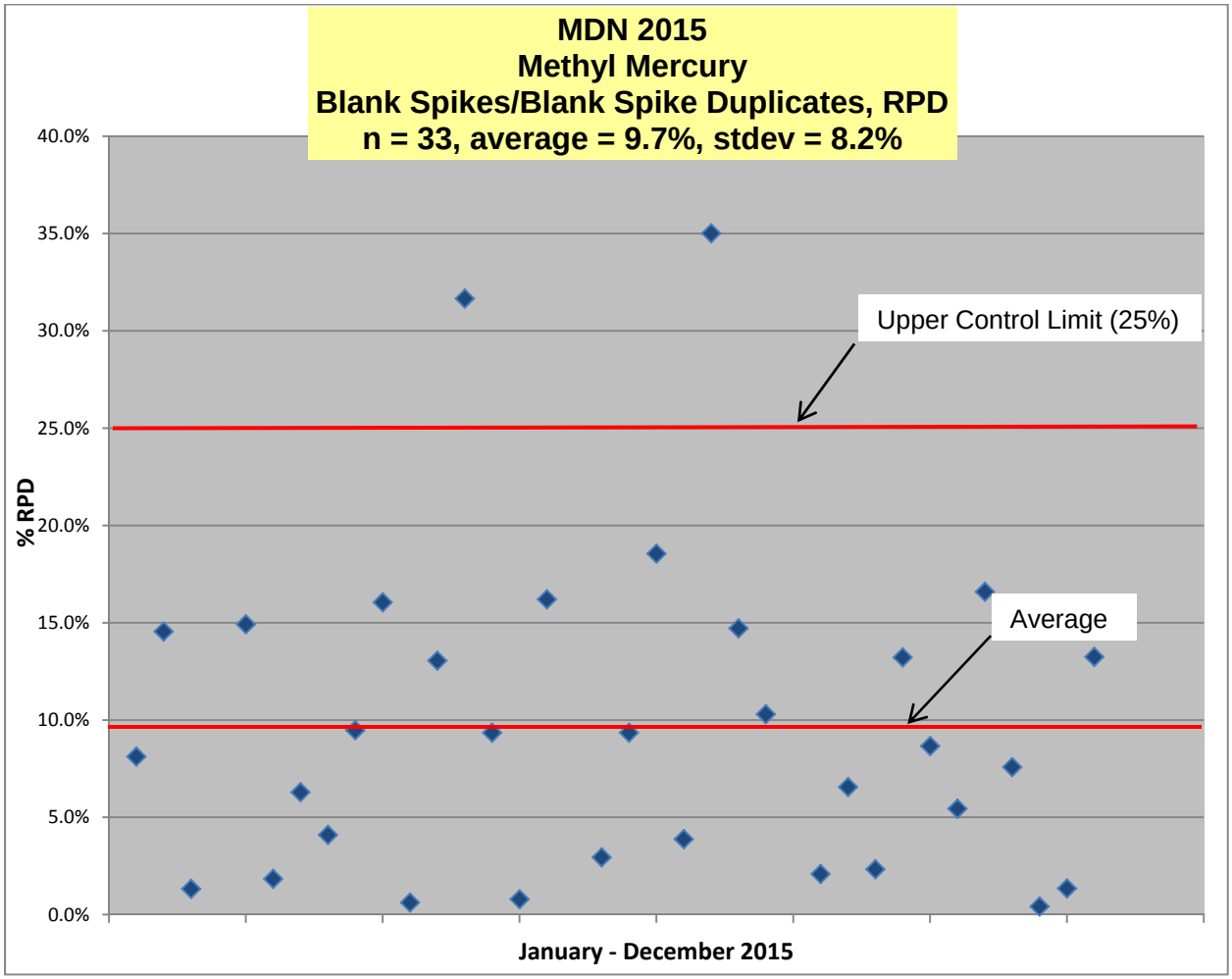

Figure 17 - Control Chart for Methyl Mercury Relative Percent Difference (%RPD) in Blank Spikes/Blank Spikes Duplicates Samples During 2015

3. Calculations

3.1 Calculation: Gross MDN Sample Concentration

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

Sample PA = sample peak area (PA units)

Ave BB = average bubbler 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 * Concentration

Subppt: Substituted Precip, mm

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

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

If this is selected then Subppt is

=BottleCatch (ml) * 25.4 (mm/inch)*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 *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

ConcHg = ((sampleHgMass – quarterly BottleBlank) / tmpVol) * 1000

Where:

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

SampleHgMass = AliquotHg * (FullMass – EmptyMass) / AliquotVol

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 participates in two water and two soils pollution proficiency tests each year. 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 purchased from a licensed and approved commercial provider. 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.

The HAL laboratory is participating in inter-laboratory comparison studies provided by USGS on a monthly basis. Samples are submitted for mercury analysis in both spiked and ultrapure deionized water.

5.1 Proficiency Tests

The proficiency tests listed in table 9 were completed by EFGS during 2015, 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 9 - Proficiency Tests

Proficiency Test	Organization	Open-close date	Scored Total Hg Results
HW0715	Phenova	7/28/2014 – 9/11/2014	Passed
WP0715	Phenova	7/1/2014 – 8/21/2014	Passed
HW0115	Phenova	1/27/2014 – 3/13/2014	Passed
WP0115	Phenova	1/6/2014 – 2/20/2014	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 total mercury. 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 22 samples in 2015 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 total mercury was converted to ng/bottle (using 20mL charge volume/bottle) in Table 2 to accommodate comparisons with the bottle blank data. In 2015, the mean of 75 Field Bottle Blanks was 0.031 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 exceeded the PQL about 50% of the time and generally exceeded the MDL all of the time. Figure 19 shows field bottle blanks NV0220150224 and AB1420150414 with elevated mercury values of 0.169 and 0.208 ng, respectively.

Both AB14 and NV02 have ACM collectors. For AB14 there were a total of 3 field blanks and for NV02 there were a total of 2 field blanks. The blanks with elevated mercury from AB14 and NV02 were interspersed between several with low mercury values. 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.

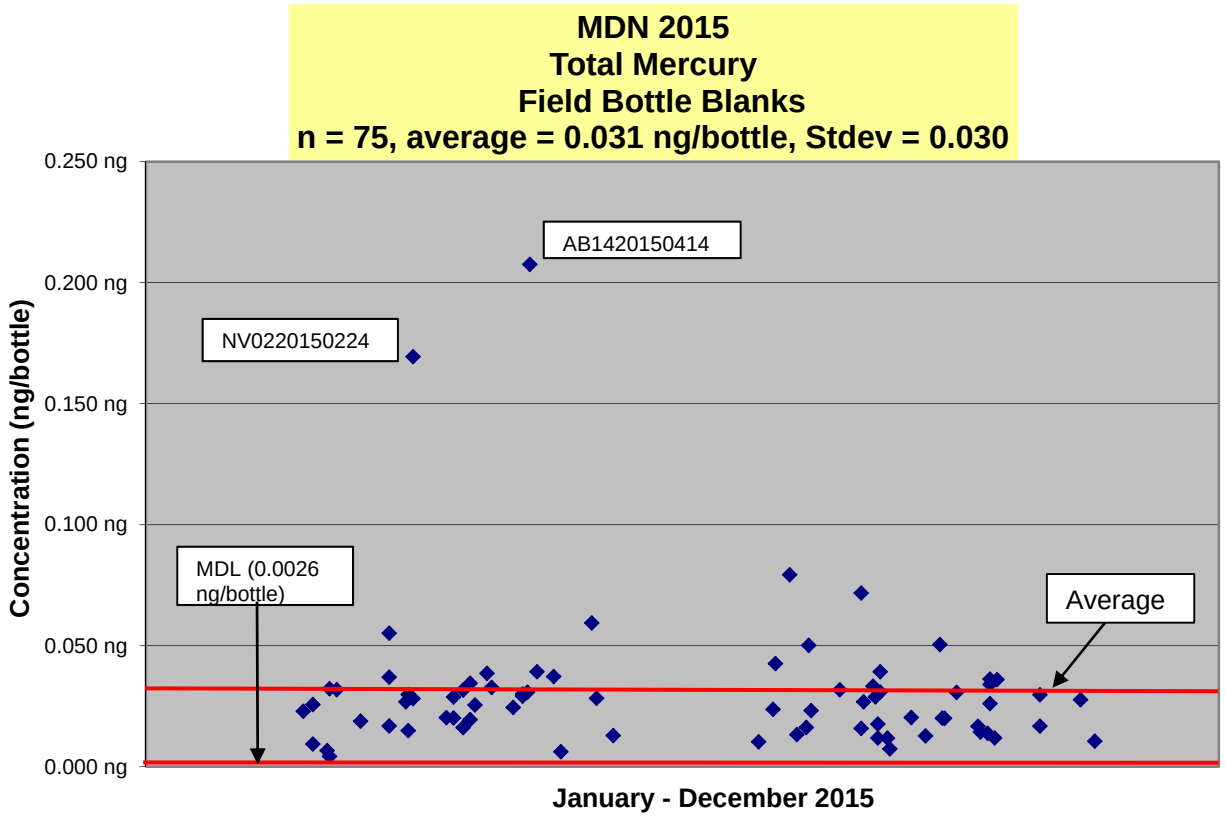

Figure 19 - Time Series Plot of Total Mercury Concentrations in Field Bottle Blanks During 2015

6.2 Field System Blanks

6.2.1 Description

A field system blank is essentially a field bottle blank in which a solution (DI-water) is poured through the wet side collection sample train that was installed in the field for an entire week with no precipitation and no unexplained collector openings. The system blank total mercury concentration is compared to the total mercury 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 total mercury convert to 0.0064 ng/aliquot and 0.025 ng/aliquot, respectively. In 2015, the mean of 40 system blanks was 0.044 ng/aliquot with a standard deviation of 0.169 ng/aliquot compared to the control sample with a mean of 0.009 ng/aliquot and a standard deviation of 0.050 ng/aliquot. Similar to laboratory bottle blank results, field system blanks are not corrected for BrCl and method blanks. The mean for the field systems blanks is not comparable to the mean for the laboratory bottle blanks (0.008 ng/bottle) because of a statistical outlier (figure 20). When that outlier is removed (figure 21), the mean of the 39 remaining system blanks was 0.018 ng/aliquot with a standard deviation of 0.026.

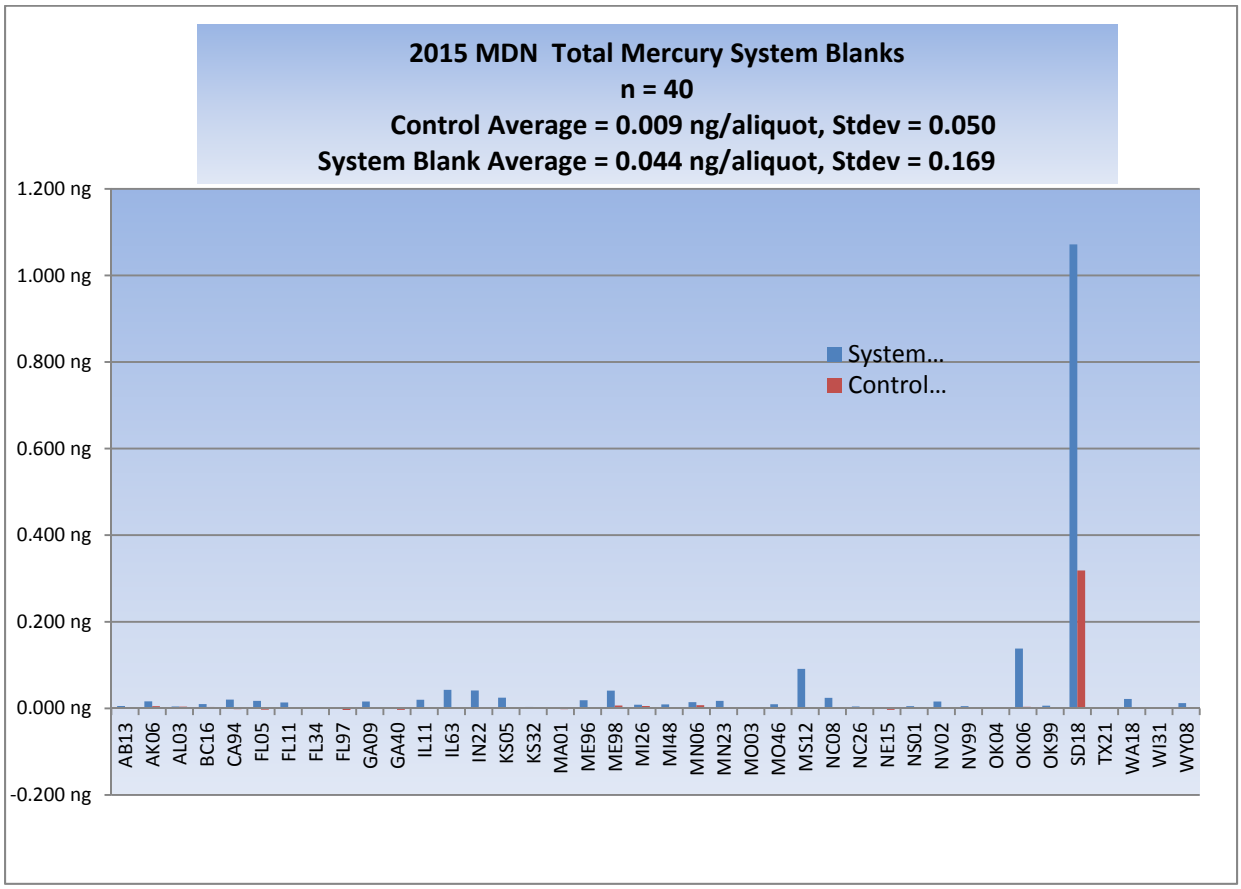

Figure 20 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2015 with the Statistical Outlier

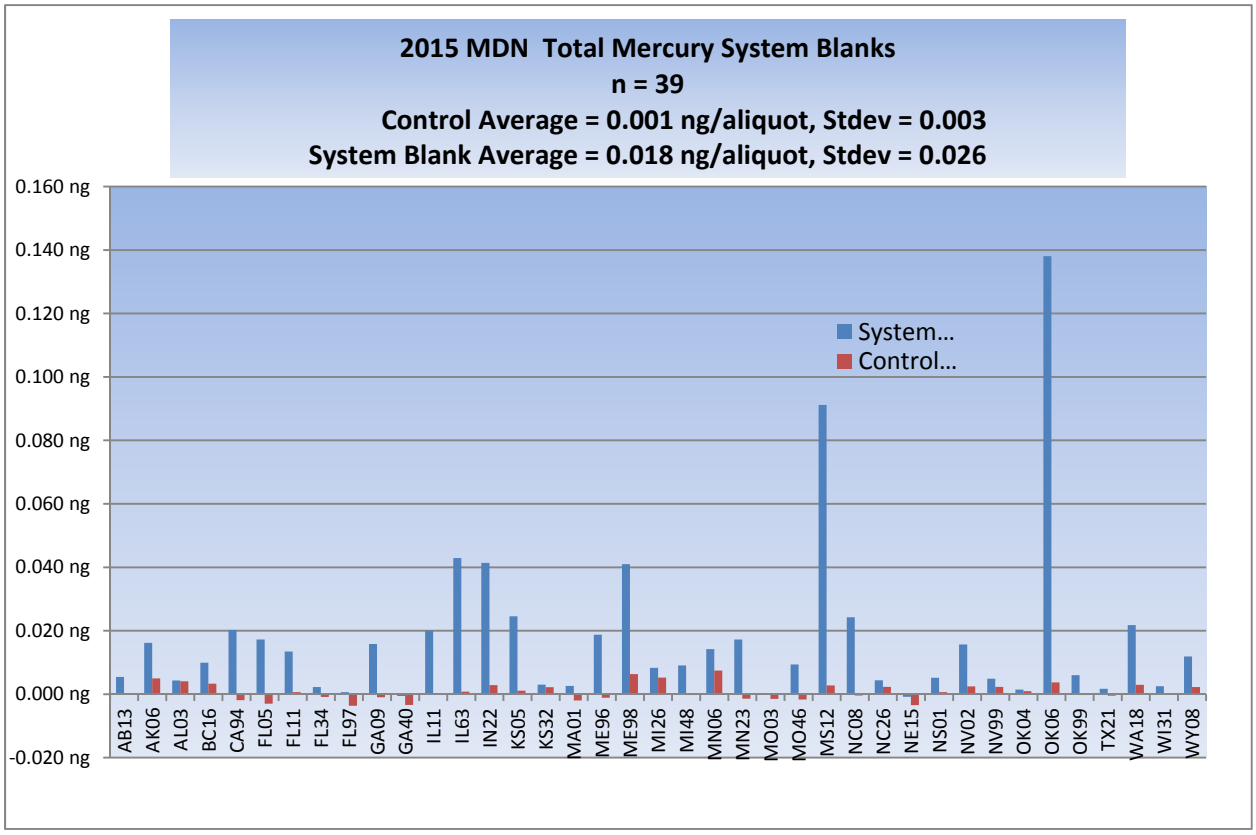

Figure 21 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2015 without the Statistical Outlier

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 average concentrations and deposition.

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

The HAL processed 5974 samples in 2015, which is comparable to the 6120 samples that were processed during 2014. There were 694 samples that received a QR code of "A" while 4922

samples received a "B" QR code, and 358 samples received a "C" QR code. This distribution is illustrated in figure 21. HAL continued to maintain and demonstrate acceptable quality control in 2015. This comparison is based on the HAL's assessment of the QR codes. These codes can later be changed by the NADP Program Office (PO).

Of the 358 "C" coded samples for 2015, 12 samples were originally disqualified due to laboratory issues/errors. However, after a closer examination, 5 of the 12 samples should have been disqualified due to field issues or sample conditions. Of the 7 samples disqualified due to laboratory issues/errors, breakage was responsible for 4 disqualifications and QC failures were responsible for 3.

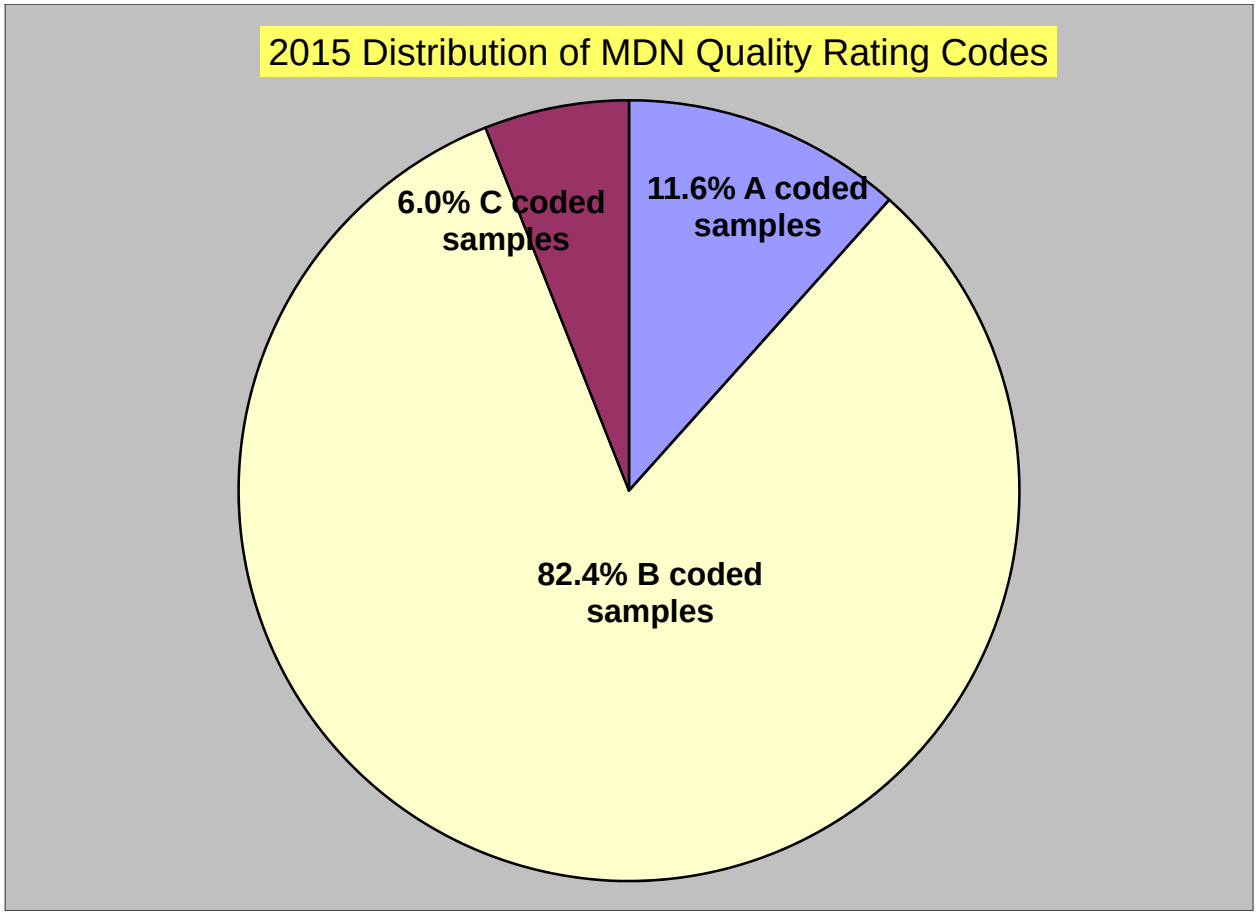

Figure 22 - Distribution of Quality Rating Codes for Samples Received in 2015

8. Summary and Conclusions

The HAL continued to maintain and demonstrate acceptable quality control in 2015. The five DQOs (precision, accuracy, representativeness, comparability, and completeness) were met. The MDL for total Hg was 0.129 ng/L at a PQL of 0.50 ng/L, and the MDL for MMHg was 0.021 ng/L at a PQL of 0.05 ng/L. Average bottle blank Hg and MMHg content was quantified at 0.008 ng Hg/bottle and -0.007 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=75) and system blanks (n=40) 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

AIRMoN	Atmospheric Integrated Research Monitoring Network
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
CVAFS	Cold Vapor Atomic Fluorescence Spectrometry
DI	Deionized Water
DMR-QA	Discharge Monitoring Report-Quality Assurance
DQO	Data Quality Objectives
EPA	Environmental Protection Agency
EFGS	Eurofins Frontier Global Sciences
HAL	Mercury (Hg) Analytical Laboratory
IAEA	International Atomic Energy Agency
ICB	Initial Calibration Blank
ICV	Initial Calibration Verification
IDL	Instrument Detection Limit
ISO/IEC	International Organization for Standardization (ISO) / International Electrotechnical Commission (IEC)
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MD	Matrix Duplicate
MDL	Method Detection Limit
MDN	Mercury Deposition Network
MMHg	Methyl Mercury
MRL	Method Reporting Limit
MS/MSD	Matrix Spike/ Matrix Spike Duplicate

NADP	National Atmospheric Deposition Program
NADP PO	National Atmospheric Deposition Program/Program Office
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
NIST	National Institute of Standards and Technology
NOS	Network Operations Subcommittee
NPDES	National Pollutant Discharge Elimination System
NRCC	National Research Council Canada
PO	Program Office
PQL	Practical Quantitation Limit
PT	Proficiency Test
QA	Quality Assurance
QC	Quality Control
QR	Quality Rating
QCS	Quality Control Sample
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
TNI	The NELAC Institute
THg	Total Mercury (Hg)
TV	True Value
USGS	United States Geological Survey

10. Appendix A:

10.1 QC Criteria

Table 10 - 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

eurofins | Frontier Global Sciences	**MDL Study: Total Mercury in Water (EPA 1631E, EFGS-137)**

Analyzed by Lou Anne McKown: LouAnn McKown

Report Prepared by Allison Kazlauskas: Allison Kazlauskas

Report Reviewed by David Wunderlich: David A. Wunderlich

MDL Study Data for Total Mercury in Waters
Sequence: 5K02019
Batch: F511017
Date: 11/03/15

Objective

To verify the method detection limit (MDL) for Total Mercury in water on instrument CV-AFS 2600-1 following an instrument conversion to in-vial sparging (IVS). The MDL study was performed using the analysis method EPA 1631 E (EFGS-137) and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for Total Mercury in water was determined to be **0.1293 ng/L**.

Analytical Method

A calibration was performed according to EPA 1631 E (EFGS-137). 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.

Reagent water was spiked with a 1 ng/mL Hg standard (LIMS #1505112). The MDL study consisted of ten aliquots (replicates) of this solution, with each replicate having a final spike level of 0.5035 ng/L of THg.

The results of these measurements are found in the table on page 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 in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$MDL = t^*\sigma = (2.821)^*(0.046) = \mathbf{0.1293ng/L}.$$

MDL Validation

The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, RSD CF, etc.) passed.

In accordance with EFGS-094 and the EFGS Quality Manual, an MDL must be verified whenever instrument hardware or operating conditions change (as with the IVS conversion). To verify an existing 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 **3.895.** Additionally, MDL verification requires that the calculated MDL be within 2x the existing MDL. Twice the existing MDL is 0.16 ng/L. The calculated MDL of **0.1293 ng/L** meets the verification criteria.

11/3/15
~~8/17/2015~~ 151102-1 KPK 11/3/15
THg26001-~~150817-1~~
Sequence: ~~5H18003~~ 5K02019
Batch: F511017

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

Sample	[THg], ng/L
F511017-BLK1	0.022
F511017-BLK2	0.017
F511017-BLK3	0.060
Mean	0.033
SD	0.023

Limits:
75-125%

	[THg], ng/L	[TV], ng/L	[%Rec]
F511017-BS3	0.585	0.504	116.2%
F511017-BS4	0.467	0.504	92.8%
F511017-BS5	0.508	0.504	100.9%
F511017-BS6	0.503	0.504	99.9%
F511017-BS7	0.485	0.504	96.3%
F511017-BS8	0.584	0.504	116.0%
F511017-BS9	0.571	0.504	113.4%
F511017-BSA	0.497	0.504	98.7%
F511017-BSB	0.483	0.504	95.9%
F511017-BSC	0.478	0.504	94.9%
Mean	0.516	0.504	102.5%
SD	0.046	0.000	9.10%

MDL	0.1293
TV/MDL	3.895
FMDL in LIMS	0.08
2x LIMS FMDL	0.16
FPQL in LIMS	0.50

Matrix Specific MDL Study: Total Mercury in Water According to EPA 1631 E, FGS-137

Analyzed by: Lou Anne Mcknown Lou Anne Mcknown 12/18/15
Report Prepared by: Allison Kazlauskas Allison Kazlauskas 12/18/15
Mercury Laboratory Manager: Ryan Nelson Ryan Nelson 12/18/15
QA Manager: Dave Wunderlich David A. Wunderlich 12/18/2015

Sequence: 5L15018 (THg26002-151215-1)
Batch: F512190
Date: 12/15/15

Objective

Verify the method detection limit (MDL) for total mercury in water (CVAFS 2600-2), using the preservation method FGS-012 and analysis method EPA 1631 E (FGS-137), and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for Total Mercury in water was determined to be **0.064ng/L THg**.

Analytical Method

A calibration was performed according to EPA 1631 E (FGS-137). 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 waster spiked with a 10 ng/mL Hg standard (LIMS # 1506990) 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 0.500 ng/L of THg oxidized to 1% with BrCl.

The results of these measurements are found in the table on the page 3, as well in the raw data sheets (ID#THg26002-151215-1). All results are reported corrected for the instrument blanks and the 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, where σ is the standard deviation of the results obtained on replicates.

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

The MDL calculated for the 0.500 ng/L spike is (2.821)*(0.023, or **0.064 ng/L**.

Matrix Specific MDL Study: Total Mercury in Water According to EPA 1631 E, FGS-137

MDL 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 **7.84**. 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 **0.064ng/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, FGS-137

MDL Summary Table
Total Mercury for Waters
MDL Study Data for THg2600-2
Eurofins North Creek Pkwy North, Suite 400
Bothell, WA 98011

Date: 12/15/15
Dataset ID:THg26002-151215-1
Sequence: 5L15018
Batch: F512190

Sample	[THg], ng/L		
F512190-BLK1	0.07		
F512190-BLK2	0.02		
F512190-BLK3	0.01		
Mean	**0.033**		Limits:
SD	**0.032**		75-125%
Sample	**[THg], ng/L**	**Spike Level, [TV], ng/L**	**[%Rec]**
F512190-BS3	0.43	0.50	86.0%
F512190-BS4	0.40	0.50	80.0%
F512190-BS5	0.46	0.50	92.0%
F512190-BS6	0.46	0.50	92.0%
F512190-BS7	0.48	0.50	96.0%
F512190-BS8	0.46	0.50	92.0%
F512190-BS9	0.44	0.50	88.0%
F512190-BSA	0.45	0.50	90.0%
F512190-BSB	0.45	0.50	90%
F512190-BSC	0.47	0.50	94.0%
Mean	**0.450**	**0.50**	**90.0%**
SD	**0.023**	**0.000**	**4.3%**

MDL:	**0.064**
TV/MDL	**7.84**
FMDL in LIMS	**0.08**
2x LIMS FMDL	**0.16**
FPQL in LIMS	**0.50**

Quality Assurance\MDLs PQLs & RLs\Complete Reports of MDL Studies by Analyte and Matrix\Current\ MDL Study (THg)\MDL THg2600_2 water 1631 5L15018

eurofins | Frontier Global Sciences	**MDL Study:** **Total Mercury in Water (EPA 1631E, EFGS-137)**

Analyzed by: Blake Cassidy 7/13/15
Report Prepared by: Kristine Teffeau 7/13/15
Report Reviewed by: Dave Wunderlich 7/17/15

Sequence: 5F04013 (THg26003-150604-2)
Batch: F506060
Date: 6/4/15

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. The MDL study was performed using the preservation method EFGS-012 and analysis method EPA 1631 E (EFGS-137), and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for Total Mercury in water was determined to be **0.0561 ng/L**.

Analytical Method

A calibration was performed according to EPA 1631 E (EFGS-137). 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.

Reagent water was spiked with a 1 ng/mL Hg standard (LIMS #1503484) and preserved with BrCl. The MDL study consisted of ten aliquots (replicates) of this solution, with each replicate having a final spike level of 0.4028 ng/L of THg oxidized to 1% with BrCl. The PQL study replicates were prepared similarly using a 10 ng/mL Hg standard (LIMS #1502994) for a final spike concentration of 0.5035 ng/mL.

The results of these measurements are found in the table on pages 2-3, 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 0.500 ng/L spike was (2.821)*(0.038), or **0.0561 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 7.177. 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 0.0561 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 0.5035 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 Study
6/4/2015
THg26003-150604-2
Sequence: 5F04013
Batch: F506060

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

Sample	[THg], ng/L
F506060-BLK1	0.086
F506060-BLK2	0.000
F506060-BLK3	0.000
Mean	0.043
SD	0.061

	[THg], ng/L	[TV], ng/L	Limits: 75-125% [%Rec]
F506060-BSD	0.487	0.4028	121%
F506060-BSE	0.440	0.4028	109%
F506060-BSF	0.423	0.4028	105%
F506060-BSG	0.447	0.4028	111%
F506060-BSH	0.441	0.4028	109%
F506060-BSI	0.429	0.4028	107%
F506060-BSJ	0.433	0.4028	108%
F506060-BSK	0.412	0.4028	102%
F506060-BSL	0.449	0.4028	111%
F506060-BSM	0.438	0.4028	109%
Mean	0.440	0.403	109%
SD	0.020	0.000	4.94%

MDL	0.0561
TV/MDL	7.177
FMDL in LIMS	0.08
2x LIMS FMDL	0.16

PQL Study
6/4/2015
THg26003-150604-2
Sequence: 5F04013
Batch: F506060

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

Sample	[THg], ng/L		
F506060-BLK1	0.086		
F506060-BLK2	0.000		
F506060-BLK3	0.000		
Mean	0.043		Limits:
SD	0.061		75-125%
	[THg], ng/L	[TV], ng/L	[%Rec]
F506060-BS3	0.531	0.5035	105%
F506060-BS4	0.527	0.5035	105%
F506060-BS5	0.525	0.5035	104%
F506060-BS6	0.544	0.5035	108%
F506060-BS7	0.522	0.5035	104%
F506060-BS8	0.533	0.5035	106%
F506060-BS9	0.530	0.5035	105%
F506060-BSA	0.547	0.5035	109%
F506060-BSB	0.548	0.5035	109%
F506060-BSC	0.541	0.5035	108%
Mean	0.535	0.504	106%
SD	0.010	0.000	1.89%

FPQL in LIMS 0.50

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

Analyzed by: Don Moran Don Moran 2-9-16
Mercury Supervisor: Ryan Nelson 2/9/16
Report Prepared by: Allison Kazlauskas 2/9/16
Report Reviewed by: David Wunderlich D. Wunderlich 2/9/2016

MDL Study Data for Methyl Mercury in Precipitation Samples
Preparation Method: EFGS-013
Analysis Method: EFGS-070
Dataset: MMHg15-151217-1

Objective To verify the existing Method Detection Limit (MDL). This MDL verification study applies to Methyl Mercury in precipitation samples as prepared by method EFGS-013 and analyzed by method EFGS-070. 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 **0.02095 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 0.8046 was used and the calibration was performed according to EFGS-070.

The MDL study consisted of a 0.050 ng/L MHg solution divided into ten replicates, which were distilled 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 were **corrected** for the instrument blanks (0.20 units). All final concentrations were **corrected** for the preparation blanks (0.001 ng/L).

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 in the following equation, where σ is the standard deviation of the results obtained on the replicates.

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

The MDL calculated from these data is (2.821)*(0.007), or **0.02095 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 **2.389** 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 10 replicates were spiked at the current PQL (0.050 ng/L) and recovered within the control limits.

02/08/16
MMHg15-151217-1
MDN MDL Study

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

Sample	[MHg], ng/L		
F512207-BLK1	-0.004		
F512207-BLK2	-0.004		
F512207-BLK3	0.000		
Mean	0.001		
SD	0.002		65-135%
	[MHg], ng/L	[TV], ng/L	[%Rec]
F512207-BS2	0.043	0.050	85.9%
F512207-BS3	0.048	0.050	95.9%
F512207-BS4	0.050	0.050	99.9%
F512207-BS5	0.061	0.050	121.9%
F512207-BS6	0.066	0.050	131.9%
F512207-BS7	0.048	0.050	95.9%
F512207-BS8	0.043	0.050	85.9%
F512207-BS9	0.048	0.050	95.9%
F512207-BSA	0.052	0.050	103.9%
F512207-BSB	0.055	0.050	109.9%
Mean	0.051	0.050	102.7%
SD	0.007	0.000	14.8%

MDL	0.02095
TV/MDL	2.389
Current MDL	0.026
2x Current MDL	0.052
PQL	0.050