National Atmospheric Deposition Program

Mercury Analytical Laboratory

2014 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 110 active sites in the United States and Canada at the end of 2014. In 2014, 4 sites were shut down, 4 new sites were added and no sites were re-started.

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

EFGS continued to maintain and demonstrate acceptable quality control (QC) in 2014. 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 2014:

- Senior analyst Phil Kilner resigned in August; S&R technician Richard Hedelund resigned in October; senior analyst David Westby resigned in November; temporary MDN technicians Ivy Butler (S&R) and Connor Foote (Equipment Cleaning) began their assignments in November; sample prep technician Duyen Hinh was on vacation in November and December; analyst Owen Valentine resigned in December; and two new analysts – Don Moran and Lou Anne McKown started in January 2015.
- A new Tekran 2600 instrument (2600_3) was installed in July 2014.
- A new Tekran 2700 instrument (2700_1) equipped with an auto-sampler was installed in July 2014, but the analysis of MDN samples for methyl mercury was still accomplished by the bubbler instrument throughout 2014.

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 2014. 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 instrument 2600-1 and 2600-2 (datasets THg26001-141014-1and THg26002-141014-1), were performed at 0.50 ng/L (the PQL is 0.50 ng/L). The TV/MDL ratios for both instruments were less than 10, but the MDL on 2600-2 did not fall within 2X the previously established MDL. Since only the study on 2600-1 was valid, 0.129 ng/L will be used to evaluate data.

A MDL study was performed for methyl mercury on instrument #15 in dataset MMHg15-150430-1 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 0.02166 ng/L will be used to evaluate data.

Table 1 - MDL Studies for 2014 Summary Table

Instrument	Dataset	MDL (ng/L)	PQL (ng/L)	PQL/MDL
FI-AFS 2600-1	THg26001-141014-1	0.129	0.50	3.87
FI-AFS 2600-2	THg26002-141014-1	0.174*	0.50	2.88
CV-GC-AFS #15	MMHg15-150430-1	0.022	0.050	2.309

* - did not verify previously established MDL.

1.3 Accreditations

Eurofins Frontier Global Sciences currently holds certifications through departments in eight states: California Department of Public Health, Florida Department of Health, State of Louisiana Department of Environmental Quality, State of New York Department of Health, State of New Jersey Department of Environmental Protection, Washington Department of Ecology, Wisconsin Department of Natural Resources, and State of Nevada Division of Natural Resources. Since July 2011, Louisiana's Department of Environmental Quality has been Eurofins Frontier Global Sciences' primary accreditation body for the National Environmental Laboratory Accreditation Program (NELAP). Frontier is also ISO/IEC 17025:2005 and Department of Defense accredited through Perry Johnson Laboratory Accreditation.

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 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. However, sample and laboratory bottle blank results are not corrected for BrCl and method blanks.

There were four laboratory bottle blanks that exceeded the MDL and PQL for methyl mercury. 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

2014 Laboratory Bottle Blanks	n	Average (ng/bottle)	Standard Deviation	MDL (ng/bottle)	PQL (ng/bottle)
Total Mercury	90	0.011	0.006	0.0026	0.010
Methyl Mercury	12	0.007	0.018	0.00044	0.001

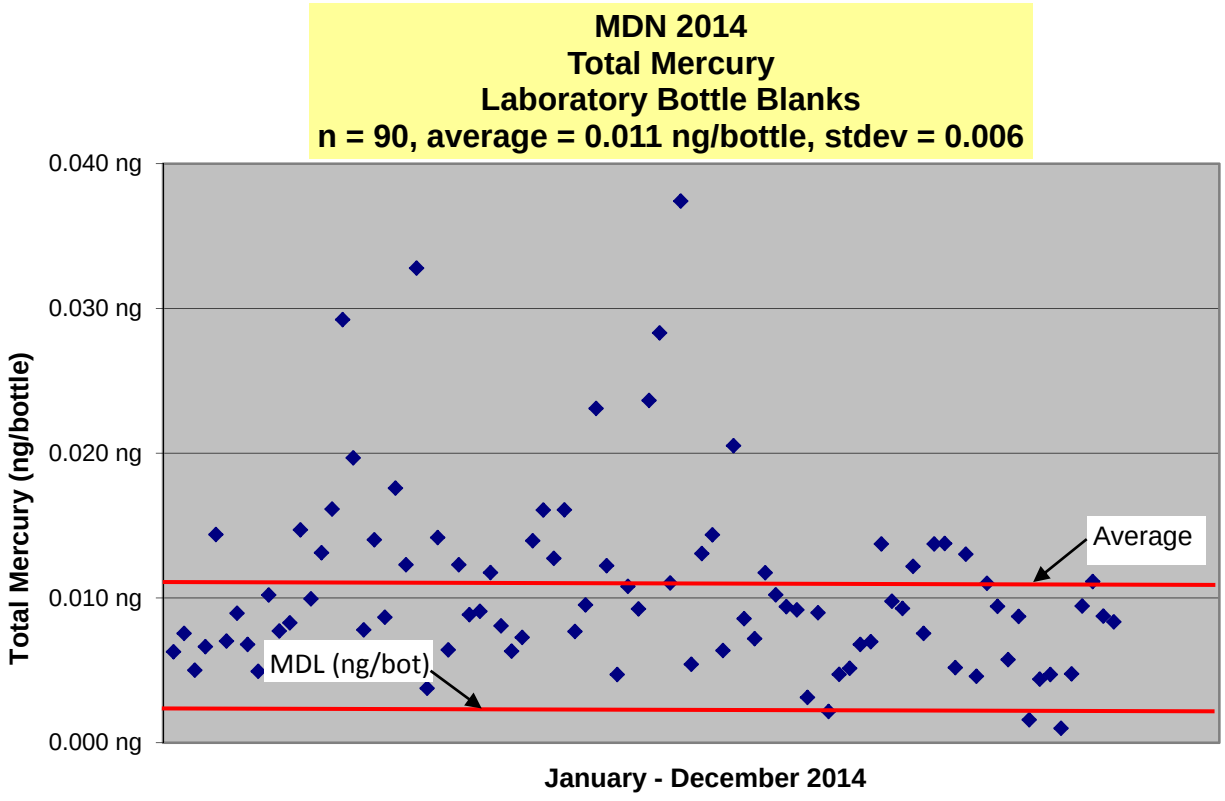

Figure 1 - 2014 Plot of Total Mercury Mass in Laboratory Bottle Blanks for 90 Samples

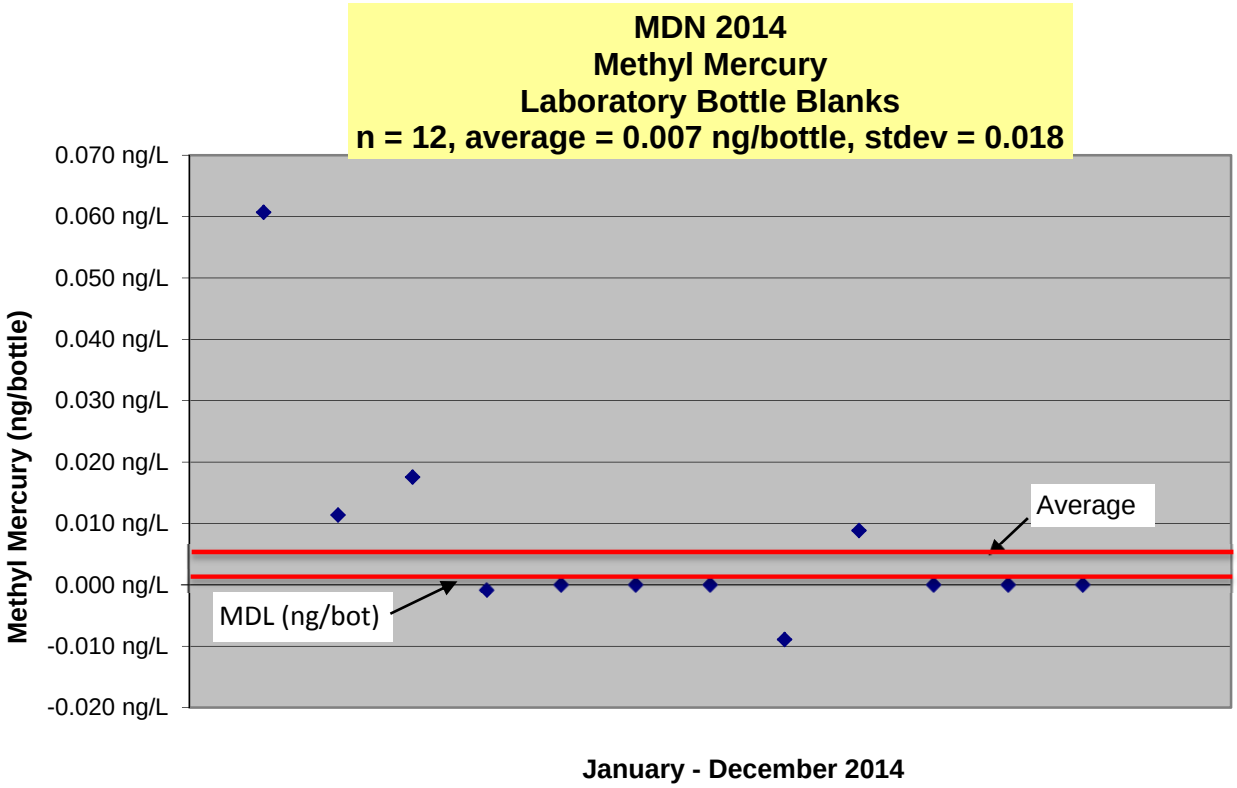

Figure 2 - 2014 Plot of Methyl Mercury Mass in Laboratory Bottle Blanks for 12 Samples

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. Consequently, 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, and 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. 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 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).

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 the preparation blanks analyzed for total mercury during 2014 were less than the control limit of <0.25 ng/L used at the laboratory and less than the EPA criteria of 0.50 ng/L (table 3 and figure 3). Higher values (but less than the control limit) for preparation blanks in the fourth quarter could be caused by samples from environmental remediation projects that were being processed by the lab at that time.

All of the preparation blanks analyzed for methyl mercury during 2014 were less than the EFGS control limit of 0.045 ng/L (figure 4). The standard deviation for 2014 of 0.013 ng/L is less than the EPA requirement of <0.015 ng/L.

Table 3 - Preparation Blanks Summary Table

2014 Preparation Blanks	n	Average (ng/L)	Std Dev (ng/L)	MDL (ng/L)	HAL Control Limit (ng/L)	EPA 1631E/1630
Total Mercury	564	-0.016	0.046	0.129	0.25	< 0.50
Methyl Mercury	63	0.0016	0.0128	0.022	0.045	Mean <0.045 σ<0.015

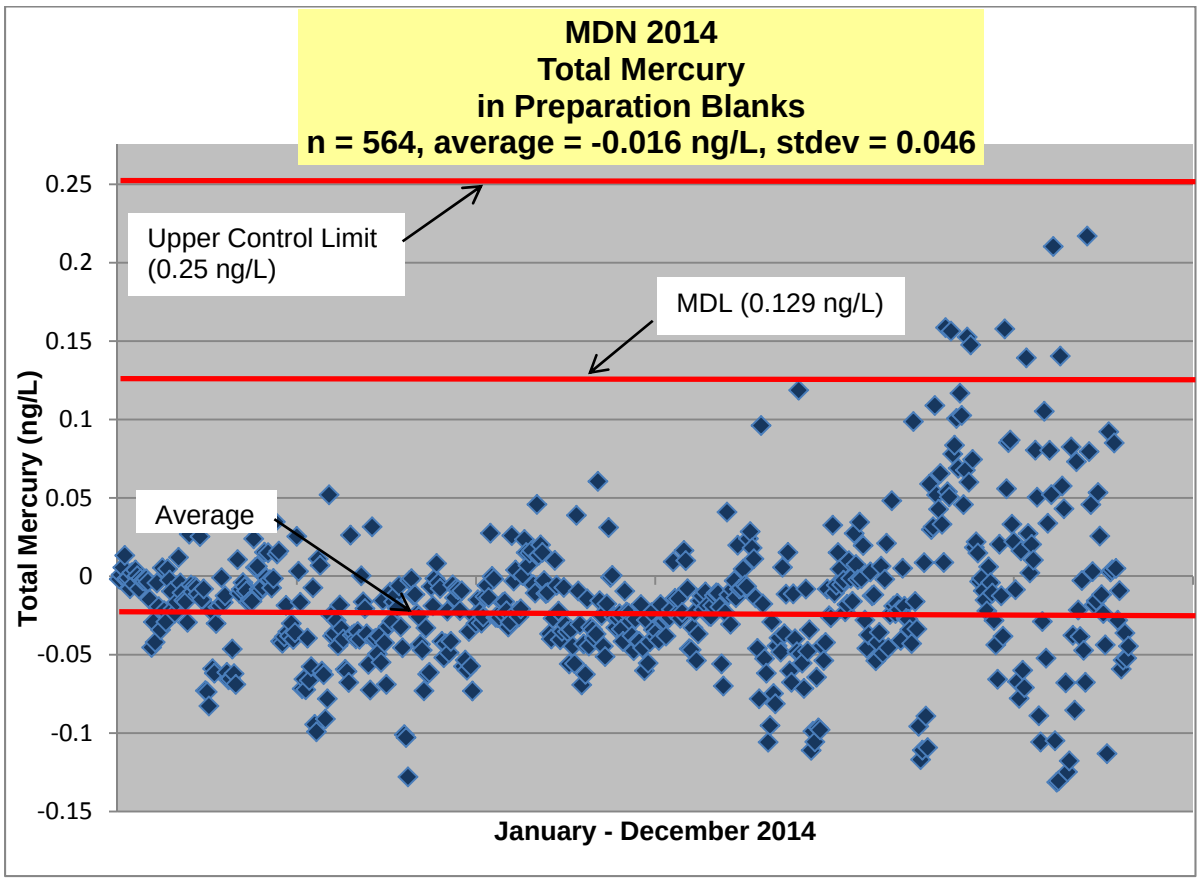

Figure 3 - 2014 Control Chart for Total Mercury Concentration in Reagent Preparation Blanks

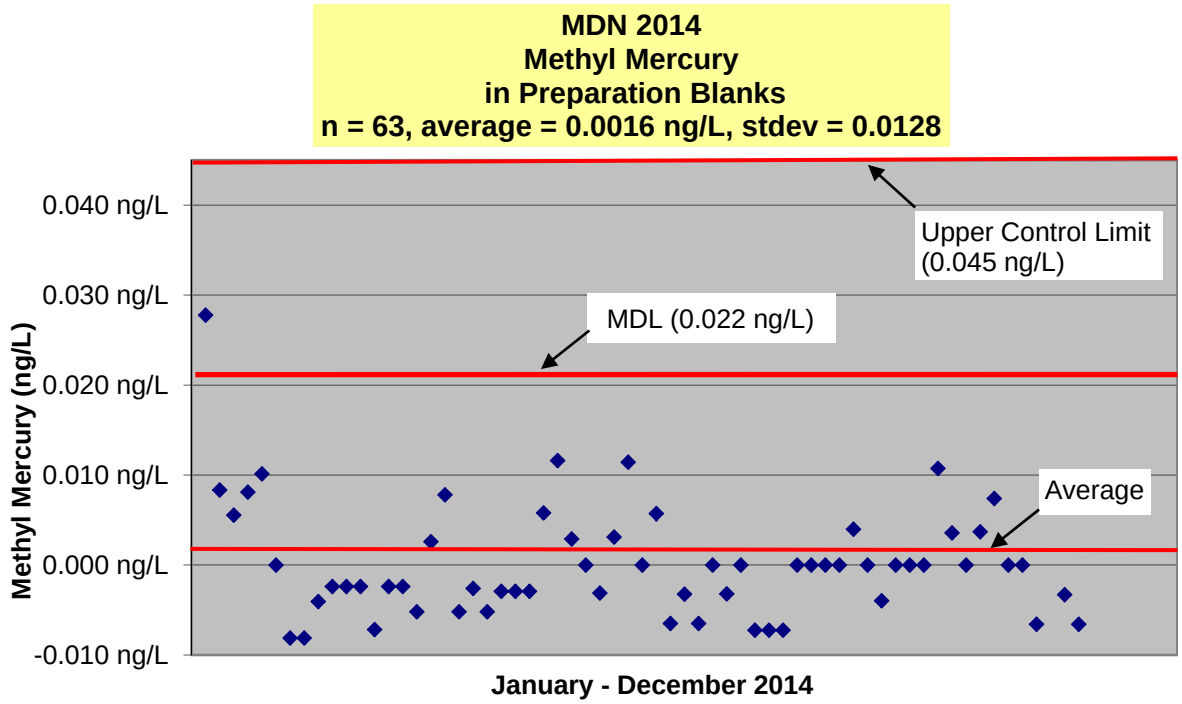

Figure 4 - 2014 Control Chart for Methyl Mercury Concentration in Reagent Preparation Blanks

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 95-102%. 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 (figure 5).

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

Table 4 - Continuing Calibration Standard Summary Table

2014 Continuing Calibration Standard	n	Average recovery (%)	Std dev of recovery (%)	Control Limit (%)	EPA 1631E/1630 Control Limits (%)
Total Mercury	629	102.0	5.7	77-123	77-123
Methyl Mercury	162	88.1	11.0	67-133	67-133

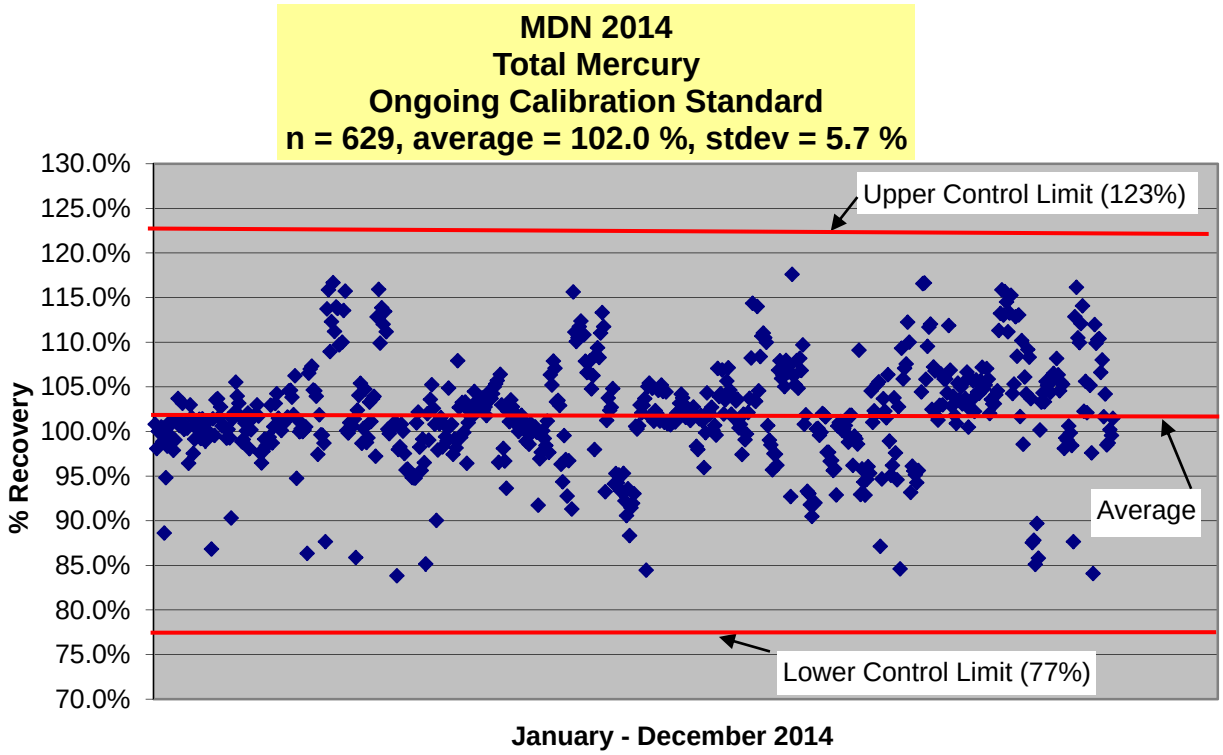

Figure 5 - 2014 Control Chart for Total Mercury Continuing Calibration Standard Percent Recovery

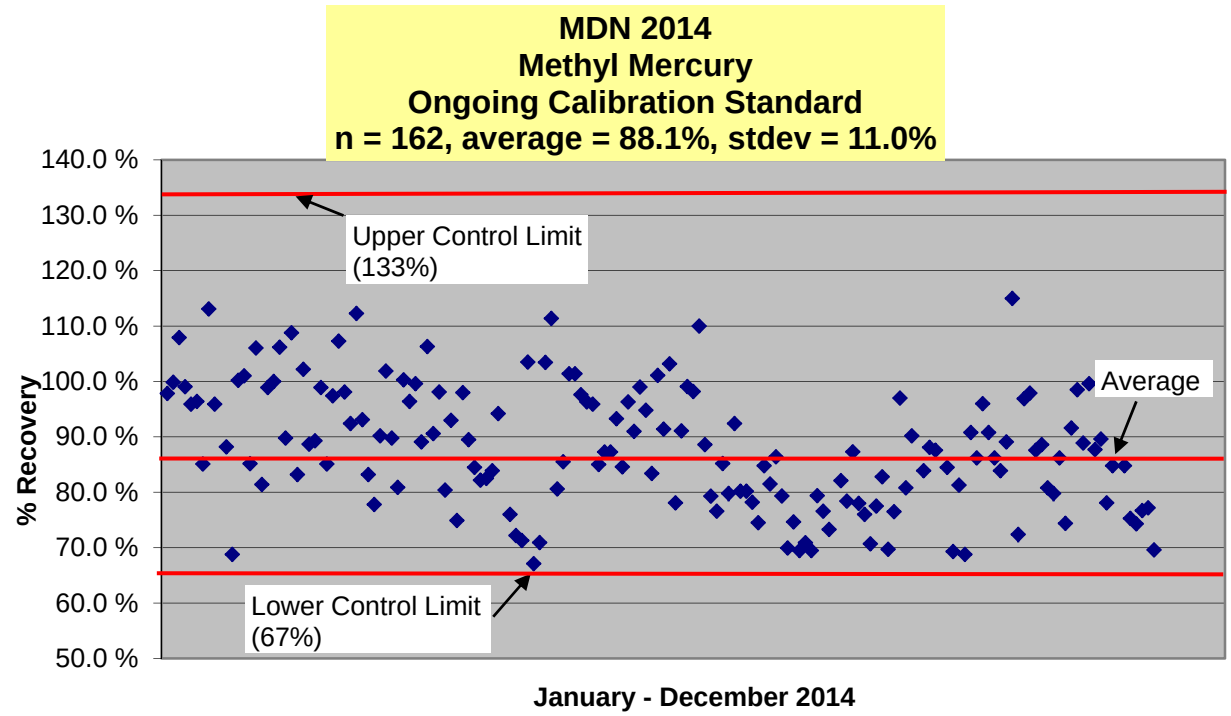

Figure 6 - 2014 Control Chart for Methyl Mercury Ongoing Calibration Standard Percent Recovery

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).

All of the ongoing CCBs for methyl mercury were less than 0.025 ng/L, which is the control limit used for MDN analysis at HAL.

Table 5 - Ongoing Calibration Blanks Summary Table

2014 Ongoing Calibration Blanks	n	Average (ng/L)	Std Dev (ng/L)	MDL (ng/L)	HAL Control Limits
Total Mercury	626	0.0260	0.049	0.129	Individually <0.50 ng/L, mean <0.25 ng/L with a standard deviation <0.10 ng/L
Methyl Mercury	128	-0.001	0.003	0.022	0.025

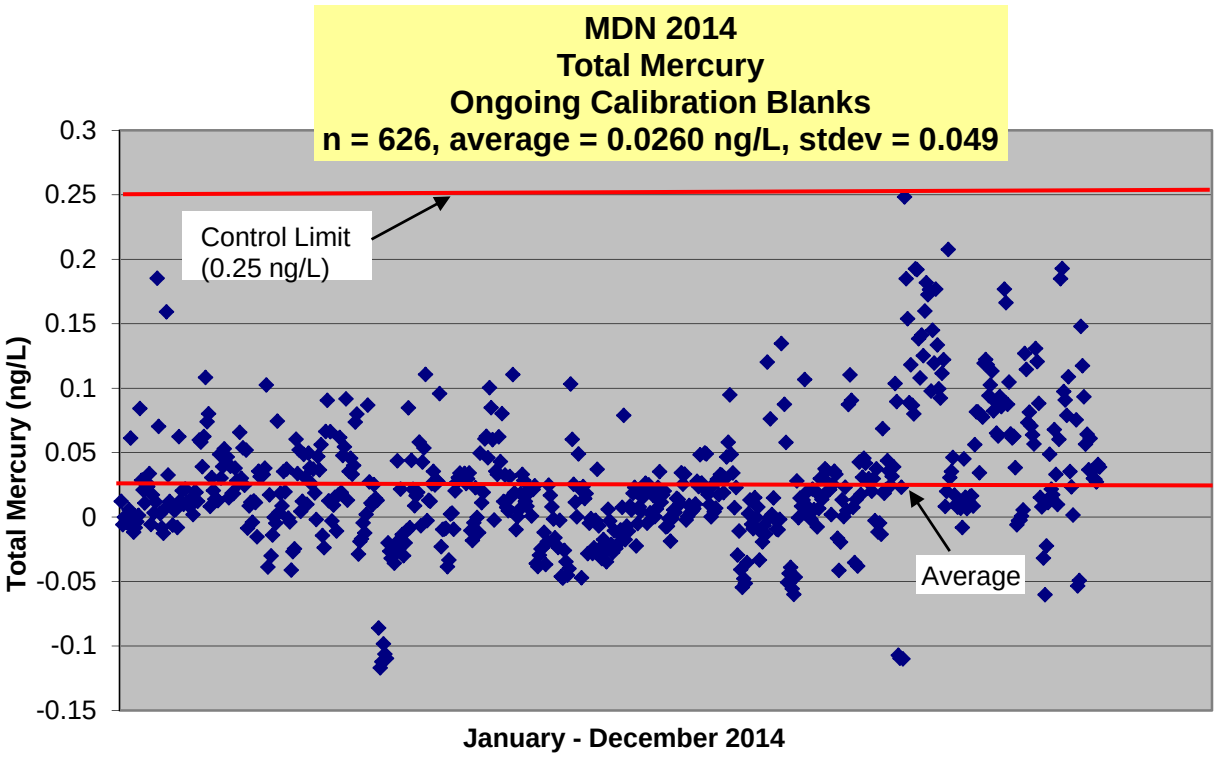

Figure 7 - 2014 Control Chart for Total Mercury Continuing Calibration Blanks

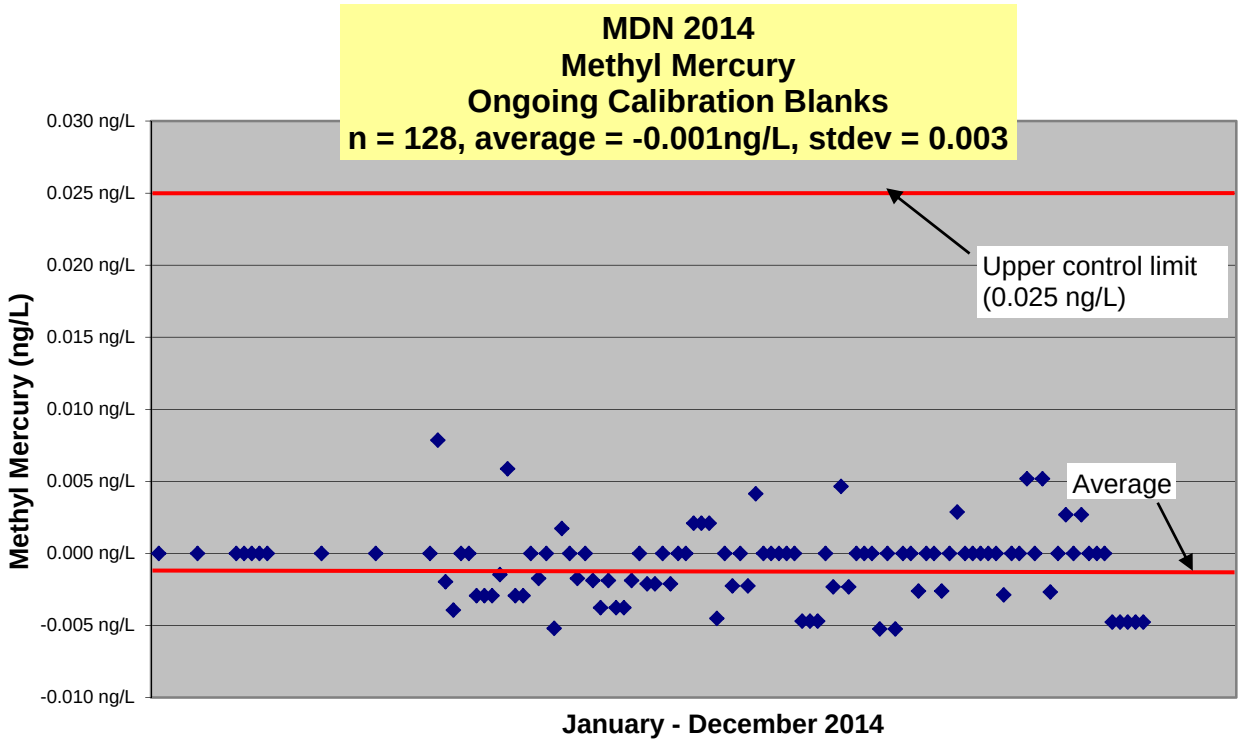

Figure 8 - 2014 Control Chart for Methyl Mercury Continuing Calibration Blanks

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, one of the RPDs calculated for duplicate pairs exceeded the control limit of 25% RPD (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 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 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 2014

2014 Matrix Duplicates	n	Average RPD (%)	Std Dev (%)	HAL control Limit (%)	EPA 1631E/1630 Control Limits
Total Mercury	566	2.6	3.1	25	NA
Methyl Mercury	17	11.4	5.4	25	NA

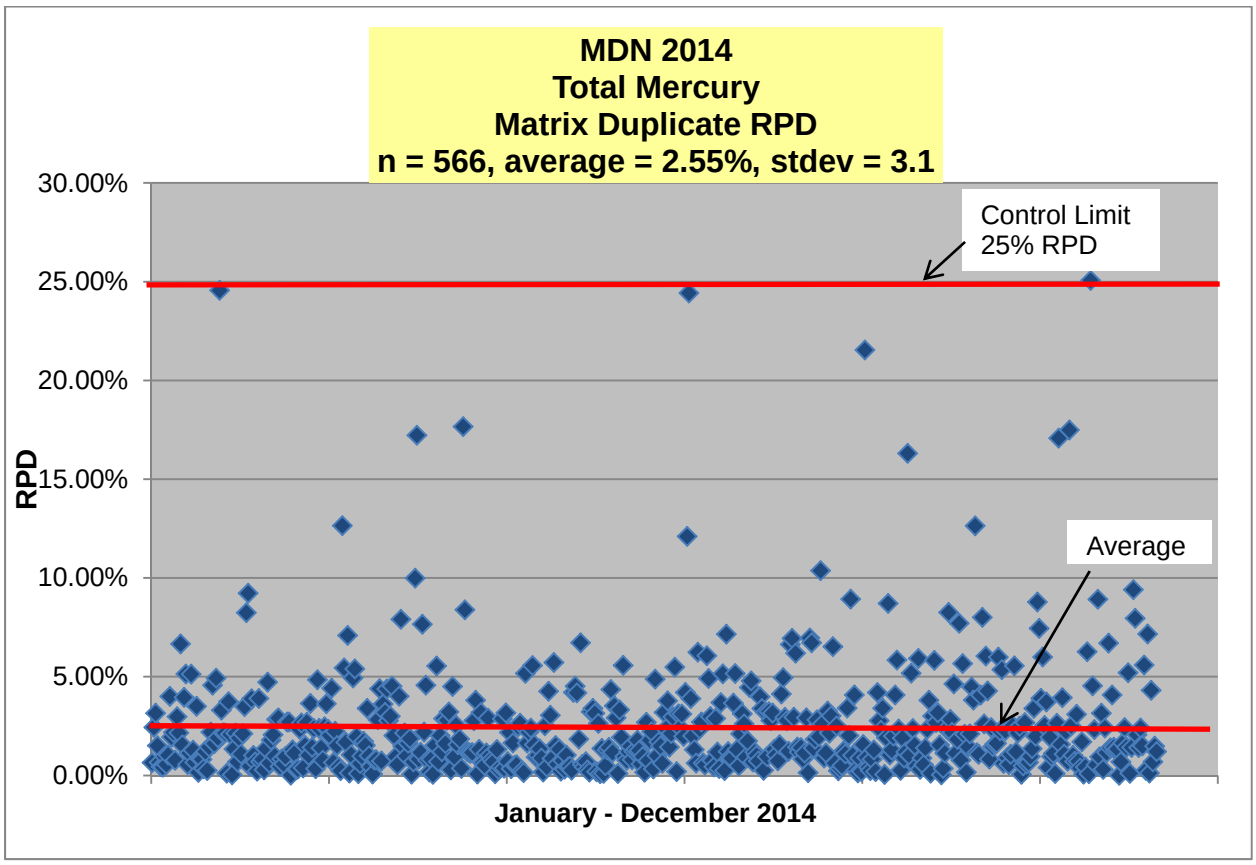

Figure 9 - 2014 Control Chart of the Relative Percent Differences for Total Mercury Concentrations in Matrix Duplicates

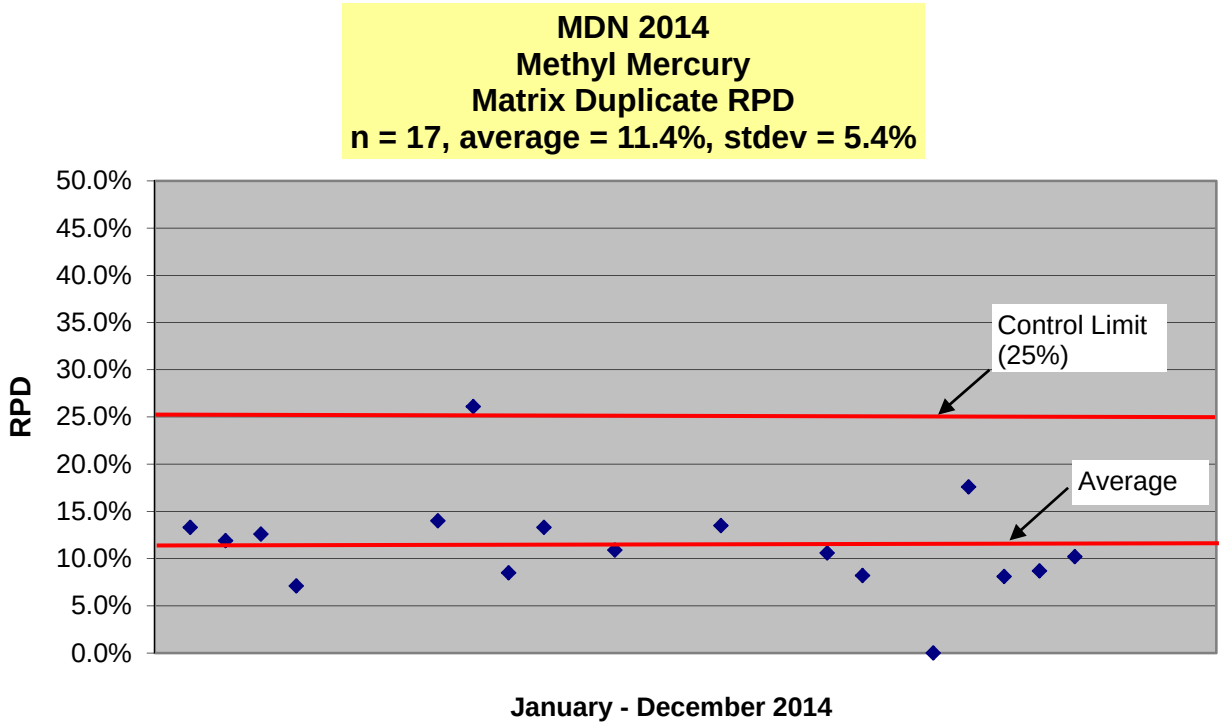

Figure 10 - 2014 Control Chart of the Relative Percent Differences for Methyl Mercury Concentrations in Matrix Duplicates

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 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. 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).

Six RPD values for methyl mercury exceeded the 25% control limit used at HAL (table 8 and figure 13).

Table 7 - Matrix Spike Recoveries for 2014 Samples

2014 Matrix Spikes	n	Average Recovery (%)	Std Dev of Recovery (%)	HAL Control Limits	EPA 1631E/1630 Control Limits (%)
Total Mercury	565	103.6	5.9	75-125	71-125
Methyl Mercury	102	103.9	13.2	65-135	65-135

Table 8 - Matrix Spike/Matrix Spike RPD for 2014 Samples

2014 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	48	12.8	9.3	<25	<35

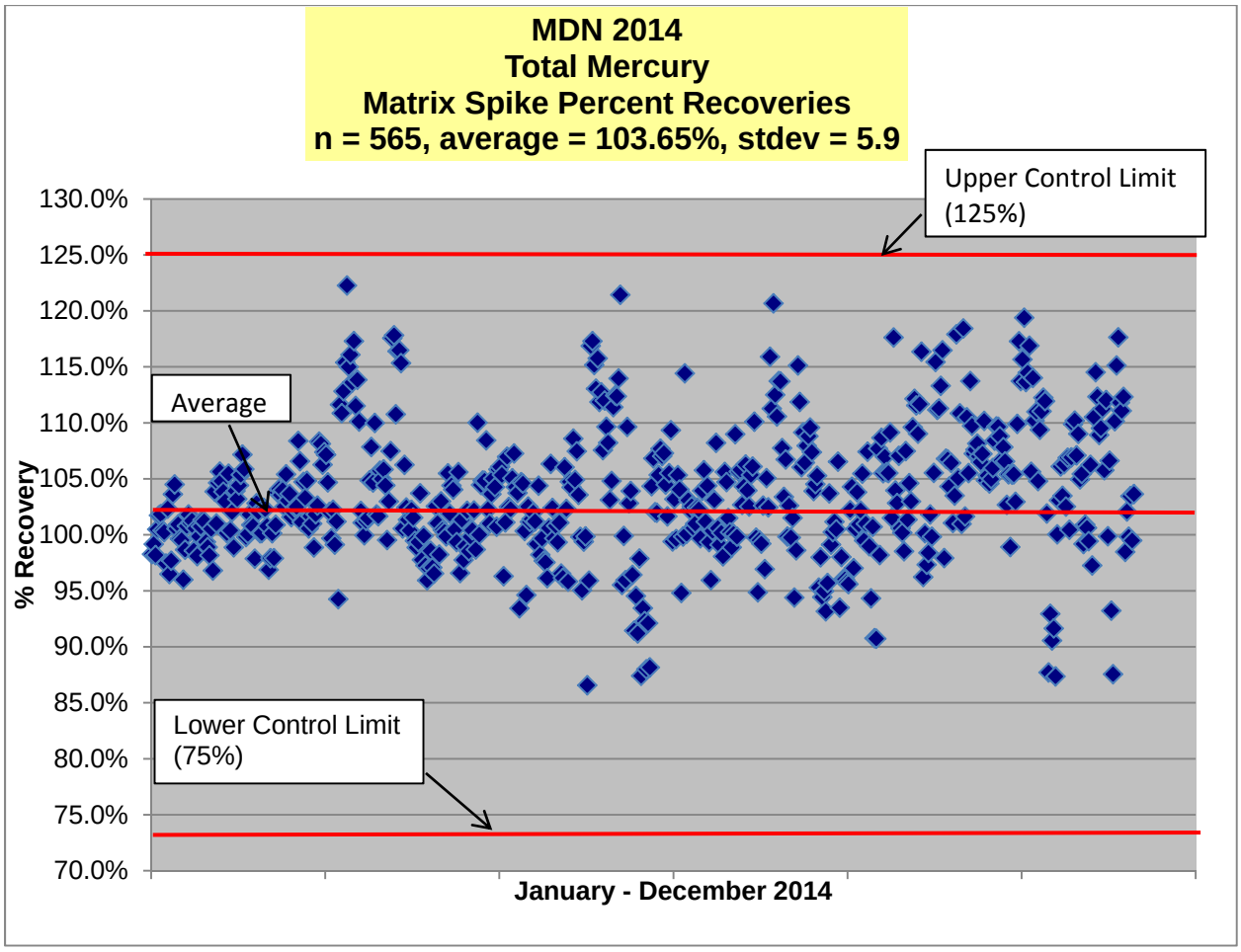

Figure 11 - Control Chart for Total Mercury Percent Recovery in Matrix Spikes During 2014

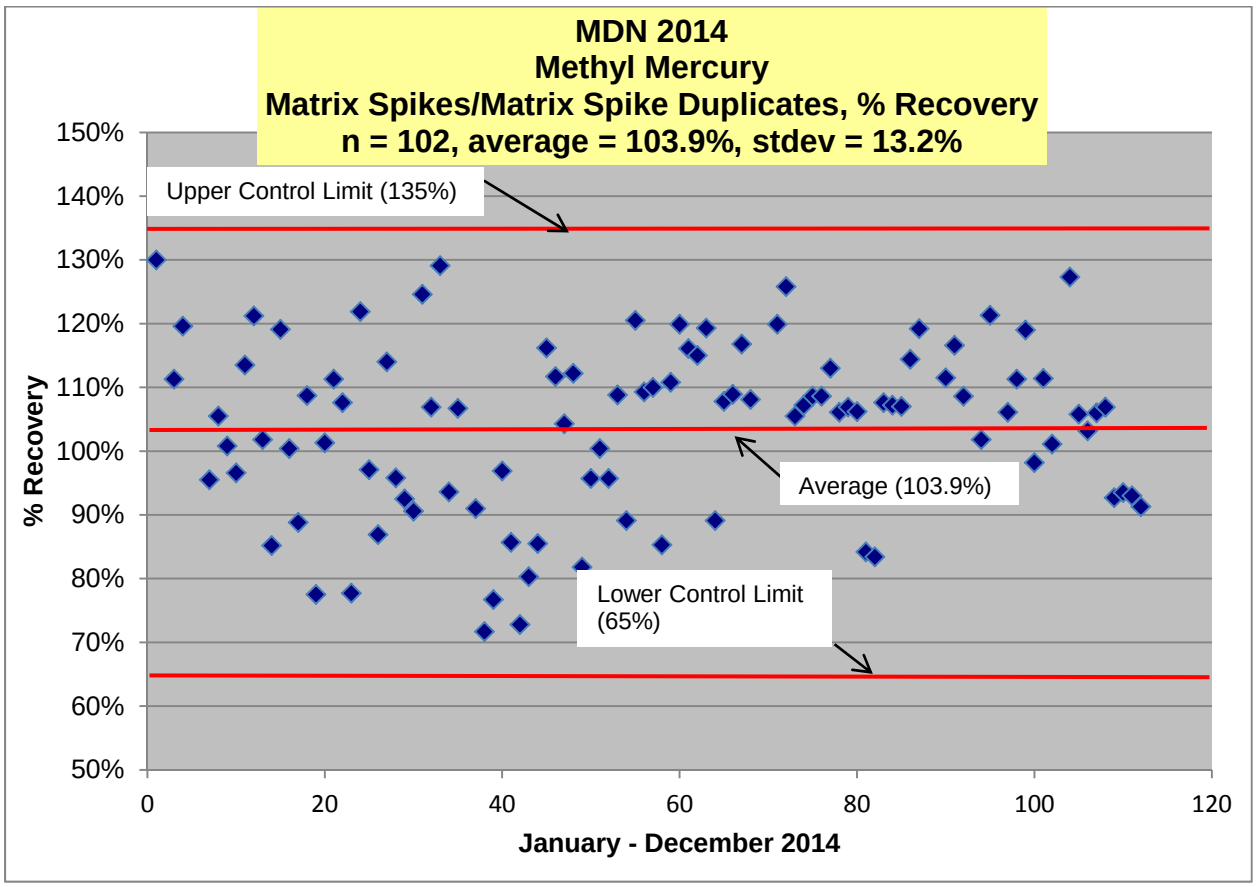

Figure 12 - Control Chart for Methyl Mercury Percent Recovery in Matrix Spikes During 2014

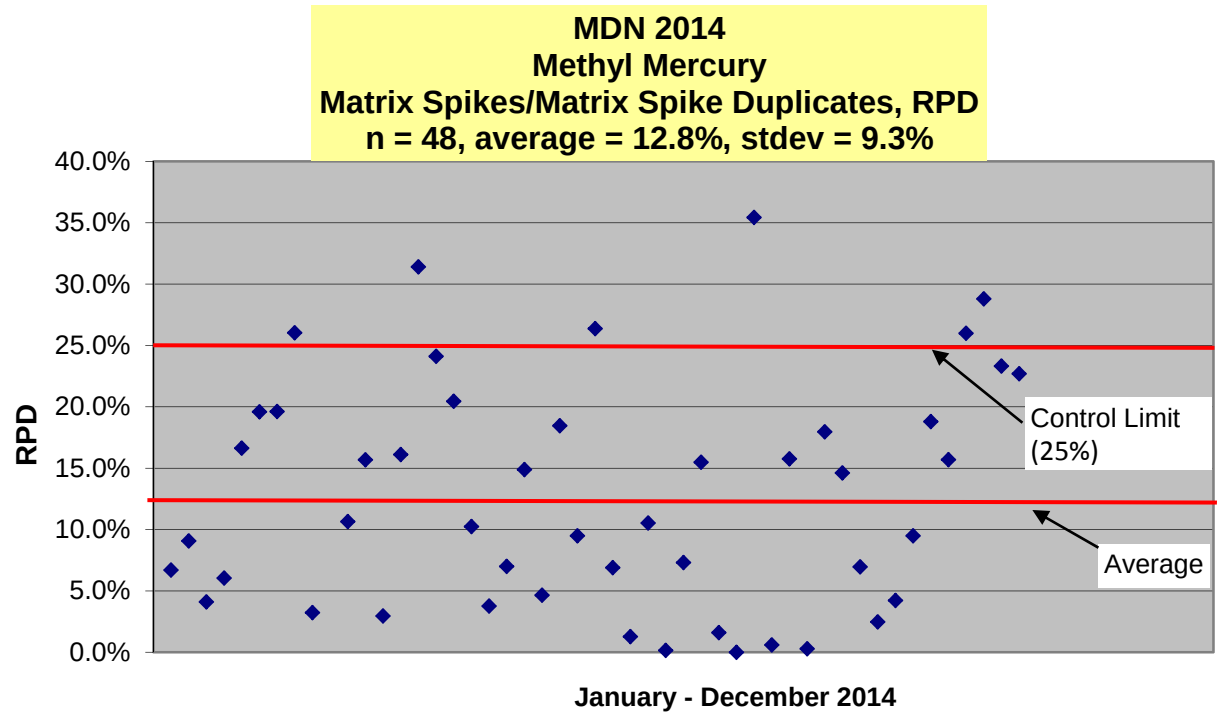

Figure 13 - Control Chart of the Relative Percent Differences for Methyl Mercury Matrix Spike / Matrix Spike Duplicate Pairs during 2014.

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%. The 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 378 certified reference material recoveries for total mercury was 102.8% with a standard deviation of 5.3% (figure 14). All CRM values were within the actual control limit of 75-125% used in the laboratory. The average RPD value for the CRM/CRM duplicate was 2.3% (n=189), with a standard deviation of 2.6%. All of the RPD values were below the 25% limit used in the laboratory, demonstrating good precision between the CRMs and CRM duplicates (figure 15).

The mean recovery of 56 blank spikes and blank spike duplicates (BS/BSD) for methyl mercury was 104.1% with a standard deviation of 13.1% (figure 16). All recovery values are within the 70-130% control limit used at HAL. The average RPD value for the BS/BSD was 11.7% (n=26) with a standard deviation of 9.5%. One RPD value was above the 25% limit used in the laboratory (figure 17).

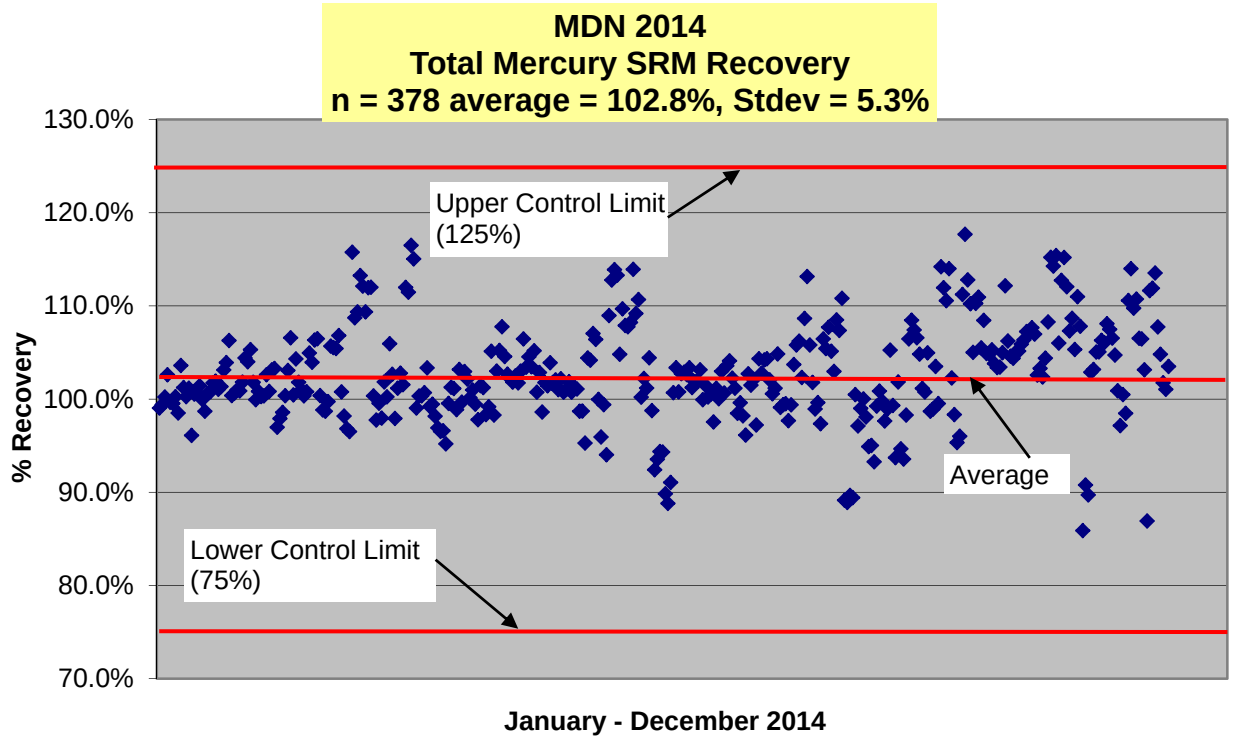

Figure 14 - Control Chart for Total Mercury Percent Recovery in Certified Reference Material Samples During 2014

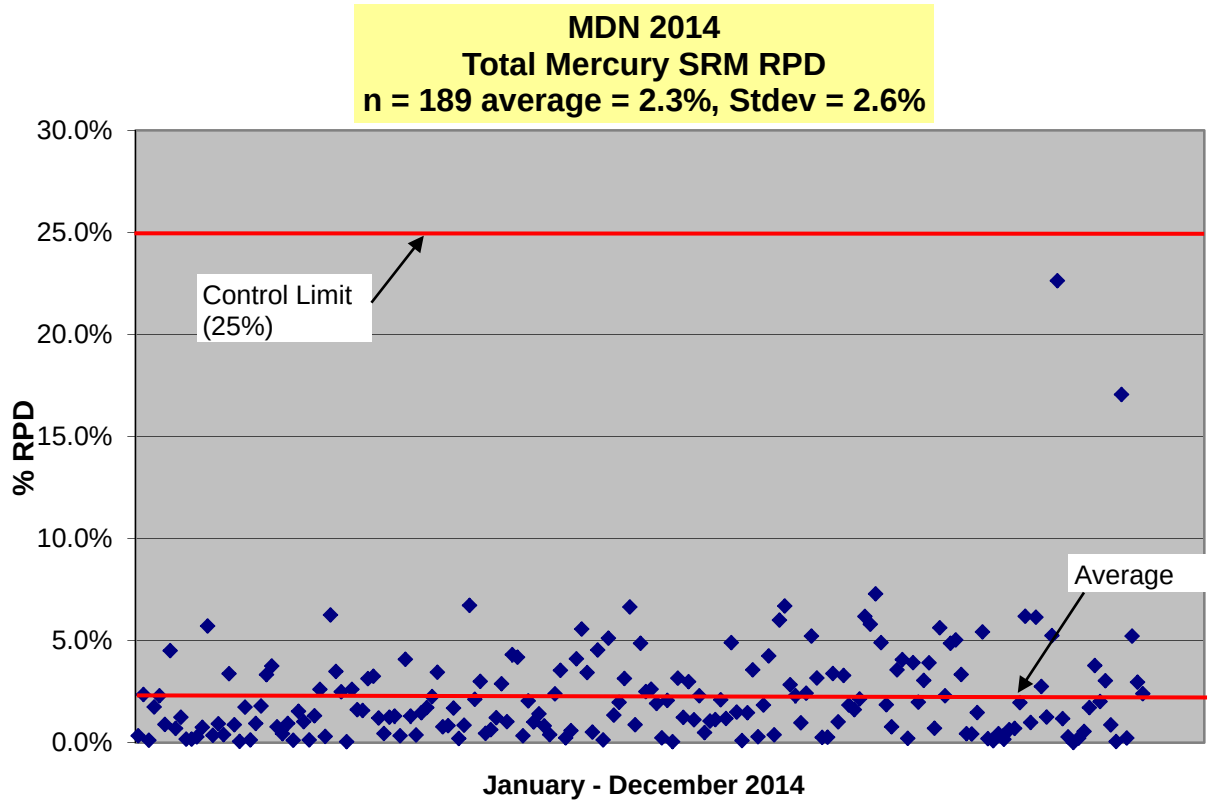

Figure 15 - Control Chart for Total Mercury Relative Percent Difference (%RPD) in CRM /CRM Duplicates Samples During 2014

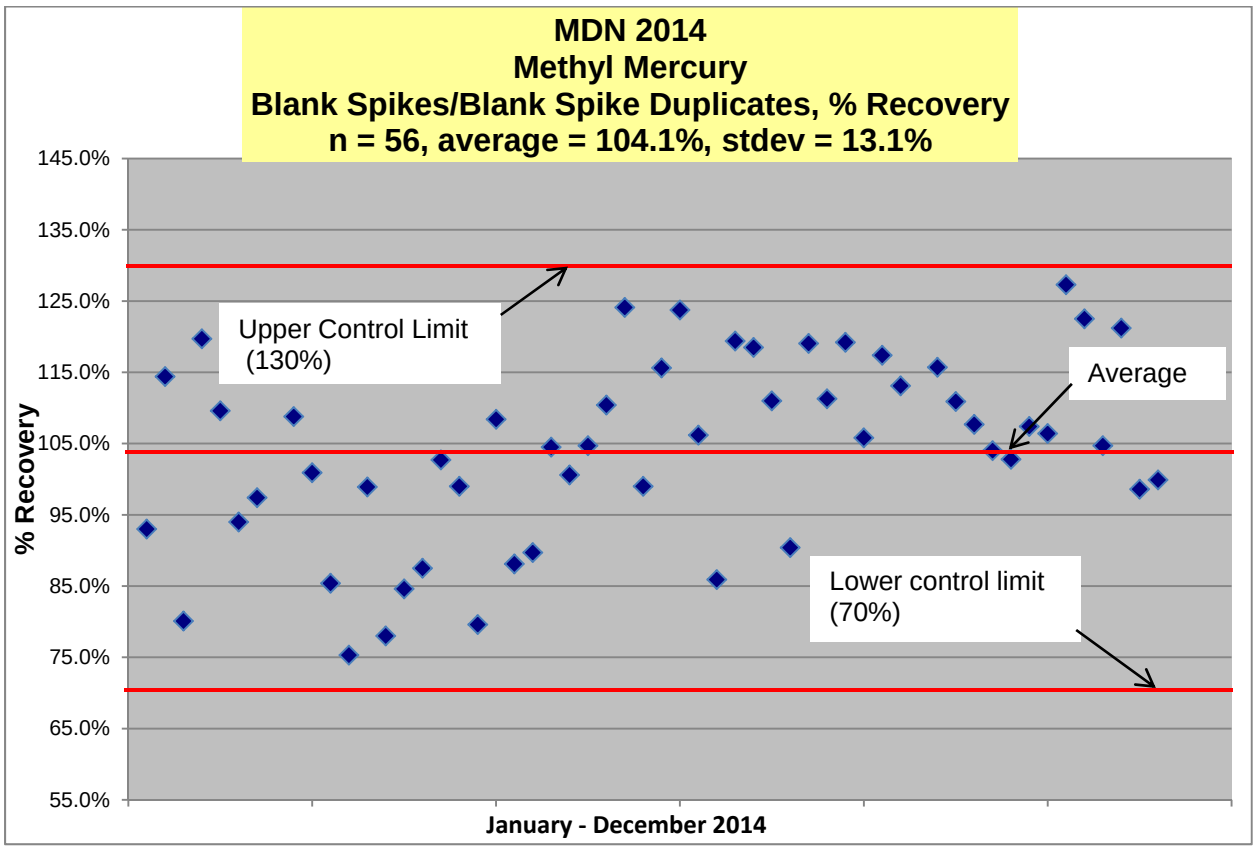

Figure16 - Control Chart for Methyl Mercury Percent Recovery in Blank Spikes/Blank Spikes Duplicates Samples During 2014

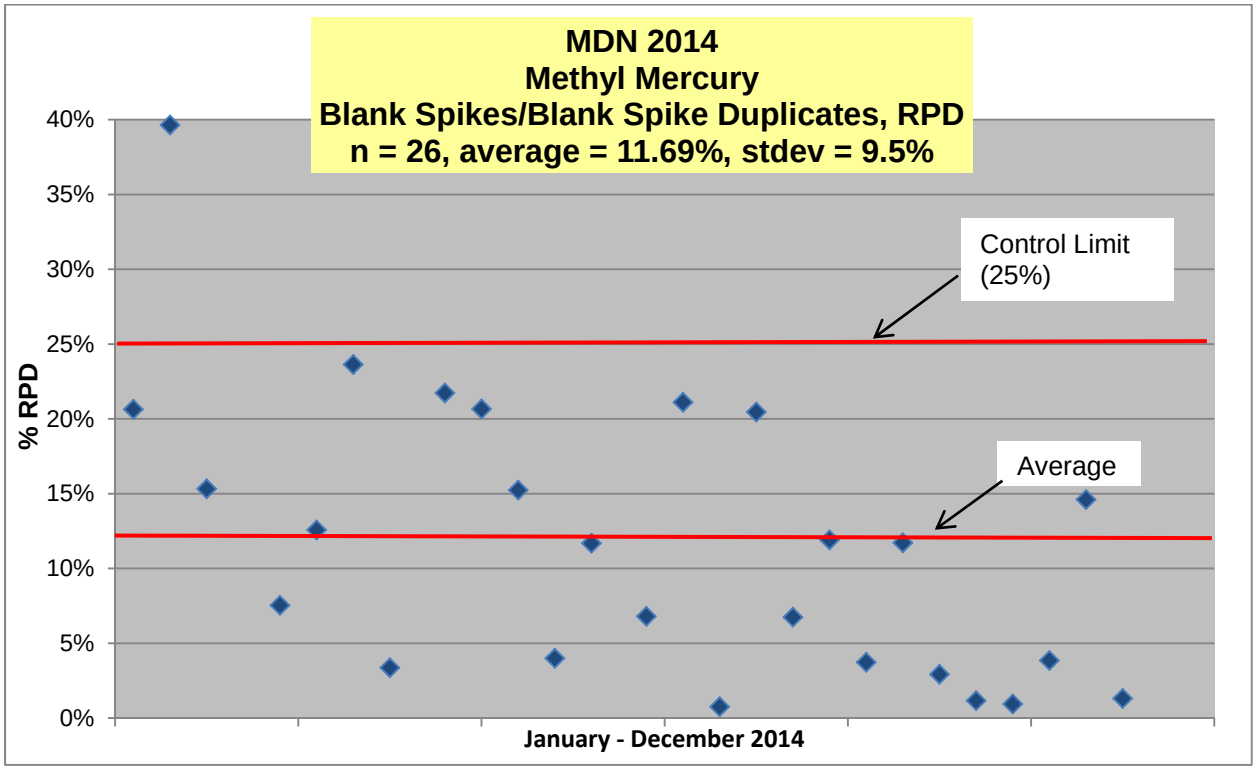

Figure 17 - Control Chart for Methyl Mercury Relative Percent Difference (%RPD) in Blank Spikes/Blank Spikes Duplicates Samples During 2014

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 2014, 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 http://bqs.usgs.gov.

Table 9 - Proficiency Tests

Proficiency Test	Organization	Open-close date	Scored Total Hg Results
WP1014	Phenova	10/7/2014 – 11/21/2014	Passed
HW0714	Phenova	7/28/2014 – 9/11/2014	Passed
WP0714	Phenova	7/1/2014 – 8/21/2014	Passed
HW0114	Phenova	1/27/2014 – 3/13/2014	Passed
WP0114	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). 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 52 samples in 2014 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 2014, the mean of 129 Field Bottle Blanks was 0.037 ng/bottle with a standard deviation of 0.027 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 CO9920140121, CO9920140318, CA7520140701 and CO9920141007 with elevated mercury values of 0.129, 0.158, 0.141 and 0.190 ng, respectively.

Both CA75 and CO99 have ACM collectors. For CO99 there were a total of 10 field blanks. The three blanks from CA099 with elevated mercury values 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. For CA75 there were a total of 13 field blanks. This suggests that neither site had systemic issues of contamination (bad lid seal, handling, etc.).

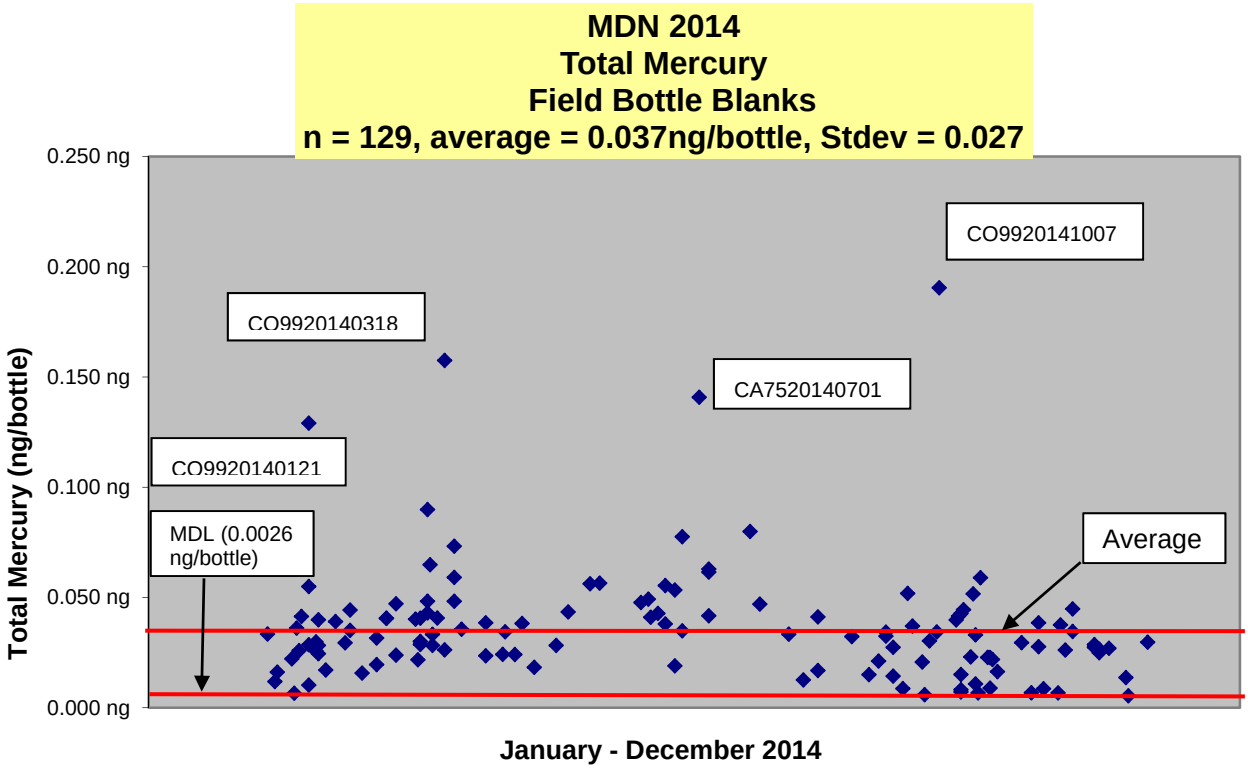

Figure 19 - Time Series Plot of Total Mercury Concentrations in Field Bottle Blanks During 2014

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. 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 2014, the mean of 44 system blanks was 0.014 ng/aliquot with a standard deviation of 0.015 ng/aliquot compared to the control sample with a mean of 0.000 ng/aliquot and a standard deviation of 0.003 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 comparable to the mean for the laboratory bottle blanks (0.011 ng/bottle). One location (WA18) had a higher level of mercury in its

control sample compared to the system blank. Figure 20 illustrates the system blank results for 2014.

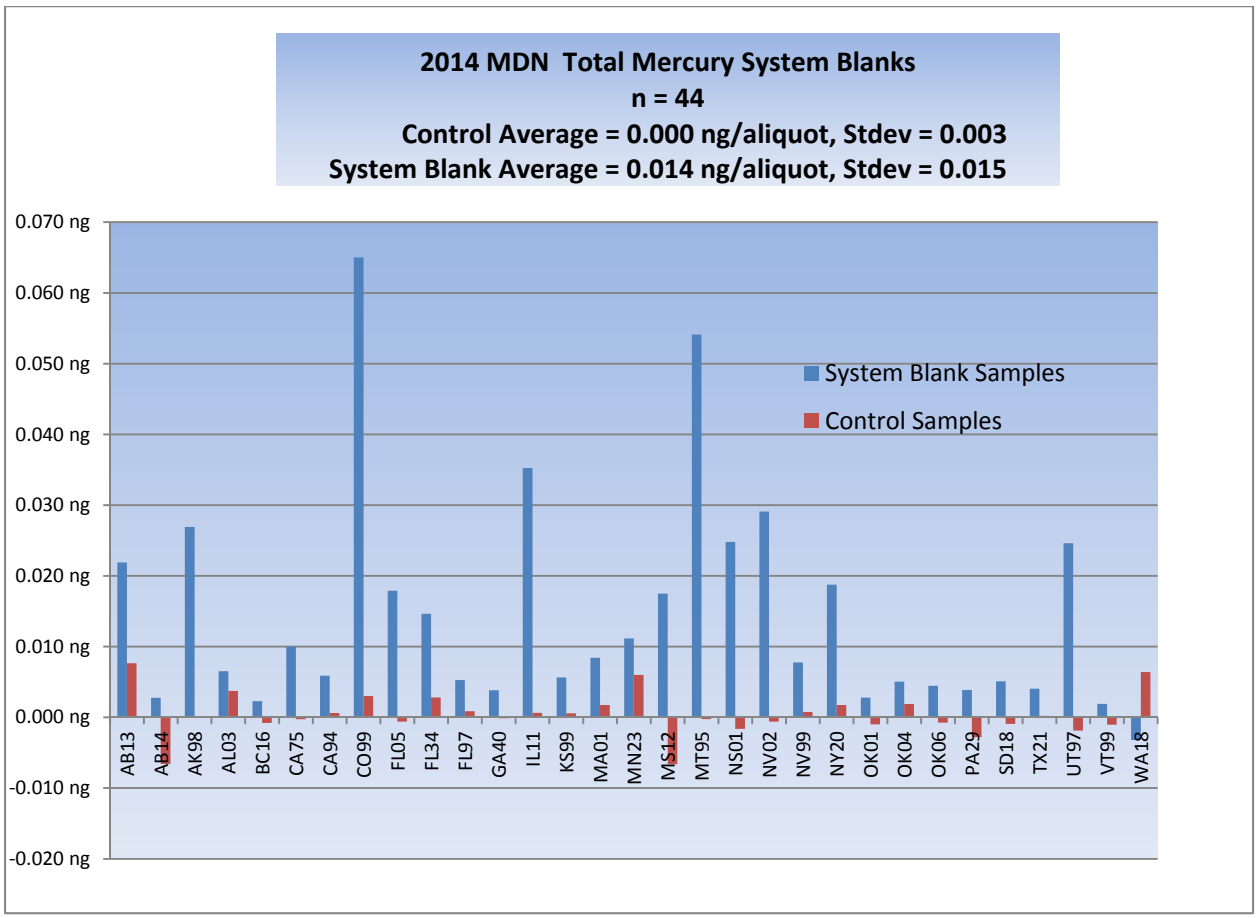

Figure 20 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2014

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 contaminants such as 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 6120 samples in 2014, which is comparable to the 6008 samples that were processed during 2013. There were 1095 samples that received a QR code of "A" while 4691 samples received a "B" QR code, and 378 samples received a "C" QR code. This distribution is illustrated in figure 21. HAL continued to maintain and demonstrate acceptable quality control in 2014. This comparison is based on HAL assessing the QR codes. These codes can later be changed by the NADP Program Office (PO).

Of the 378 "C" coded samples for 2014, no samples were disqualified due to laboratory issues/errors.

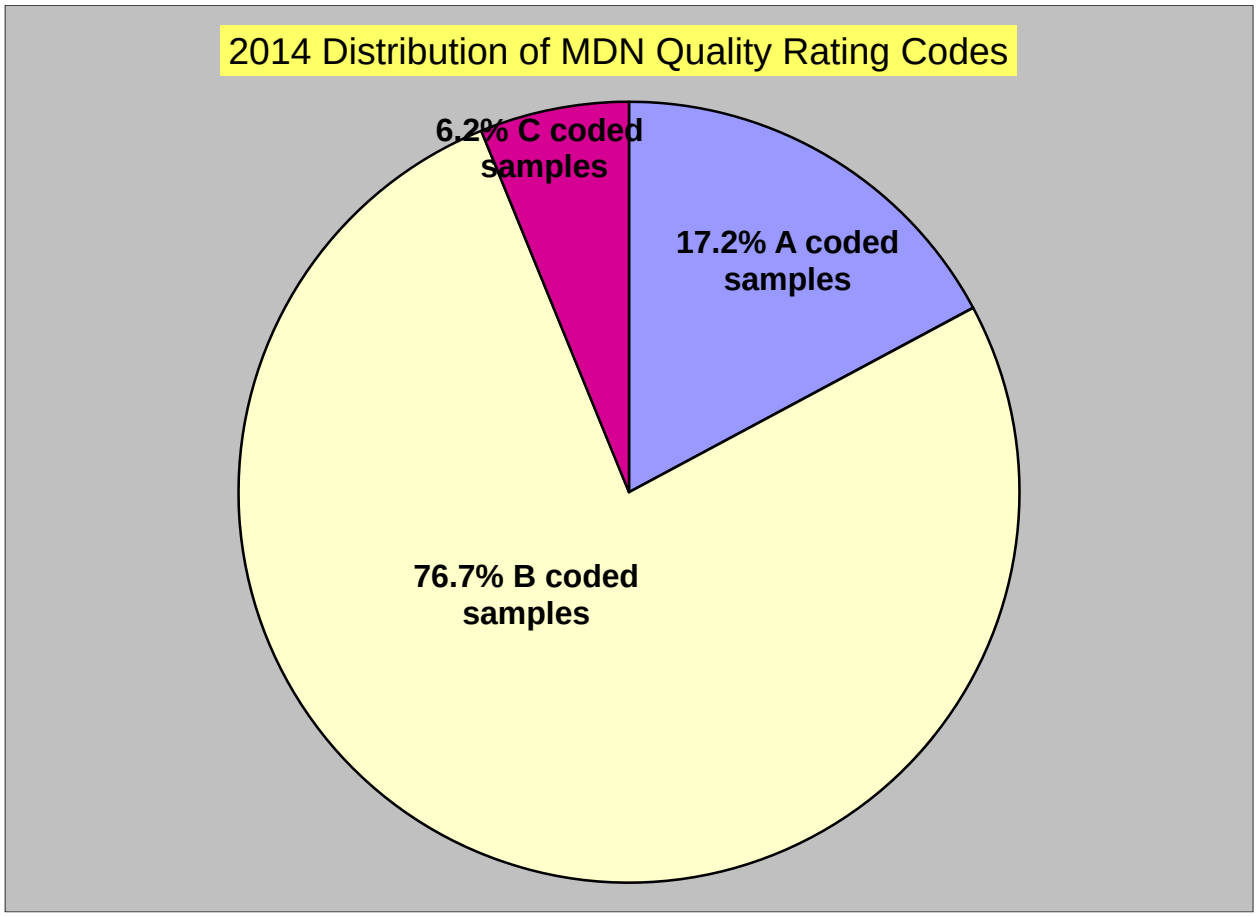

Figure 21 - Distribution of Quality Rating Codes for Samples Received in 2014

8. Summary and Conclusions

The HAL continued to maintain and demonstrate acceptable quality control in 2014. Four of 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 0.022 ng/L at a PQL of 0.05 ng/L. Average bottle blank Hg and MMHg content was quantified at 0.011 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 were within control limits. RPDs for MDs and BSDs for total mercury were less than $\pm$25%. However, at least one RPD exceeded control limits for MDs, MSDs and BSDs for methyl mercury. .

Field bottle blanks (n=129) and system blanks (n=44) generally indicated that field contamination levels continue to be low. However, some field-blank and system-blank samples identified site-specific contamination issues that appear to be field-related, especially at CO99 and CA75.

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
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	Matrix Specific MDL Study: Total Mercury in Water by Flow Injection Atomic Fluorescence Spectroscopy (FI-AFS)

Analyzed by: David Westby by NL for David Westby

Mercury Laboratory Manager: Ryan Nelson by NL

Report Prepared by: Kristine Teffeau KE Teffeau 7/13/15

Objective

To verify the Method Detection Limit (MDL) for total mercury (THg) in water on FI-AFS 2600-1. This instrument is used analyze samples received from the Mercury Deposition Network (MDN). Regulations for the MDN require an annual MDL study on each instrument used to analyze MDN samples.

Replicates for the MDL study were prepared in accordance with FGS MDN-04.04 and analyzed in accordance with FGS-121.02 (EPA 1631). The MDL study was performed following the protocols outlined in 40 CFR 136, Appendix B. As detailed below, the MDL for THg in water samples was determined to be **0.1290** ng/L THg for 2600-1.

Analytical Method

An instrument calibration was performed according to EFGS-121.03. Briefly, this method involves oxidation of the sample through the addition of BrCl, the reduction of Hg to elemental Hg with stannous chloride. The elemental Hg was then purged onto gold traps. This Hg was analyzed by thermal desorption into an atomic fluorescence detector using dual amalgamation.. The MDL study consisted of the oxidation and analysis of ten water replicates of a 0.500 ng/L solution.

The results for the replicates are listed in the table on the page 2, as well in the raw data sheets for dataset THg26001-141014-1. All results are reported corrected for the method and instrument blanks.

MDL Calculation

Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked replicates. In this case, n = 10 replicates (9 degrees of freedom) and 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 for the spiked replicates at the current PQL.

MDL = t*σ = (2.821) * (0.02033) = 0.1290 ng/L.

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

A valid MDL study requires that the ratio of the spike level (TV) to the calculated MDL be 10 or less. Additionally, to verify an existing MDL, the newly-calculated MDL must be less than twice the existing MDL. This MDL study was valid with a TV/MDL ratio of 3.8746. The existing MDL was also verified with a newly-calculated MDL less than the 2x current MDL.

MDN MDL Study

Dataset ID: **THg26001-141014-1**

Sample	[THg], ng/L
BLK1	-0.0460
BLK2	-0.0320
BLK3	-0.0140
Mean	-0.0307
SD	0.0160

Rec Limits
70-130%

	Result ng/L	Spike Level, [TV], ng/L	[%Rec]
BS2	0.63467	0.500	127%
BS3	0.53534	0.500	107%
BS4	0.49559	0.500	99.1%
BS5	0.52360	0.500	105%
BS6	0.48987	0.500	98.0%
BS7	0.51344	0.500	103%
BS8	0.50535	0.500	101%
BS9	0.48227	0.500	96.5%
BSA	0.48918	0.500	97.8%
BSB	0.48059	0.500	96.1%
Mean	0.51499	0.500	103%
SD	0.04575	0.000	9.1%

MDL	0.1290
PQL/MDL	3.8746
Current MDL	0.08
2x Current MDL	0.16
Current PQL	0.50

eurofins | Frontier Global Sciences	Matrix Specific MDL Study: Total Mercury in Water by Flow Injection Atomic Fluorescence Spectroscopy (FI-AFS)

Analyzed by: David Westby Ryan Nelson for David Westby Ry N

Mercury Laboratory Manager: Ryan Nelson Ry N

Report Prepared by: Kristine Teffeau KE Teffeau 7/13/15

Objective

To verify the Method Detection Limit (MDL) for total mercury (THg) in water on FI-AFS 2600-2. This instrument is used to analyze samples received from the Mercury Deposition Network (MDN). Regulations for the MDN require an annual MDL study on each instrument used to analyze MDN samples.

Replicates for the MDL study were prepared in accordance with FGS MDN-04.04 and analyzed in accordance with FGS-121.02 (EPA 1631). The MDL study was performed following the protocols outlined in 40 CFR 136, Appendix B. As detailed below, the MDL for THg in water samples was determined to be **0.1735** ng/L THg for 2600-2.

Analytical Method

An instrument calibration was performed according to FGS-121.02. Briefly, this method involves oxidation of the sample through the addition of BrCl, the reduction of Hg to elemental Hg with stannous chloride. The elemental Hg was then purged onto gold traps. This Hg was analyzed by thermal desorption into an atomic fluorescence detector using dual amalgamation.. The MDL study consisted of the oxidation and analysis of ten water replicates of a 0.500 ng/L solution.

The results for the replicates are listed in the table on the page 2, as well in the raw data sheets for dataset THg26002-141014-1. All results are reported corrected for the method and instrument blanks.

MDL Calculation

Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked replicates. In this case, n = 10 replicates (9 degrees of freedom) and 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 for the spiked replicates at the current PQL.

MDL = $t^*\sigma$ = (2.821) * (0.03684) = 0.1735 ng/L.

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

A valid MDL study requires that the ratio of the spike level (TV) to the calculated MDL be 10 or less. Additionally, to verify an existing MDL, the newly-calculated MDL must be less than twice the existing MDL. This MDL study was valid with a TV/MDL ratio of 2.8816. However, the existing MDL was not verified because the newly-calculated MDL exceeded twice the current MDL.

MDL Study Data for 2600-2

Dataset ID: **THg26002-141014-1**

Sample	[THg], ng/L
BLK1	-0.0597
BLK2	-0.0575
BLK3	-0.0530
Mean	-0.0568
SD	0.0034

Rec Limits
70-130%

	Result ng/L	Spike Level, [TV], ng/L	[%Rec]
BS2	0.65870	0.500	132%
BS3	0.51525	0.500	103%
BS4	0.48262	0.500	96.5%
BS5	0.46514	0.500	93.0%
BS6	0.48898	0.500	97.8%
BS7	0.48265	0.500	96.5%
BS8	0.44796	0.500	89.6%
BS9	0.44669	0.500	89.3%
BSA	0.47469	0.500	94.9%
BSB	0.46885	0.500	93.8%
Mean	0.49315	0.500	98.6%
SD	0.06151	0.000	12.3%

MDL	0.1735
PQL/MDL	2.8816
Current MDL	0.08
2x Current MDL	0.16
Current PQL	0.50

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Matrix Specific MDL Study: Methyl Mercury in Precipitation Samples by CV-GC-AFS

Analyzed by: Ryan Nelson 7/27/15
Mercury Supervisor: Ryan Nelson 7/27/15
Report Prepared by: Kristine Teffeau
Report Reviewed by: David Wunderlich 7/24/15

MDL Study Data for Methyl Mercury in Precipitation Samples
Preparation Method: EFGS-013
Analysis Method: EFGS-070
Dataset: MMHg15-150430-1

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 **0.02166 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)*(0.00438), or **0.02166 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 2.309 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.

4/30/2015
MMHg15-150430-1
MDN MDL Study

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Sample	[MHg], ng/L		
F504384-BLK1	0.003		
F504384-BLK2	0.000		
F504384-BLK3	0.000		
Mean	0.001		
SD	0.002		65-135%
	[MHg], ng/L	[TV], ng/L	[%Rec]
F504384-BS1	0.057	0.050	114.0%
F504384-BS2	0.041	0.050	82.0%
F504384-BS3	0.060	0.050	120.0%
F504384-BS4	0.054	0.050	108.0%
F504384-BS5	0.060	0.050	120.0%
F504384-BS6	0.041	0.050	82.0%
F504384-BS7	0.054	0.050	108.0%
F504384-BS8	0.041	0.050	82.0%
F504384-BS9	0.047	0.050	94.0%
F504384-BSA	0.050	0.050	100.0%
Mean	0.051	0.050	101.0%
SD	0.008	0.000	15.4%

MDL	0.02166
TV/MDL	2.309
Current MDL	0.026
2x Current MDL	0.052
PQL	0.05