

# National Atmospheric Deposition Program

## Mercury Deposition Network

Mercury Analytical Laboratory  
2010 Annual Quality Assurance Report

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## Definitions of Abbreviations and Acronyms

<b>AIRMoN</b>	Atmospheric Integrated Research Monitoring Network
<b>APDC</b>	Ammonium PyrrolidineDithioCarbamate
<b>AS/ASD</b>	Analytical Spike/ Analytical Spike Duplicate
<b>BS</b>	Blank Spike/ Blank Spike Duplicate
<b>CCB</b>	Continued Calibration Blank
<b>CCV</b>	Continued Calibration Verification
<b>CFR</b>	Code of Federal Regulations
<b>CRM</b>	Certified Reference Material
<b>CVAFS</b>	Cold Vapor Atomic Fluorescence Spectrometry
<b>DMRQA</b>	Discharge Monitoring Report-Quality Assurance
<b>DQO</b>	Data Quality Objectives
<b>EPA</b>	Environmental Protection Agency
<b>FGS</b>	Frontier Global Sciences
<b>HAL</b>	Mercury (Hg) Analytical Laboratory
<b>IAEA</b>	International Atomic Energy Agency
<b>ICB</b>	Initial Calibration Blank
<b>ICV</b>	Initial Calibration Verification
<b>ISO/IEC</b>	International Organization for Standardization (ISO)/ International Electrotechnical Commission (IEC)
<b>LCS</b>	Laboratory Control Sample
<b>LCSD</b>	Laboratory Control Sample Duplicate
<b>MD</b>	Matrix Duplicate
<b>MDL</b>	Method Detection Limit
<b>MDN</b>	Mercury Deposition Network
<b>MMHg</b>	Methyl Mercury
<b>MRL</b>	Method Reporting Limit
<b>MS/MSD</b>	Matrix Spike/ Matrix Spike Duplicate
<b>NADP</b>	National Atmospheric Deposition Program
<b>NELAP</b>	National Environmental Laboratory Accreditation Program
<b>NIST</b>	National Institute of Standards and Technology
<b>NPDES</b>	National Pollutant Discharge Elimination System
<b>NRCC</b>	National Research Council Canada
<b>OPR</b>	Ongoing Precision and Recovery
<b>PO</b>	Program Office
<b>PQL</b>	Practical Quantitation Limit
<b>PT</b>	Proficiency Test
<b>QA</b>	Quality Assurance
<b>QC</b>	Quality Control
<b>QR</b>	Quality Rating
<b>QCS</b>	Quality Control Sample
<b>RPD</b>	Relative Percent Difference
<b>RSD</b>	Relative Standard Deviation
<b>THg</b>	Total Mercury (Hg)
<b>TV</b>	True Value
<b>USGS</b>	United States Geological Survey

## Introduction

Since January 1996, Frontier Global Sciences Inc. (FGS) has served as the Mercury Analytical Laboratory (HAL) and Site Liaison Center for the Mercury Deposition Network (MDN). MDN, 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 network ended 2010 with 113 active sites in the United States and Canada (Figure 1) compared to 119 active sites at the end of 2009.

The HAL analyzes weekly precipitation samples for total mercury from all of its active sites and methyl mercury from 25 MDN 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 Method 1631 "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" final validation study.

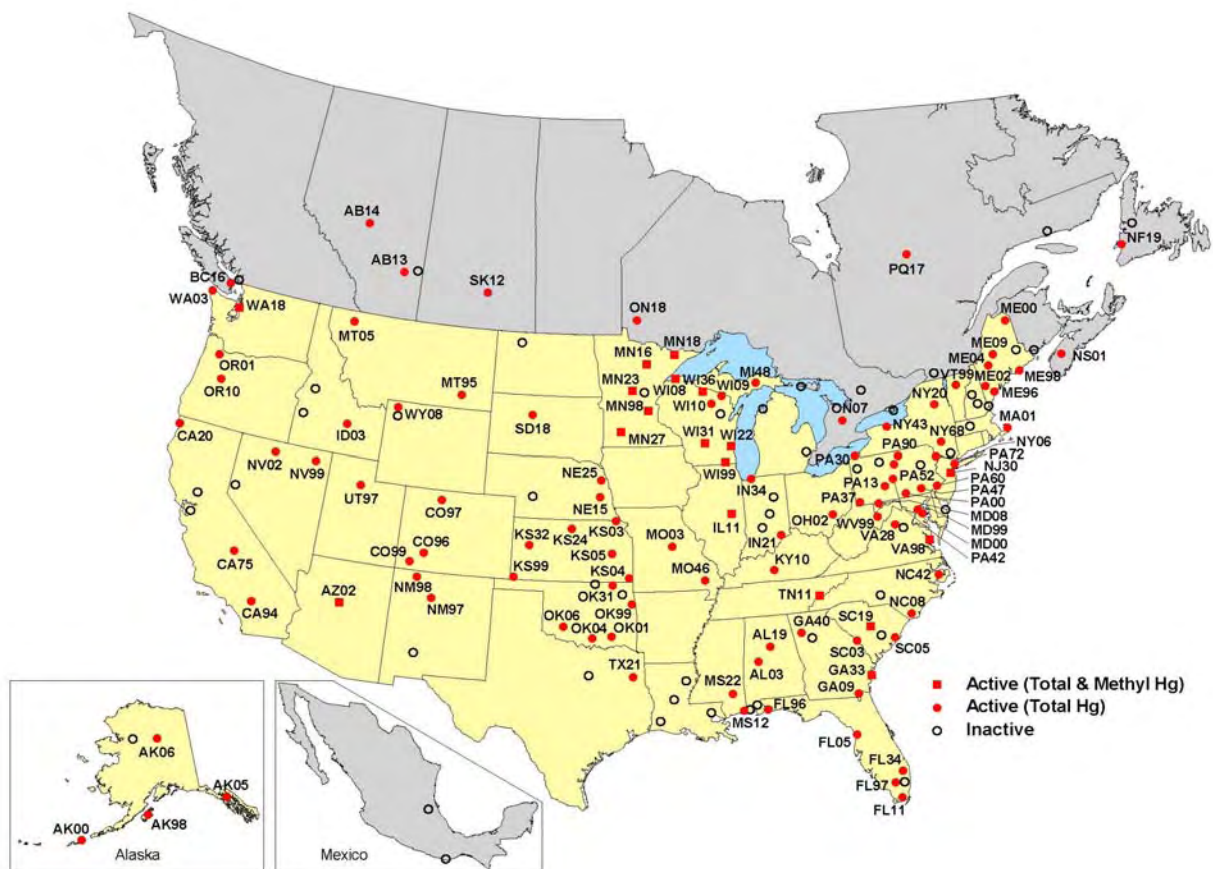


Figure 1 - Locations of MDN Sites During 2010

FGS continued to maintain and demonstrate acceptable quality control in 2010. FGS demonstrated consistency and reproducibility in bottle blanks, preparation blanks, certified reference materials, matrix duplicates, and matrix spikes. All of these parameters are plotted in control charts in this report.

The following changes occurred between 2009 and 2010.

- Change in instrumentation: Instrument #10 was used until June of 2010 and was replaced with instrument 1 after a MDL study had been performed.
- At the end of 2009 the MDN network included 119 sites, and at the end of 2010 the number of sites had decreased to 113 official sites. The total number of sites decreased from 119 in 2009 to 113 in 2010.
- There was no change in laboratory personnel for MDN during 2010.

# 1. Quality Assurance

## 1.1 Philosophy and Objectives

Frontier Global Sciences Inc. (FGS) is committed to a rigorous quality assurance 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 Quality Assurance 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 FGS' 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 matrix duplicates is  $\leq 25\%$  RPD.
- **Accuracy** is a measure of how close analyzed data is to a "true" value. HAL assesses accuracy using certified reference materials and matrix spikes. The acceptance criterion for reference materials and matrix spikes is 75-125% recovery.
- **Representativeness** is a measure of how typical a sample is compared to the sample population. It is demonstrated by accurate, artifact-free sampling procedures and appropriate sample homogenization.
- **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, Section 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 that are 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 ( $\sigma$ ) is taken from the resulting data and the MDL is determined as  $t * \sigma$  of the replicates. For ten replicates, the MDL is calculated as follows:  $MDL = 2.821 * \sigma$ . 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). The PQL is determined by running ten replicate samples with a concentration that must normally meet a recovery of 70-130% (or the same recovery criteria which is applicable for the low non-standard calibration point, depending on the method). The PQL is also referred to as the Method Reporting Limit (MRL).

All MDL and PQL studies are on file with the Quality Assurance department and are available upon request.

The HAL updates MDL studies periodically for the MDN project. See Appendix A and 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 2010.

Three MDL studies were completed for the instrumentation used for analysis of MDN samples for total mercury collected during 2010. Ten replicates were originally run for MMHg15-110203-1; however sample 1012134-10 recovered significantly out of control and was removed as an outlier. In this case, the t value of 2.896 was used in the following equation  $MDL = t \cdot \sigma$ , where  $\sigma$  is the standard deviation of the results obtained on samples spiked at a level near the MDL.

**Table 1 – MDL Studies for 2010 Summary Table**

Instrument	Dataset	MDL (ng/L)	PQL (ng/L)
CV-AFS#1	THg011-101006	0.101	0.50
CV-AFS#9	THg091-100528	0.062	0.50
CV-AFS#10	THg101-100528	0.060	0.50
CV-GC-AFS #7	MMHg07-110303-1	0.018	0.050
CV-GC-AFS #15	MMHg15-110203-1	0.020	0.050

### 1.3 Accreditations

FGS currently holds certifications through departments in seven states: the California Department of Public Health, the Florida Department of Health, the State of Louisiana Department of Environmental Quality, the State of New York Department of Health, the Washington Department of Ecology, the Wisconsin Department of Natural Resources, and the State of Nevada Division of Natural Resources. The Florida Department of Health acted as FGS' primary accreditation body for the National Environmental Laboratory Accreditation Program (NELAP) during 2010. Frontier Global Sciences received ISO/IEC 17025:2005 accreditation through Perry Johnson Laboratory Accreditation, Inc. in January of 2010. Copies are available upon request.

### 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 an average 2-3 laboratory bottle blanks are analyzed each week for total mercury (the 20 mL of 1% HCl is analyzed). At least one bottle blank should be 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 must be analyzed and quantified so that it can be subtracted from final sample results. The final sample results are corrected by the average bottle blank results from the previous quarter.

#### 1.4.3 Discussion

In 2010, one laboratory bottle blank was higher than the MDL for total mercury performed for 2010 of 0.101ng/L at 0.340ng/bottle. None of the bottle blanks were above the reporting limit of 0.50ng/L.



In 2010 there was no laboratory bottle blank above the MDL for methyl mercury. The analyzed MDL for methyl mercury for 2010 was 0.020ng/L (See Table 2). Laboratory bottle blanks are expected to be at, or near, the MDL. In cases where the blanks are significantly higher, the situation is investigated. Possible contamination sources are researched and identified. Note that the values for the bottle blanks are in ng/bottle and the MDL is in ng/L. The bottle blanks are reported as ng/bottle and not ng/L. The laboratory bottle blanks are not converted to ng/L, since the 20 mL of the 1% HCl added to the bottle will be diluted to the final volume of water collected at the site.

**Table 2 - Laboratory Bottle Blank Summary Table**

2010 Laboratory Bottle Blanks	n	Average (ng/bottle)	Standard Deviation	MDL (ng/L)	PQL (ng/L)
Total Mercury	136	0.028	0.029	0.101	0.50
Methyl Mercury	12	0.00055	0.0004	0.020	0.050

**MDN 2010  
Total Mercury  
Laboratory Bottle Blanks  
n = 136, average = 0.028 ng/bottle, stdev = 0.029**

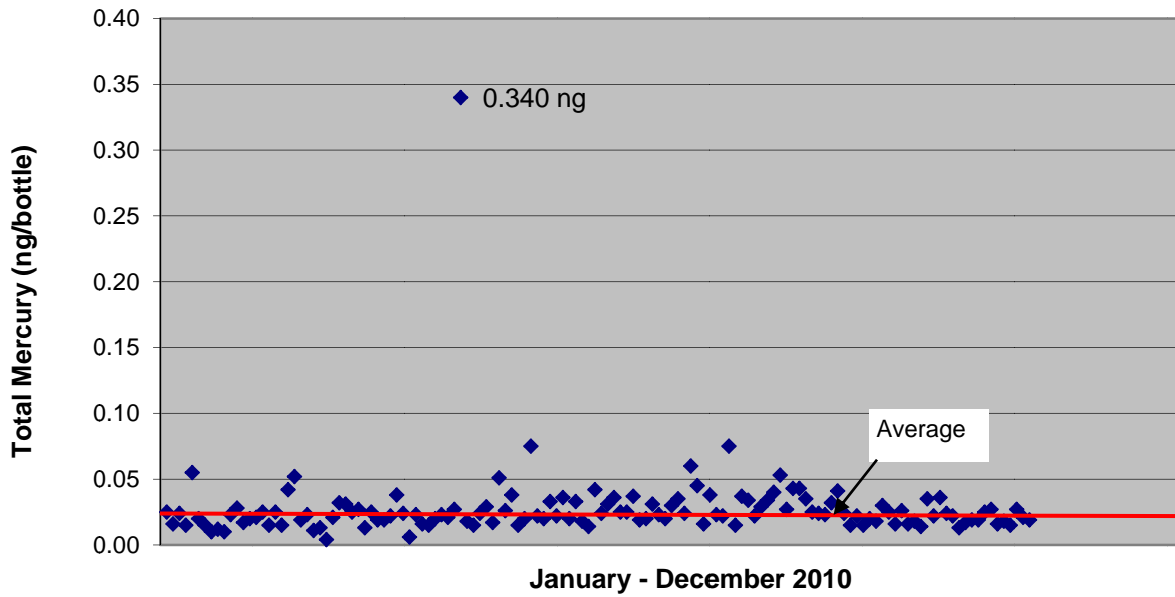


Figure 2 - Plot of Total Mercury Mass in Laboratory Bottle Blanks for 136 Samples

**MDN 2010  
Methyl Mercury  
Laboratory Bottle Blanks  
n = 12, average = 0.00055 ng/bottle, stdev = 0.0004**

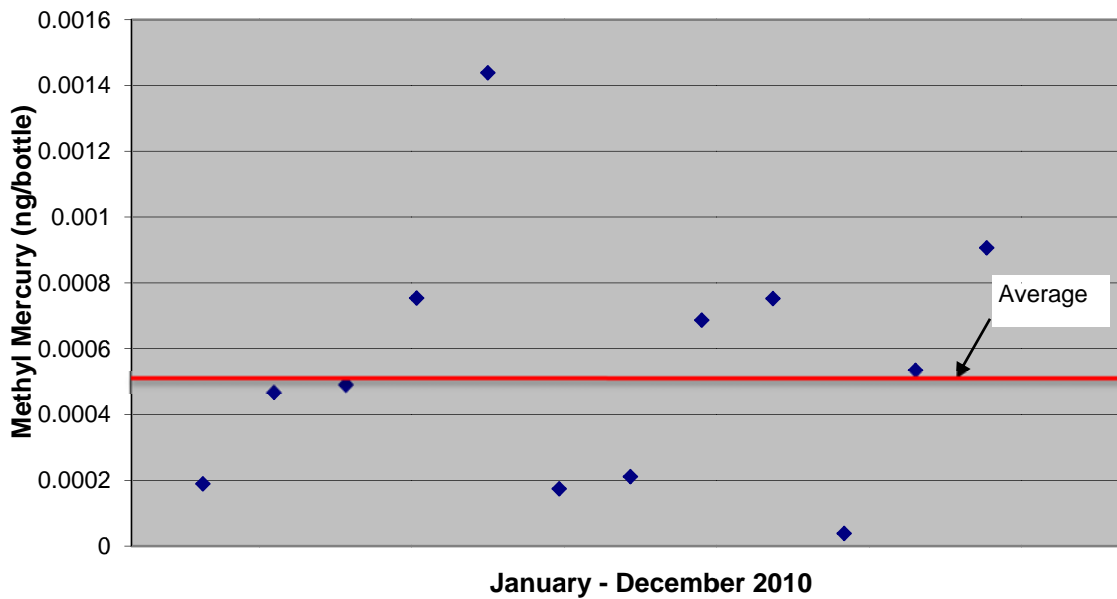


Figure 3 - Plot of Methyl Mercury Mass in Laboratory Bottle Blanks for 12 Samples

## 2. Quality Control

Quality Control (QC) samples have an expected target value that can be used to assess objectively the 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 duplicate 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 100mL of reagent water. Preparation blanks for methyl mercury consist of 45 mL reagent water, hydrochloric acid (0.4%), ammonium pyrrolidine dithiocarbamate (0.200 mL of APDC) solution, ethylating agent (38.5  $\mu$ L), acetate buffer (0.300 mL), and reagent water. The control limit used at HAL for total mercury is that the absolute value for each individual preparation blank shall be less than 0.25ng/L. This control limit is lower than the US EPA method 1631E method blank, which individually must be less than 0.5ng/L. The PQL for THg is 0.50ng/L.

The HAL control limit for methyl mercury is set to 0.045ng/L, which is the same as for EPA 1630. HAL does not have control criteria on the standard deviation; see Table 10 for a summary of QC Criteria for EPA 1631E and EPA 1630.

#### 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 from these necessary reagents. Preparation blanks also help when investigating possible sources of contamination.

#### 2.1.3 Discussion

In 2010, 13 preparation blanks for total mercury were above the calculated  $\bar{x}+3\sigma$  limit of 0.154ng/L. All the preparation blanks analyzed during 2010 were less than the control limit of <0.25 ng/L used at the laboratory and less than the EPA criteria of 0.50ng/L.

In 2010, three preparation blanks for methyl mercury were at the newly established control limit of 0.032 ng/L ( $\bar{x}+3\sigma$ ). None of the preparation blanks was higher than the control limit of 0.045ng/L. The standard deviation for 2010 of 0.0092 ng/L is less than the EPA requirement of <0.015 ng/L.

**Table 3 - Preparation Blanks Summary Table**

2010 Preparation Blanks	n	Average (ng/L)	Stdev (ng/L)	MDL (ng/L)	Mean + 3 $\sigma$ Control Limit (ng/L)	HAL Control Limit (ng/L)	EPA 1631E/1630
Total Mercury	725	0.031	0.041	0.101	0.154	0.25	< 0.50
Methyl Mercury	162	0.0048	0.0092	0.020	0.035	0.045	Mean <0.045 $\sigma$ <0.015

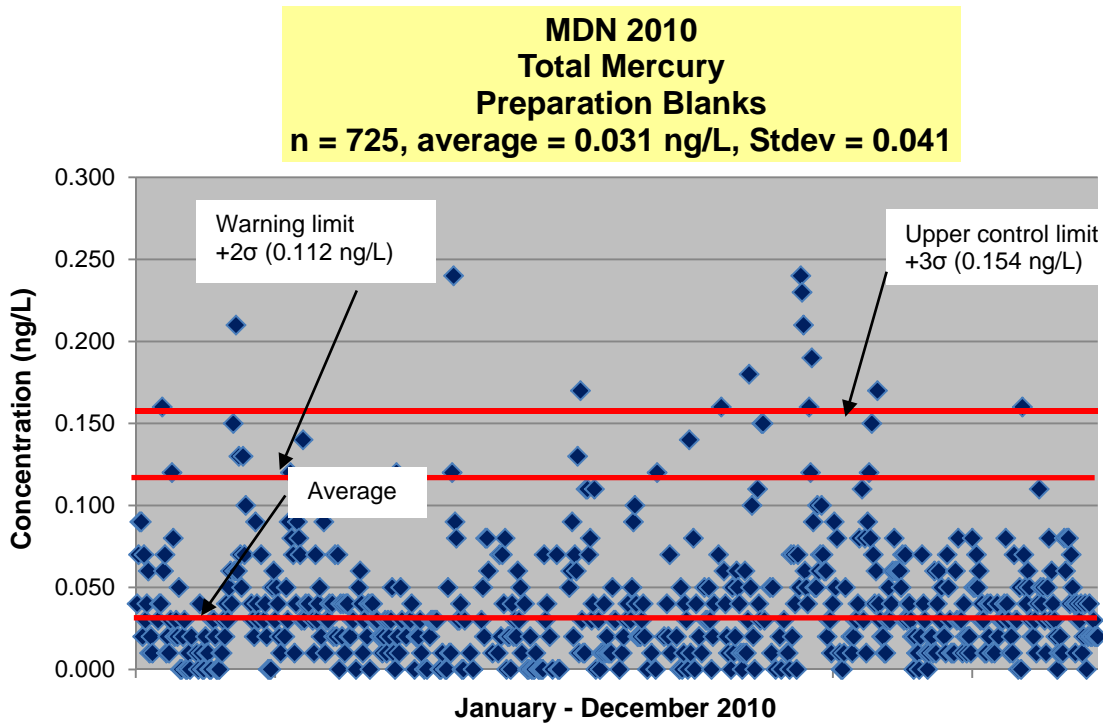


Figure 4 – Control Chart for Total Mercury Concentration in Reagent Preparation Blanks

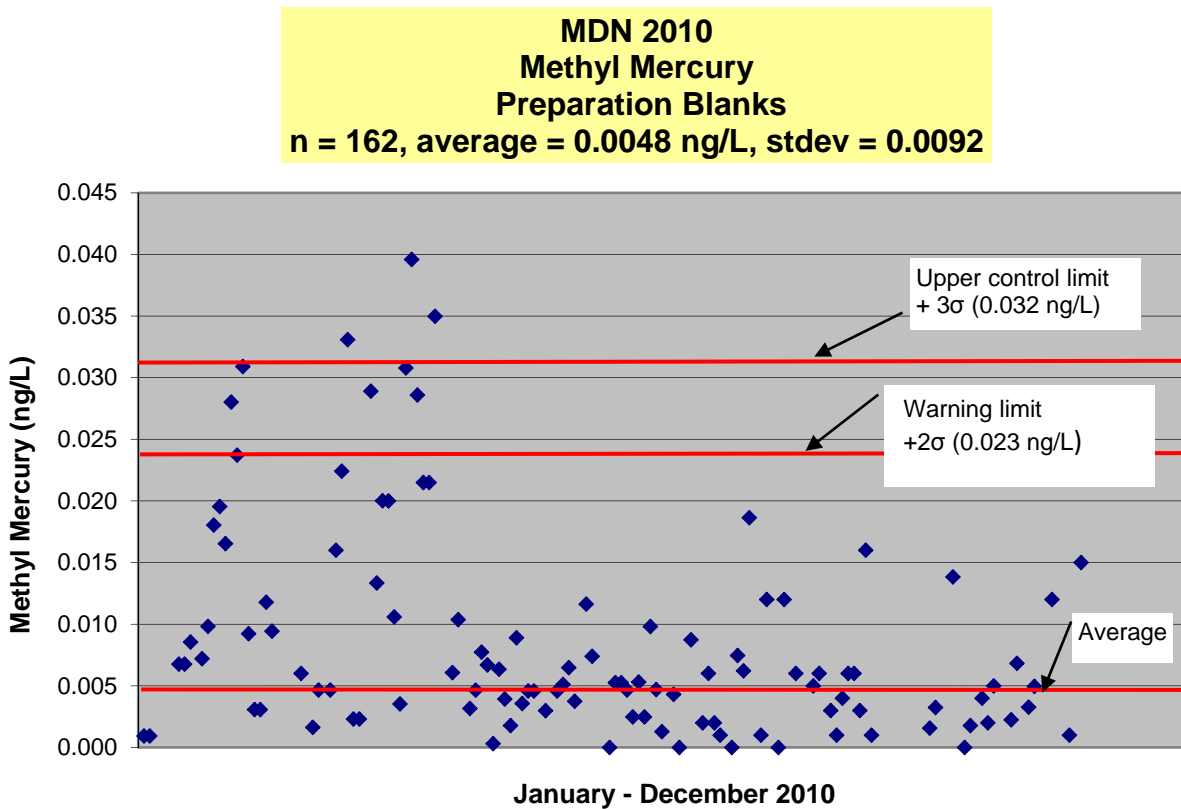


Figure 5 - Control Chart for Methyl Mercury Concentration in Reagent Preparation Blanks

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

### 2.1.4 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. The holding time for ICVs is twelve months and for CCVs three months. New working standards and standard dilutions are tested prior to use. Three reps of the new standard are analyzed at the same run as three reps 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. E.g. if the average of NIST is 97% the range for the standards are 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 2 ng/L standard for methyl mercury are analyzed as an ongoing calibration standard. The MDN control limits for ICVs and CCVs for total mercury are set to 80-120% and for methyl mercury ICVs are 80-120 and CCVs are 75-125%.

### 2.1.5 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 verify that the analytical system is in control, or demonstrate analytical drift. All ICV/CCVs reference a unique identification number and are traceable through LIMS. All raw data references a unique laboratory ID number and includes a unique identifier for each standard used in the analysis.

### 2.1.6 Discussion

Control limits are calculated using the mean value plus/minus three times the standard deviation, and for 2010 the range was between 86.2-109.3% for continuing calibration verification for total mercury. Four samples were above the calculated control limit of 109.3% ( $\bar{x}+3\sigma$ ) and one sample was below the  $\bar{x}-3\sigma$  of 86.2%. These values were all within the control limit of 80-120% used at HAL. The CCV2 for methyl mercury analyzed on March 10, 2011 recovered higher than both the  $\bar{x}+3\sigma$  control limit of 129.4% and also higher the EPA 1630 limit of 133% at 145.7%. All samples with remaining volume were reanalyzed. The volume was exhausted for ON1820101109, ON1820101130, and PQ172011116, and cannot be reanalyzed. The sample results for these three samples will be submitted to the PO with a qualifier.

**Table 4 - Continuing Calibration Standard Summary Table**

2010 Continuing Calibration Standard	n	Average (%)	Stdev (%)	$\pm 3\sigma$ Control Limit (%)	EPA 1631E/1630 Control Limits (%)
Total Mercury	855	97.8	3.8	86.2-109.3	77-123
Methyl Mercury	161	99.1	10.1	68.9-129.4	67-133

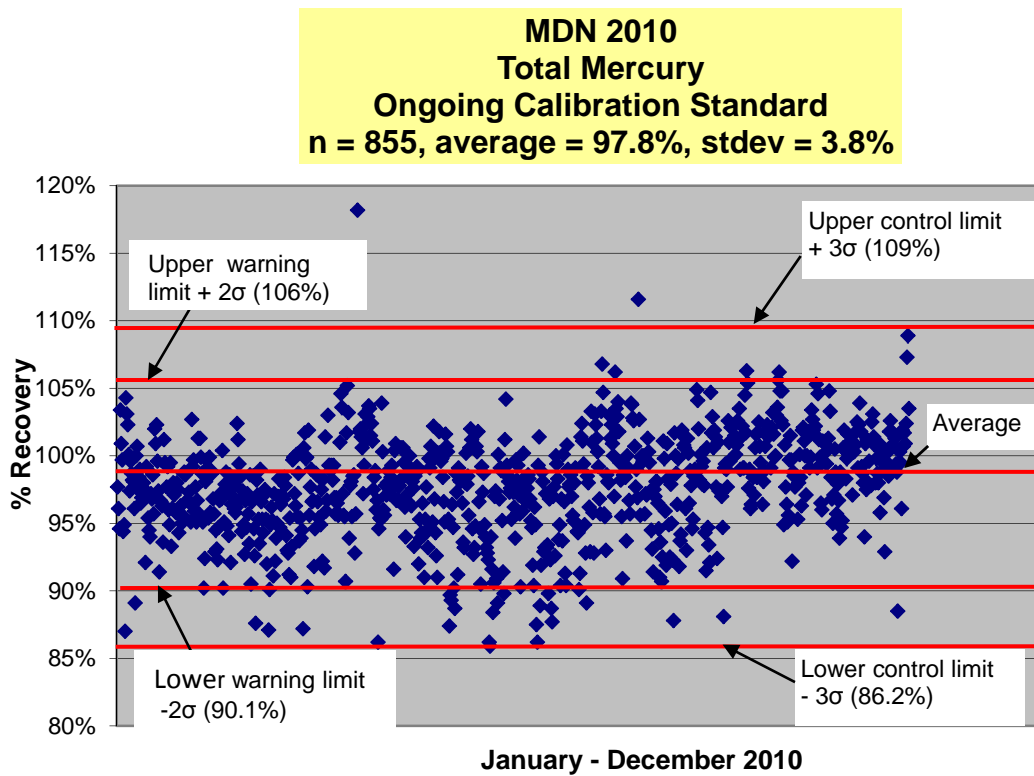


Figure 6 - Control Chart for Total Mercury Continuing Calibration Standard Percent Recovery

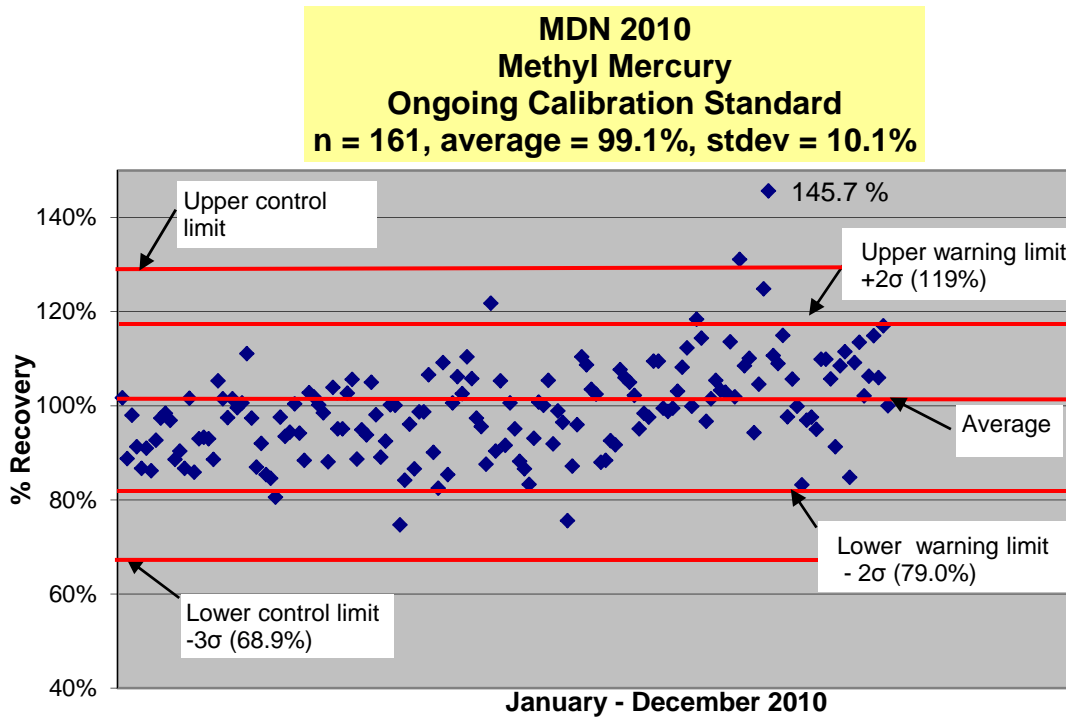


Figure 7 - Control Chart for Methyl Mercury Ongoing Calibration Standard Percent Recovery

## 2.2 Continuing Calibration Blanks

### 2.2.1 Description

Continuing Calibration Blanks (CCBs) are analyzed during the course of sample analysis, every ten or fewer samples and at the end of each analytical run. Individually, the initial and each subsequent per FGS DQOs, Continuing Calibration Blanks (ICB/CCBs) shall be less than 0.25 ng/L to be within control limits for total mercury. For MHg the mean of the Initial Calibration Blank (ICB) and CCB shall be less than 0.025ng/L.

### 2.2.2 Purpose

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

### 2.2.3 Discussion

There were several ongoing calibration blanks for the MDN project in 2010 for total mercury that were outside the calculated control limit of  $-\bar{x} \pm 3\sigma$  -0.093-0.099 ng/L. No calibration blanks exceeded 0.25ng/L, which is the control limit that is used for MDN analysis at HAL.

For 2010, a control limit for methyl mercury based on  $(\bar{x} \pm 3\sigma)$  is -0.011-0.025 ng/L. On August 10 2010, the CCB2 and the CCB3 were at 0.026ng/L, but the average was calculated to 0.022ng/L which is below the control limit of the average CCBs less than 0.025ng/L.

**Table 5 - Ongoing Calibration Blanks Summary Table**

2010 Ongoing Calibration Blanks	n	Average (ng/L)	Stdev (ng/L)	MDL (ng/L)	Control Limit (ng/L)	EPA 1631E/1630 Control Limits
Total Mercury	1818	0.003	0.032	0.101	-0.093-0.099	Individually <0.50 ng/L, mean <0.25 ng/L with a standard deviation <0.10 ng/L
Methyl Mercury	164	0.007	0.006	0.020	-0.011-0.025	NA



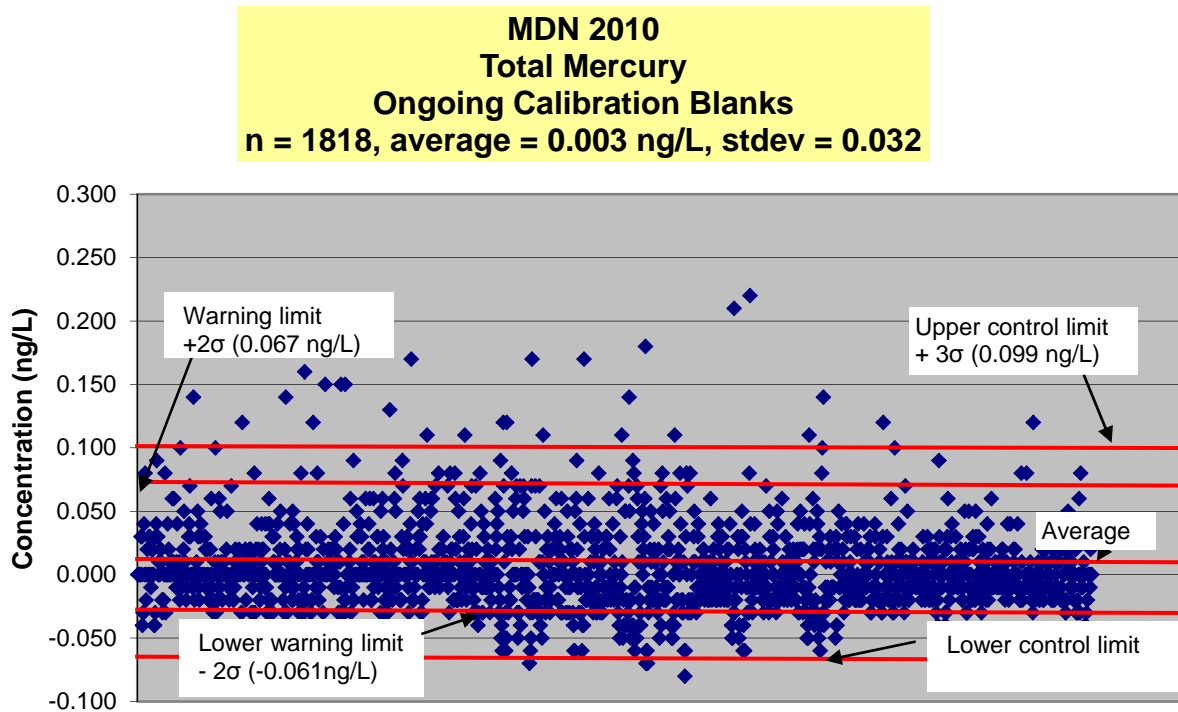


Figure 8 - Control Chart for Total Mercury Continuing Calibration Blanks 2010

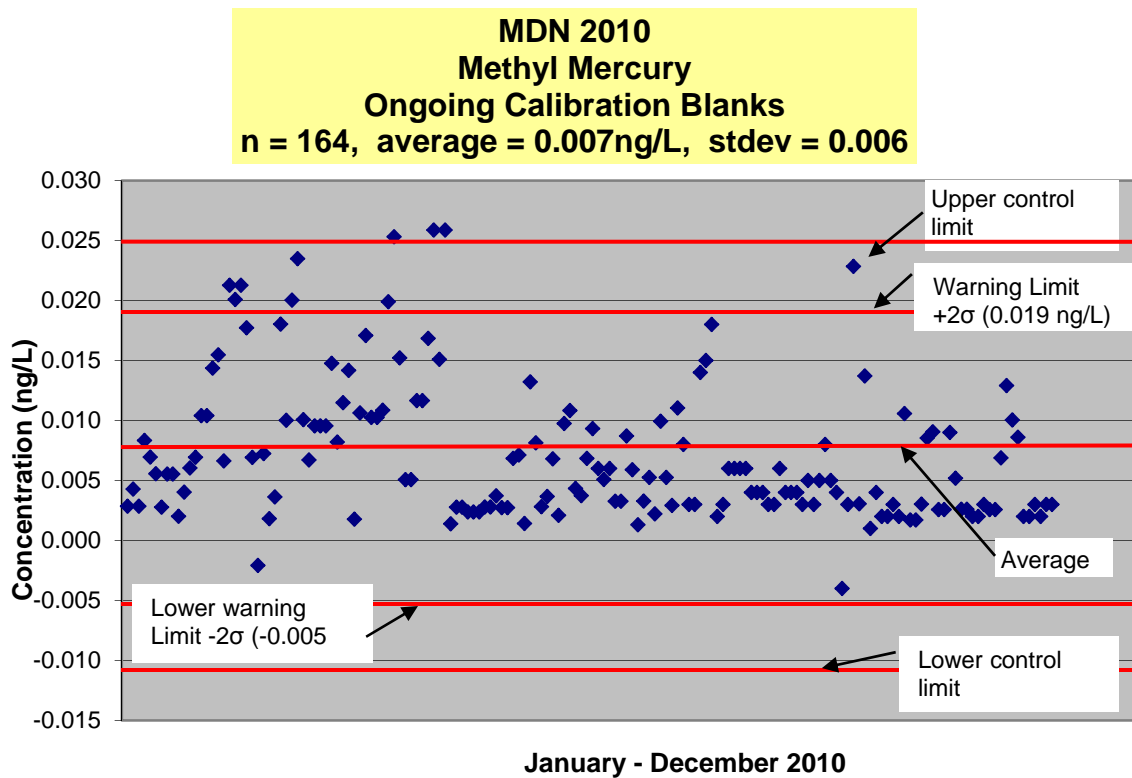


Figure 9 - Control Chart for Methyl Mercury Continuing Calibration Blanks 2010

## 2.3 Matrix Duplicates

### 2.3.1 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 Matrix Duplicates is set at 25% RPD for total mercury. US EPA methods 1630 and 1631 do not require a Matrix Duplicate. One Matrix Duplicate is performed for every ten analyzed samples and during a standard MDN THg analytical run three Matrix Duplicates are analyzed. The source samples are selected depending on the available volume. For total mercury analysis, 100 mL is needed each for the source sample, the Matrix Duplicate and the Matrix Spike, and for potential reanalysis of these QC samples.

### 2.3.2 Purpose

Replicate samples provide information about analytical precision. Matrix Duplicates 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 heterogeneous sample matrix and/or poor analytical precision.

### 2.3.3 Discussion

For 2010, for total mercury the calculated control limit based on  $\bar{x} + 3\sigma$  was 14.1% RPD. No duplicate samples were above the upper control limit of 25% RPD used at HAL.

For methyl mercury, the calculated control limit of  $\bar{x} + 3\sigma$  was 49.8% RPD and no duplicate pairs for methyl mercury were above the control limit. The actual upper control limit used in the laboratory is 25%. For many of the samples, the methyl mercury concentration is lower than, or equal to, the reporting limit of 0.05ng/L and can result in high RPD. As an example, the recovery criteria for the calibration point at the PQL (0.05 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 with QR-04.

QR-04 reads "The RPD and/or RSD value exceeded the control limit. Sample concentrations are less than 10 times the reporting limit and the difference between the QC values was less than 2 times the reporting limit."

High RPD values can also be qualified when the reproducibility is in control based on acceptable RPD values between MS/MSD and LCS/LCSD with a QR-07.

QR-07 reads "The RPD/RSD value for the matrix duplicate/triplicate was outside of acceptance limits. Batch QC acceptable based on MS/MSD and/or LCS/LCSD RPD values within control limits."

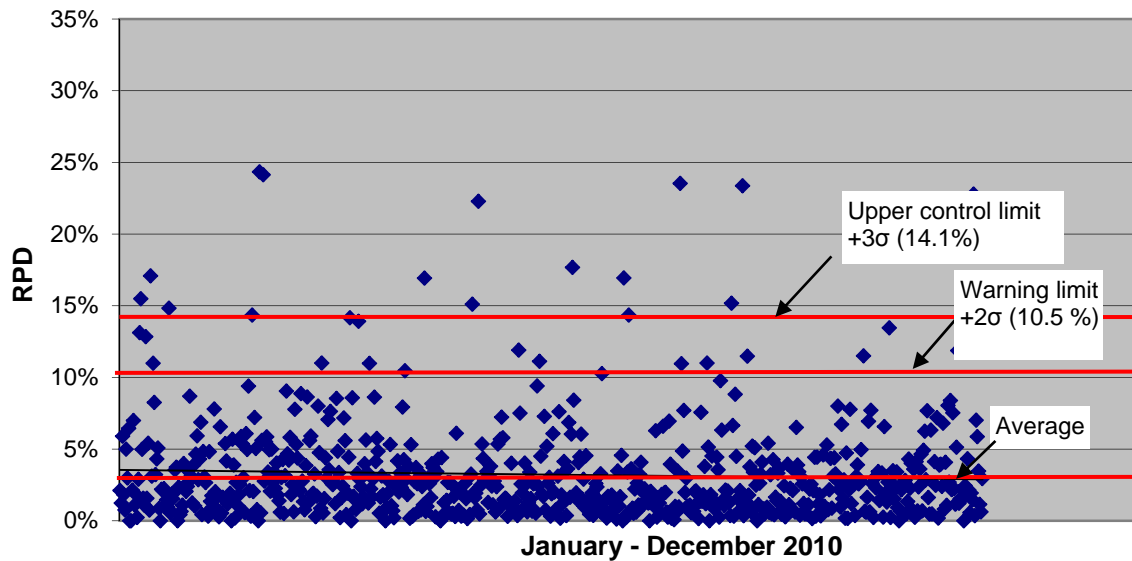
The flowcharts used to determine if a qualifier can be applied or not, are included in SOP FGS-038 "Data Review and Validation." HAL applies the same type of qualifiers on MDN data as for any other analysis of EPA 1631 E, if applicable. See Table 11 for qualifiers used at HAL.

Results below the lowest calibration point, which is below the PQL, shall not be reported without a "J" flag. The J flag reads "Detected but below the Reporting Limit; therefore, result is an estimated concentration (CLP J-Flag)." To be able to more accurately evaluate the reproducibility of the methyl mercury analysis, matrix duplicate pairs with one or both values below the PQL (qualified with QR-04) were excluded from the graph (a total of 25 pairs). These RPDs could otherwise lead to misinterpretation of the reproducibility. See Figure 11.

**Table 6 - Matrix Duplicates Summary Table 2010**

2010 Matrix Duplicates	n	Average RPD (%)	Stdev (%)	Upper control Limit +3σ (%)	EPA 1631E/1630 Control Limits
Total Mercury	707	3.22	3.62	14.1	NA
Methyl Mercury*	31	17.0	18.5	72.4	NA

**MDN 2010  
Total Mercury  
Matrix Duplicate RPD  
n = 707, average = 3.22%, stdev = 3.62%**



**Figure 10 - Control Chart of the Relative Percent Differences for Total Mercury Concentrations in Matrix Duplicates During 2010**

**MDN 2010  
Methyl Mercury  
Matrix Duplicate RPD  
n = 31, average = 17.0%, stdev = 18.5%**

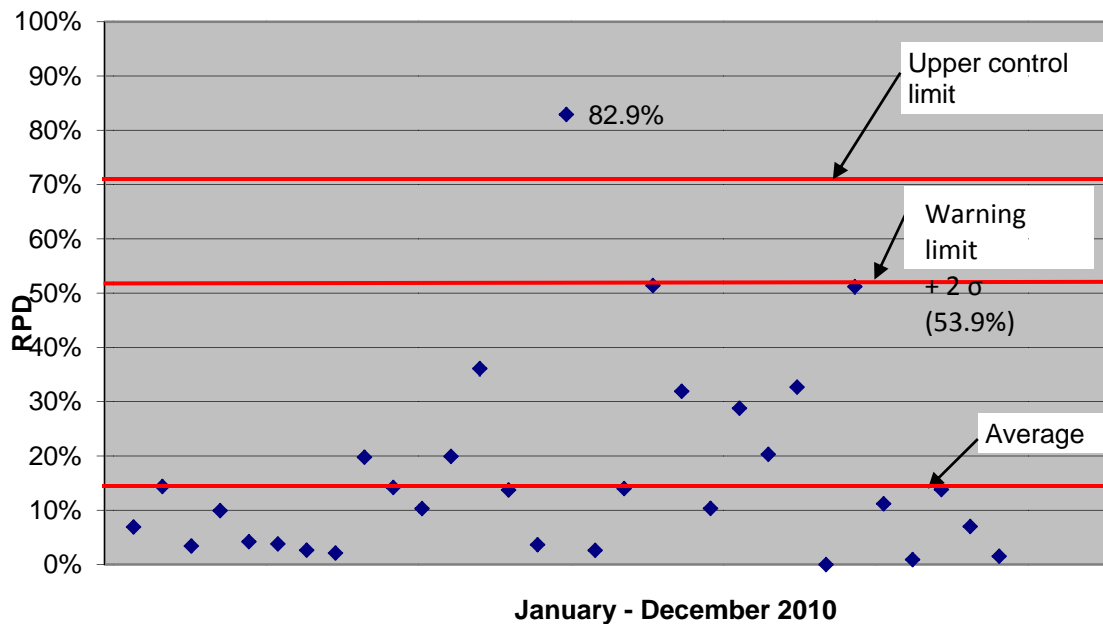


Figure 11 - Relative Percent Differences for Methyl Mercury Concentrations in Matrix Duplicates pairs above the PQL During 2010

## 2.4 Matrix Spikes

### 2.4.1 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 MHg), whichever is greater. For MDN runs, due to limited sample volume, only one matrix spike (MS) is performed for every ten analyzed samples and during a normal analytical run three matrix spikes are analyzed. The source samples are selected depending on the available volume. 100 mL is needed 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 <25%.

### 2.4.2 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 recognize 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 is a sign of matrix interference, after investigation by trap and bubbler test, the samples should be reanalyzed at a dilution. The purpose is to ascertain the largest aliquot size a sample can be analyzed at without matrix interference. The source sample shall then also be reanalyzed at the same aliquot size.

### 2.4.3 Discussion

The control limit for the recovery of the matrix spike for THg based on  $\bar{x} \pm 3\sigma$  is 81.0%-112%. For 2010, 5 values were greater, and 3 values were below these limits. All values are within the 75-125% control limit used at HAL.

For methyl mercury, a control limit 53.8%-157% was calculated based on  $\bar{x} \pm 3\sigma$  for the recovery of the matrix spike and the matrix spike duplicate. During 2010, MS % recovery was greater than the 130% (control limit in the laboratory) for five samples. Two values were below the laboratory control limit of 65% recovery and one of these values was also below the calculated low control limit of 53.8 at 48.1% recovery.

The RPDs for two matrix spike/matrix spike duplicates were above the calculated control limit of 23.6% ( $\bar{x} + 3\sigma$ ) at 26.7% and at 32.7% RPD for TN11COMP100511. For the run where TN11COMP100511 was analyzed, the recovery for both the MS and the MSD was in control at 76.9% and 107%. The Laboratory Control Samples and the Laboratory Control Duplicate Sample (LCS/LCSD) recovered in control with a RPD of 19.5% and the duplicate sample had a RPD of 19.9%. When following the laboratories internal quality control criteria, the elevated RPD could be qualified with QR-08 per SOP FGS-038 "Data Review and Validation." Qualifier QR-08 reads "The RPD value for the MS/MSD was outside of acceptance limits. Batch QC acceptable based on matrix duplicate and/or LCS/LCSD RPD values within control limits." The RPD at 23.6% was below the laboratory control limit of 25% RPD.

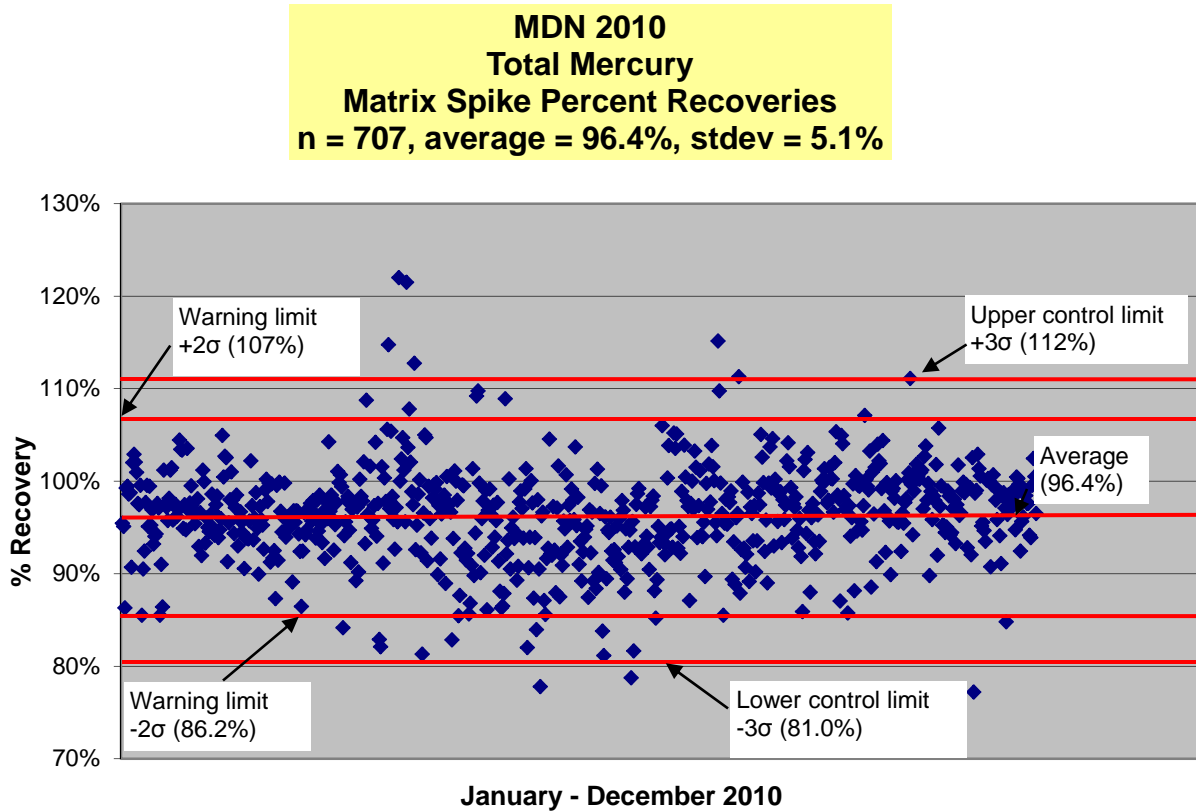
The average methyl mercury percent recovery for the matrix spikes during 2010 is 105.5%. Figure 13 shows that the majority of the results are lower than the average in the beginning of the year, higher at the end of the year, and around average during the middle of the year. The same pattern can be seen in figure 17 for the methyl mercury percent recovery in blank spikes/blank spikes duplicates samples and in figure 7 for ongoing calibration standard percent recovery. The trend is more noticeable in the QC samples that went through the distillation process than for the instrumental QC. The increase in recoveries could not be traced to new standards, analyst, new correction factor, or instrumentation. The reasons could not be determined.

**Table 7 - Matrix Spike Recoveries for 2010 Samples**

2010 Matrix Spikes	n	Average (%)	Stdev (%)	Control Limits $\pm 3\sigma$ (%)	HAL Control Limits	EPA 1631E/1630 Control Limits (%)
Total Mercury	707	96.4	5.1	81.0-112	75-125	71-125
Methyl Mercury	111	105.5	17.2	53.8-157	65-135	65-135

**Table 8 - Matrix Spike/Matrix Spike % RPD for 2010 Samples**

2010 Spikes	Matrix	n	RPD Average (%)	Stdev (%)	+3σ (%)	EPA 1630 Control limits % RPD
Methyl Mercury		55	6.7	5.6	23.6	<35%



**Figure 12 - Control Chart for Total Mercury Percent Recovery in Matrix Spikes During 2010**

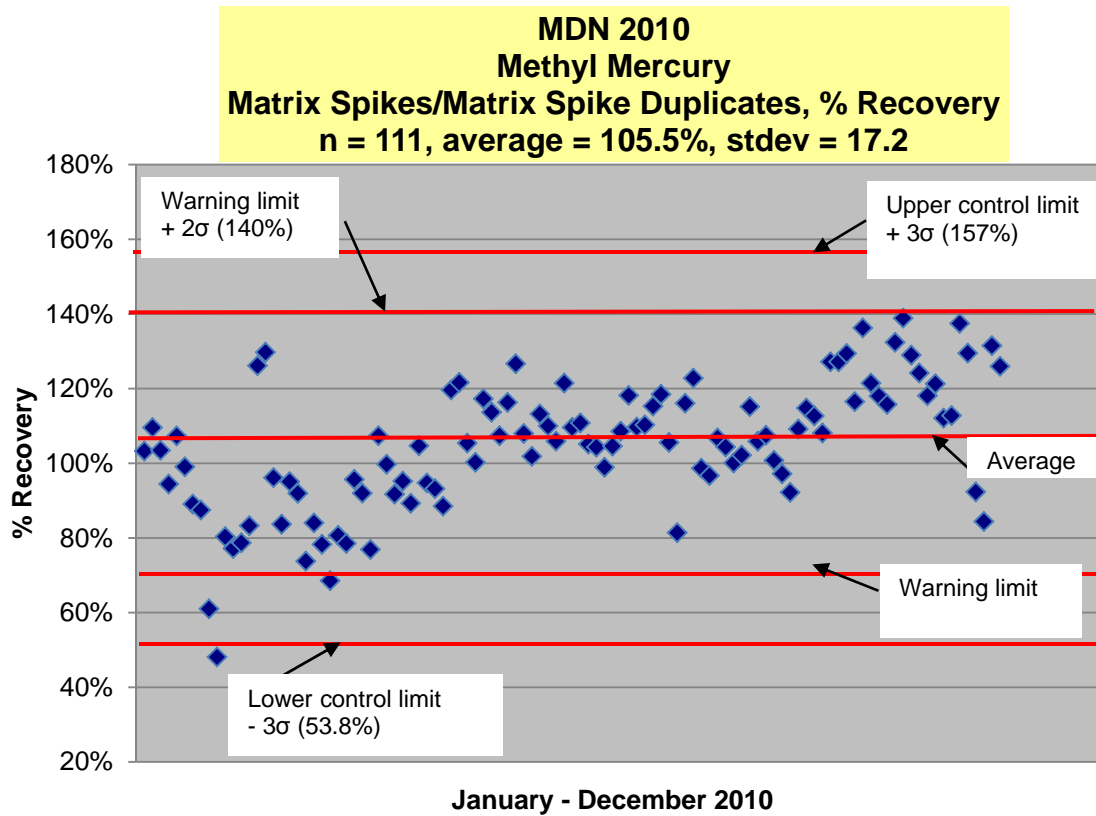


Figure 13 - Control Chart for Methyl Mercury Percent Recovery in Matrix Spikes During 2010

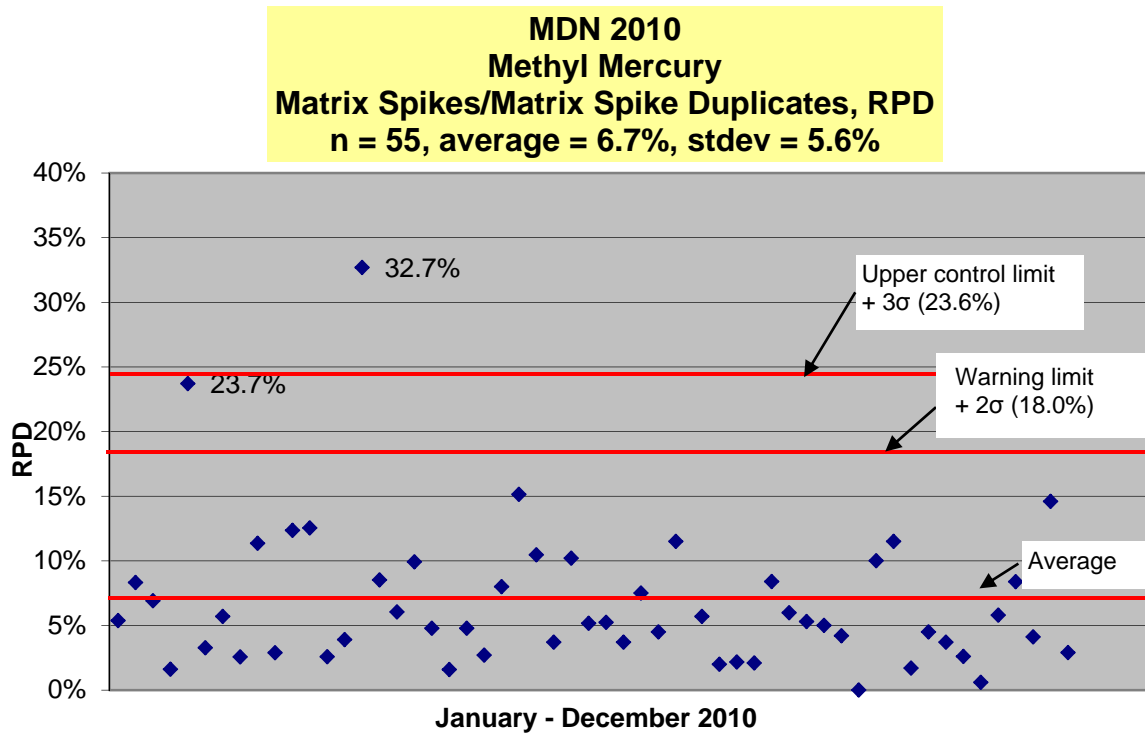


Figure 14 - Control Chart of the Relative Percent Differences for Methyl Mercury Matrix Spike/Matrix Spike Duplicate Pairs during 2010.

## 2.5 Certified Reference Materials

### 2.5.1 Description

Certified Reference Materials (CRMs) are matrix specific standards that are accompanied by a certificate of analysis for the analytes of interest. 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). Frontier maintains the position that matrix equivalent reference materials are the best measure of precision and accuracy (bias), as issues associated with matrix type and homogeneity may be assessed.

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 75-125% with a RPD of 25%. There is no CRM available for methyl mercury and 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.

### 2.5.2 Purpose

Certified Reference Materials are used to demonstrate HAL's ability to recover a target analyte from a specific matrix. The first CRM is analyzed right after the calibration curve to verify the validity of the analytical curve.

### 2.5.3 Discussion

In 2010, the mean of 471 certified reference material recoveries for total mercury was 95.3% with a standard deviation of 3.1%. There were two certified reference material recoveries above the upper control limit of 105% ( $\bar{x} + 3\sigma$ ) and one below the lower control limit of 86.0% ( $\bar{x} - 3\sigma$ ). The values were within the actual control limit of 75-125% used in the laboratory. The average RPD value for the CRM/CRM duplicate was 3.3% ( $n = 231$ ), with a standard deviation of 2.4%. One value was above the upper control limit calculated by  $\bar{x} \pm 3\sigma$  of 10.5% at 10.7%. All the RPD values were below the 25% used in the laboratory and shows high precision between the samples.

In 2010, the mean recovery of 108 blank spikes and blank spike duplicated for methyl mercury was 103% with a standard deviation of 14.5%. There was no blank spike with recovery outside the control limit of 59.4-147% based on  $\bar{x} \pm 3\sigma$  for 2010. There were two blank spikes above but no value below the actual laboratory control limits of 70-130%. The average RPD value for the BS/BSD was 11.6% ( $n = 54$ ) with a standard deviation of 9.2%. Two RPD values were above the actual control limit used in the laboratory of 25%, as well as the upper control limit based on  $\bar{x} \pm 3\sigma$  of 39.2% at 49.9% (dataset MHg15-101202-1) and 36.3% (dataset MHg07-110120-1) but were qualified based on passing MD/MS/MSD RPD values.

In Figure 17 the BS/BSD recovery is increasing in the last third part of the graph, which correlates with the time frame when the new efficiency factor of 0.8046 was applied verses the old value of 0.854. According to section 12.4.2 in EPA method 1630, the laboratory shall correct the results for recovery by applying an efficiency factor calculated based on spike recoveries from historic data produced by the laboratory.



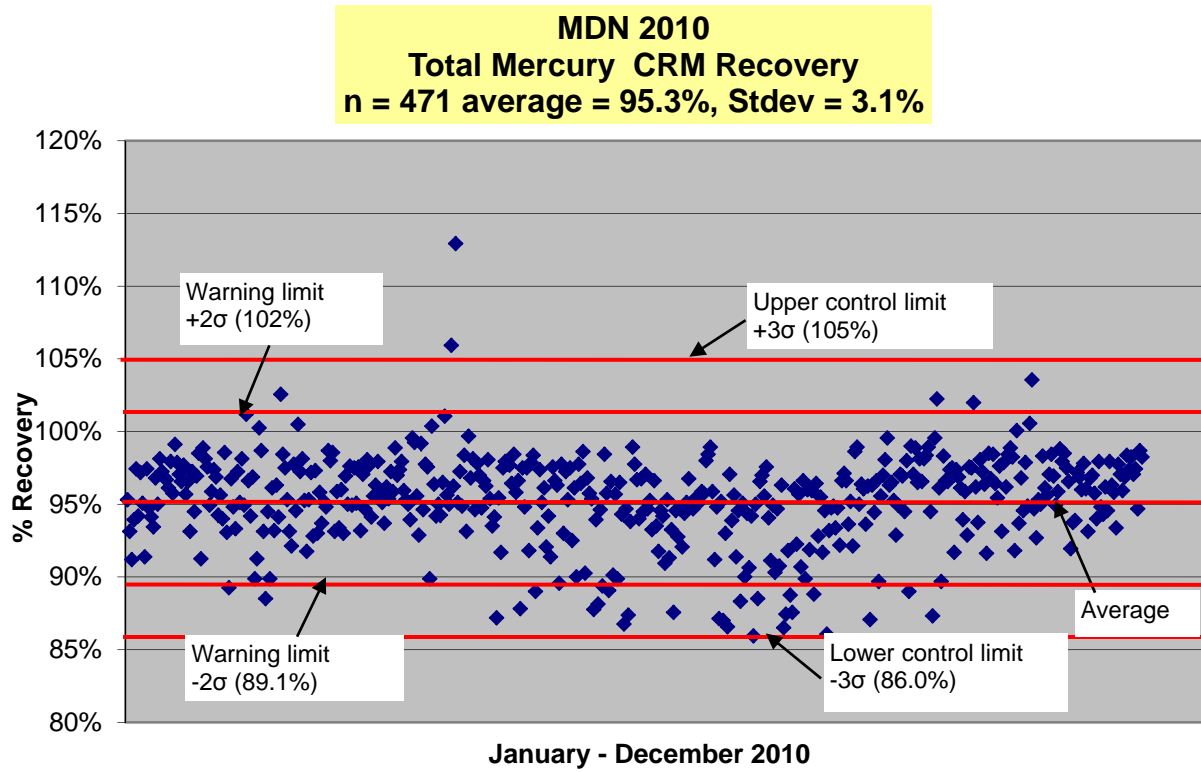


Figure 15 - Control Chart for Total Mercury Percent Recovery in Certified Reference Material Samples During 2010

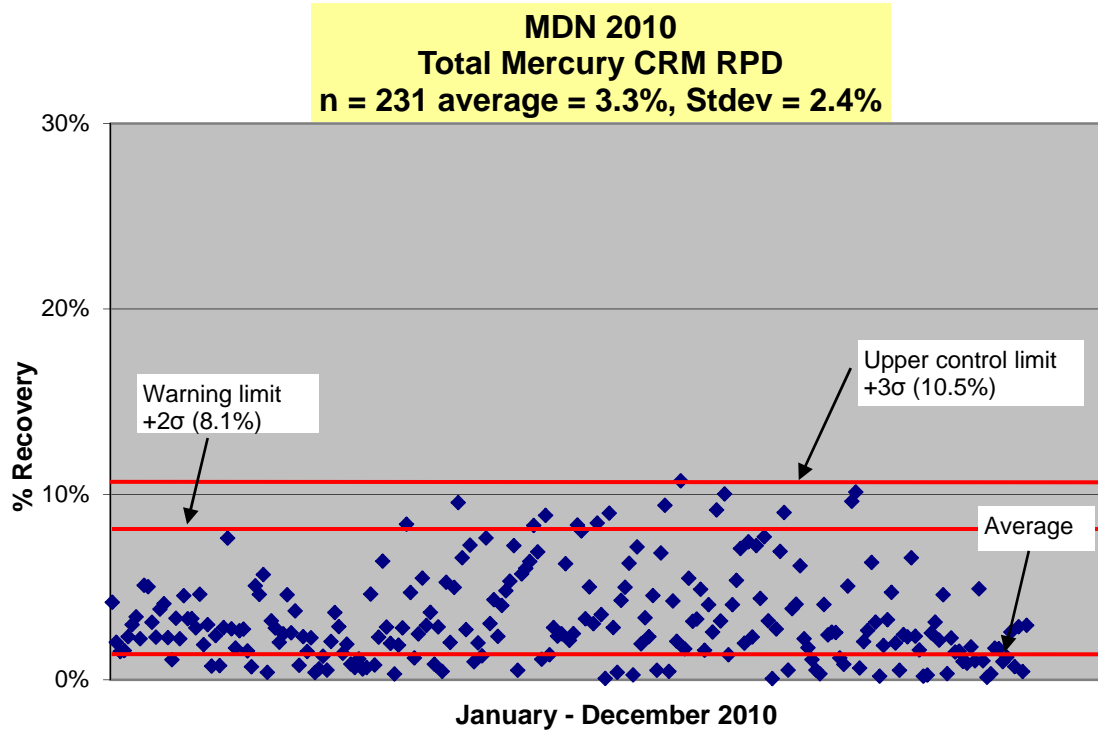


Figure 16 - Control Chart for Total Mercury Percent Relative Difference (%RPD) in CRM /CRM Duplicates Samples During 2010

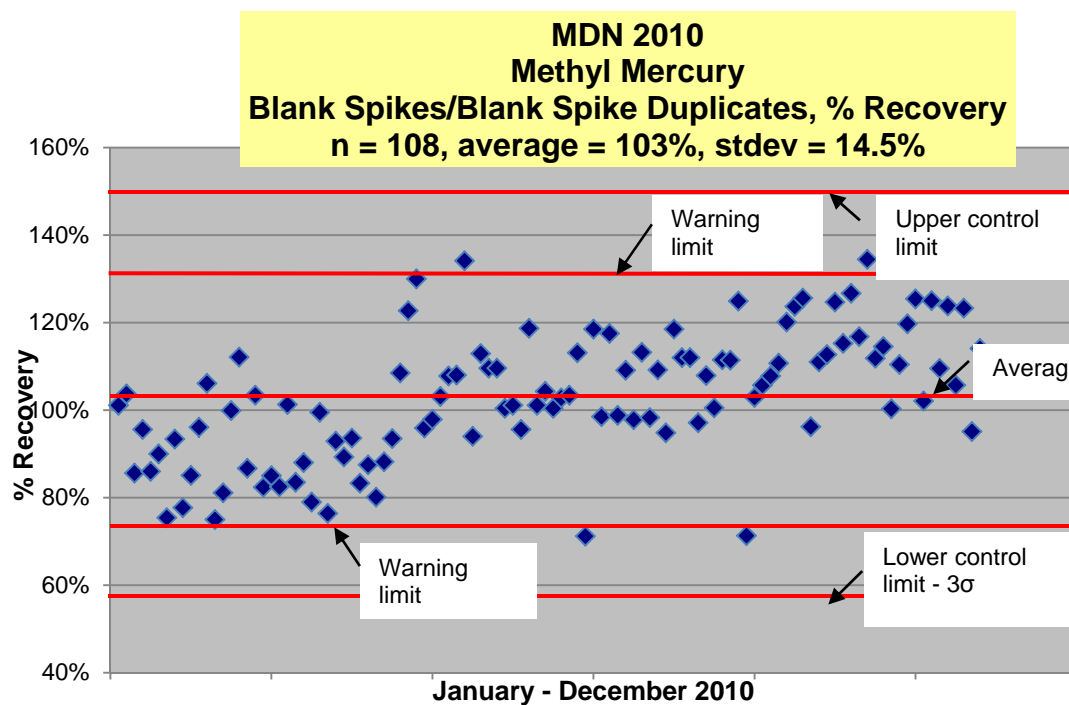


Figure 17 - Control Chart for Methyl Mercury Percent Recovery in Blank Spikes/Blank Spikes Duplicates Samples During 2010

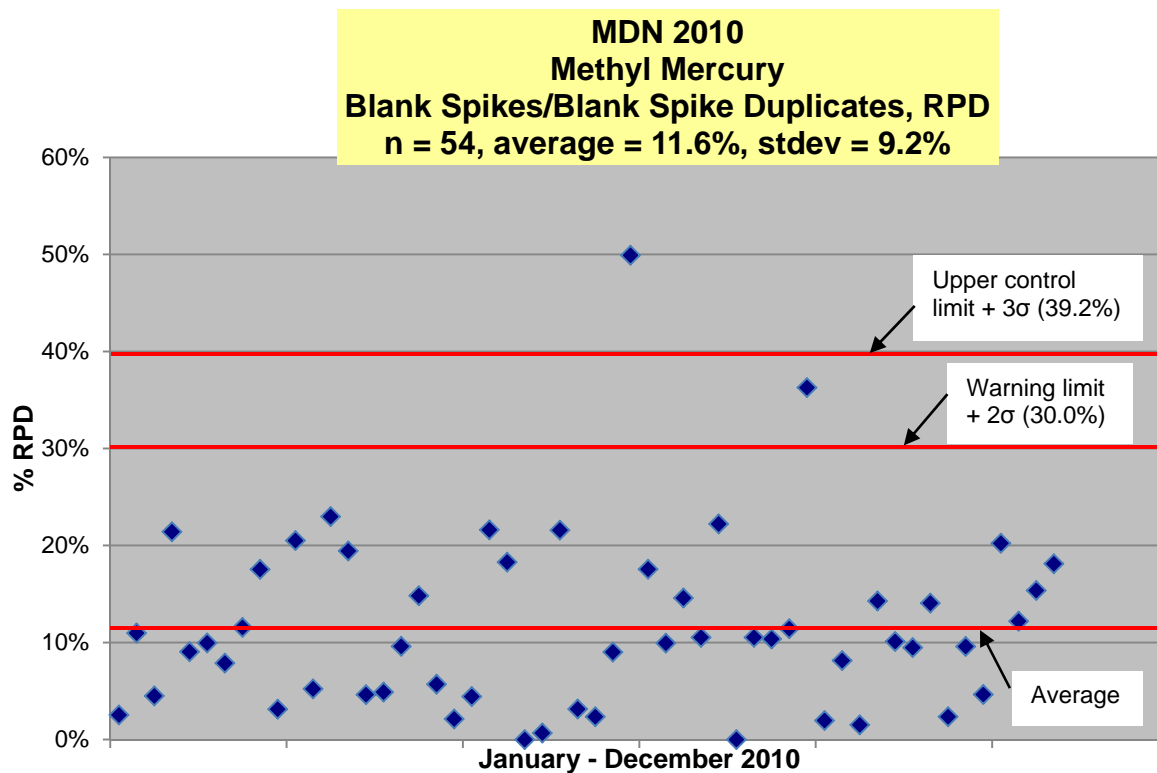


Figure 18 - Control Chart for Methyl Mercury Percent Relative Difference (%RPD) in Blank Spikes/Blank Spikes Duplicates Samples During 2010

### 3. Calculations

Calculations have been color-coded in instances where results become variables in subsequent calculations.

#### 3.1 Calculation: Gross MDN Sample Concentration

$$\text{Calc 1} \{ (\text{Sample PA} - \text{Ave BB}) / \text{Slope} \} - \{ (\text{Aliquot} * \text{BrCl RB}) / 100 \} = \text{ng Hg/aliquot (mL)}$$

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

$$\text{ng Hg/aliquot (mL)} * \text{mL} / \text{Sample Bottle} = \text{ng Hg/Sample Bottle}$$

$$\text{ng Hg/Sample Bottle} - \text{ng Hg/Quarterly Bottle Blank} = \text{net ng Hg/Sample Bottle}$$

$$\text{net ng Hg/Sample Bottle} * (\text{Sample Bottle} / \text{mL}) * 1000 = \text{net ng Hg/L}$$

#### 3.3 Calculation: MDN Deposition

$$\text{Deposition} = \text{Subppt} * \text{Concentration (ng/m}^2\text{)}$$

Subppt: Substituted Precip, mm

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

$$= \text{RainGauge (inch)} * 25.4 \text{ (mm/inch)}$$

If this is selected then Subppt is

$$= \text{BottleCatch (ml)} * 25.4 \text{ (mm/inch)} * 0.003281 \text{ (mL/inch)}$$

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

Concentration: Total Hg Concentration in Precipitation

$$\text{ConcHg} = ((\text{sampleHgMass} - \text{quarterly BottleBlank}) / \text{tmpVol}) * 1000$$

Where:

$$\text{tmpVol} = \text{FullMass} - \text{EmtyMass} - 20 \text{ (20 mL preservative)}$$

$$\text{SampleHgMass} = \text{AliquotHg} * (\text{FullMass} - \text{EmptyMass}) / \text{AliquotVol}$$

## 4. Analytical Run Sequence

HAL routinely includes the previously mentioned QC samples in all of its analyses for the MDN project. The following bench 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:				FGS DATA SET ID:						
Analyzer:				MDN LAB DATA SET CODE:						
Analyst:				REVIEWER:						
				DATE:						
Analytical Run										
D=Duplicate Analysis										
S=Sample Spike @ 1.00ng										
Trap Set:										
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 19 - Example of Sample Analysis Worksheet

## 5. Proficiency Tests and Laboratory Intercomparison Studies

Frontier Global Sciences participates in two water and two soils pollution proficiency tests each year. Frontier also participates in the DMRQA (Discharge Monitoring Report - Quality Assurance) study program each year, which is a requirement for laboratories that have clients with NPDES (National Pollutant Discharge Elimination System) permits. The Proficiency Test (PT) studies are supplied by a licensed and approved commercial provider. Results for each of these studies are submitted to all of Frontier's certifying officers 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 following proficiency tests were completed by FGS during 2010. Results for these tests are available upon request.

**Table 9 - Proficiency Tests**

Proficiency Test Name	Organization	Study Close Date
Non-Potable Water/Solid & Hazardous Waste/Air Emissions Proficiency Study 320	New York Department of Health	03/04/2010
Soil-69	ERA- Environmental Resource Associates	03/11/2010
WP-180 (water pollution)	ERA- Environmental Resource Associates	03/04/2010
Non-Potable Water/Solid & Hazardous Waste/Air Emissions Proficiency Study 325	New York Department of Health	08/26/2010
DMRQA-30 (water pollution)	ERA- Environmental Resource Associates	07/02/2010
WP-186 (water pollution)	ERA-Environmental Resource Associates	09/03/2010
Soil-71	ERA-Environmental Resource Associates	09/02/2010

## 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

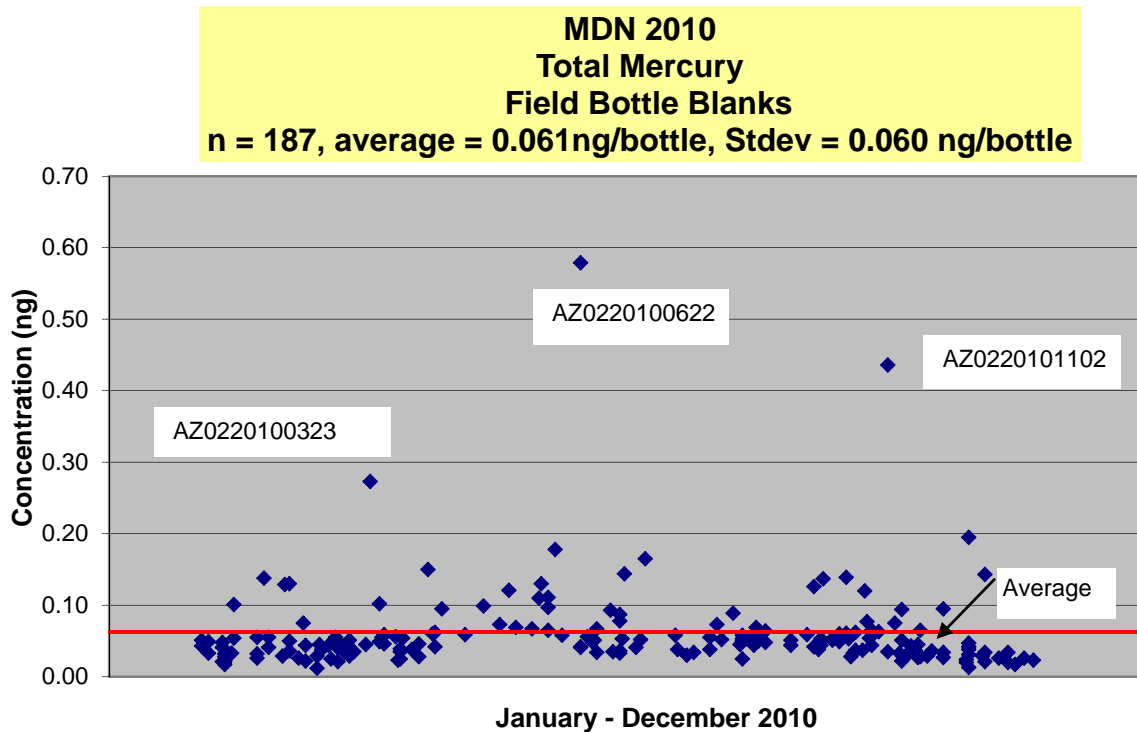
A field bottle blank has the same contents as a laboratory bottle blank. However, this blank is left exposed at the sampling site for the entire collection period without the collector being opened at any time (no rain accumulation). All field bottle blanks that maintain enough of the initial 20 mL 1% hydrochloric acid that at least 15 mL can be measured out as aliquot size, are analyzed for total mercury as a field bottle blank sample. Field blanks with a measured aliquot size less than 15 mL are not analyzed. The analysis is based on mass of sample added to the bubbler and therefore no dilution is needed. There were exactly 100 samples in 2010 that had no recorded precipitation and the event recorder showed the collector did not open, and also had less than 15 mL of preservative in the sample bottle. These results are not tabulated.

#### 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. Contamination sources from the surrounding environment are inevitable and their contributions must be quantified so that they can be subtracted from final sample results. High field blanks can be a result of 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.

#### 6.1.2 Discussion

In 2010, the mean of 187 Field Bottle Blanks was 0.061ng/bottle with a standard deviation of 0.060ng/bottle. Figure 20 shows three samples with elevated mercury values in the field blanks. These samples are AZ0220100323 (0.273 ng/bottle), AZ0220100622 (0.579 ng/bottle), and AZ0220101102 (0.436 ng/bottle). All three elevated field blanks were from the Arizona site AZ02. Of the eleven field blank samples collected from the AZ02 site, nine showed levels higher than the national average of 0.061ng/bottle. The average from the Arizona site was 0.189ng/bottle. In the monthly report for March, which was submitted in the end of May to mid June of 2010, the Site-Liaison questioned the site operator of the lid seal pad condition due to the high field bottle blank. No comment was received from the operator. The HAL mails out new lid seal pads annually to sites. HAL has no records of when the site changed their lid seal pad, since this was not noted on the MOF.



**Figure 20 - Time Series Plot of Total Mercury Concentrations in Field Bottle Blanks During 2010**

## 6.2 Field System Blanks

### 6.2.1 Description

A field system blank is essentially a field bottle blank in which a solution is poured through the wet side collection sample train that was installed in the field for an entire week with no precipitation and no 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).

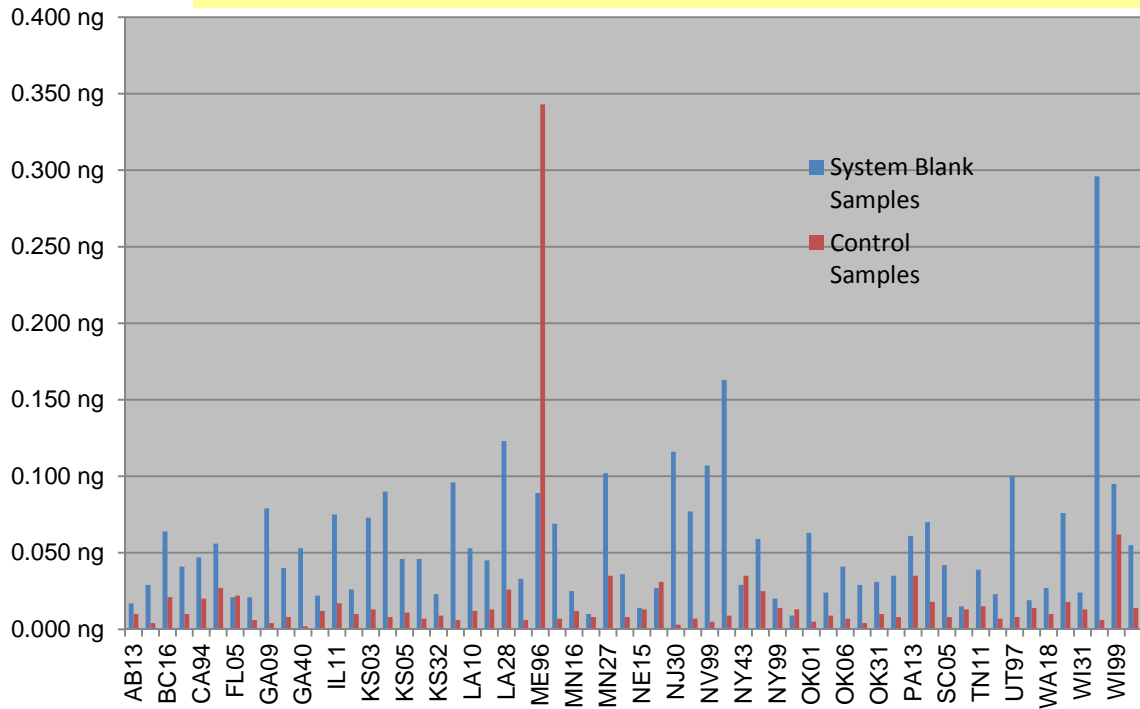
### 6.2.2 Purpose

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

### 6.2.3 Discussion

In 2010, the mean of 60 system blanks was 0.056 ng/aliquot with a standard deviation of 0.045ng/aliquot compared to the control sample with a mean of 0.019ng/aliquot and a standard deviation of 0.044ng/aliquot. The system blanks goes through all the exposed equipment in the field, while the control sample does not. Therefore, even if the system blanks have a higher value than the control sample, the MDN sample train is well protected.

**2010 MDN Total Mercury System Blanks**  
**n = 60**  
**Control Average = 0.019 ng/aliquot, Stdev = 0.044**  
**System Blank Average = 0.056 ng/aliquot, Stdev = 0.045**



**Figure 21 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2010**



## 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 what the general user of the final database will use in the evaluation of MDN data. This QR code is assigned by the computer program based on the results of the notes codes given to each MDN sample. A general description of each 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.

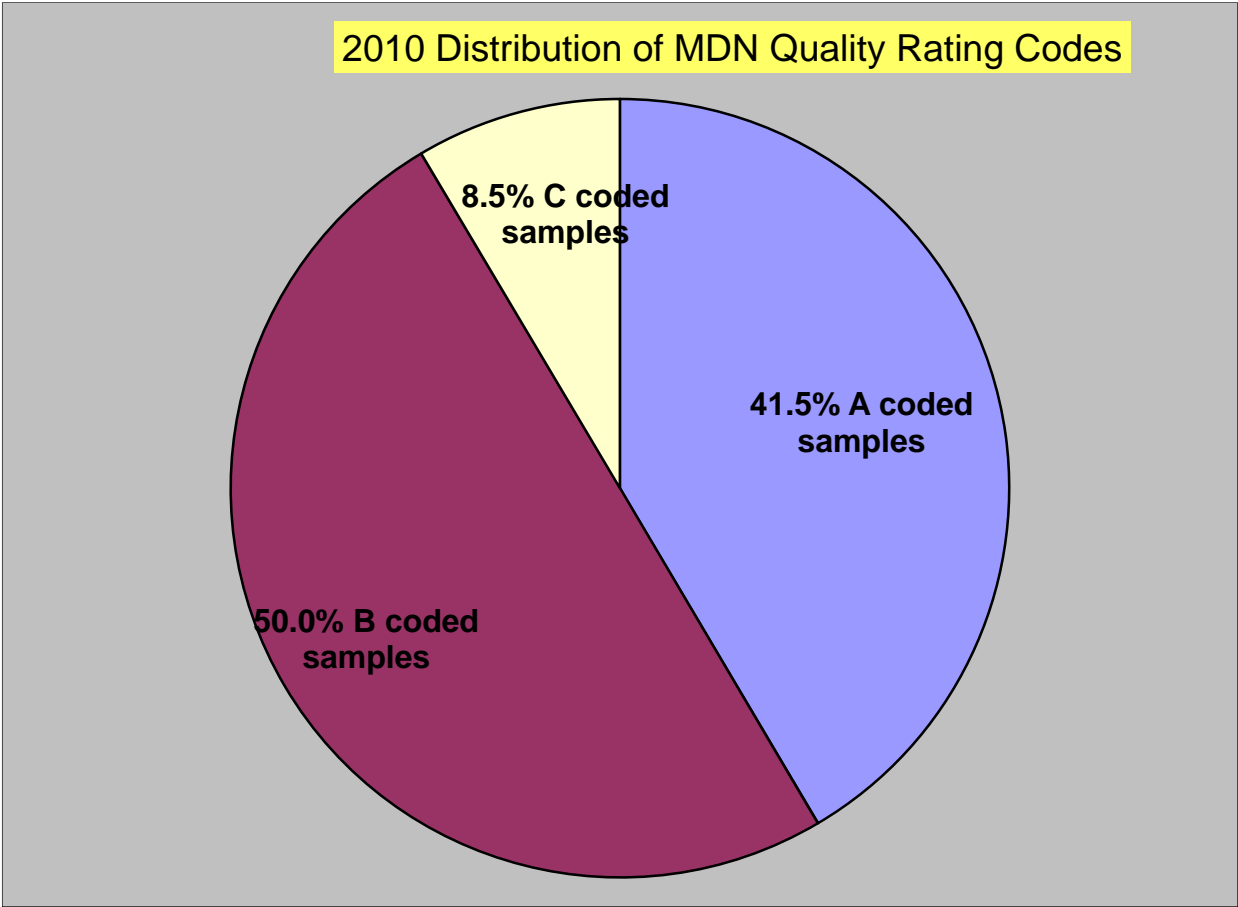
C. Invalid samples; major problems occurred; the laboratory does not have confidence in the data.

The HAL processed 6411 samples in 2010. 2661 samples received a QR code of A, 3203 received a B QR code, and 547 received a C QR code. HAL continued to maintain and demonstrate acceptable quality control in 2010. This comparison is based on HAL assessing the QR codes. These codes can later be changed by the NADP Program Office (PO).

Of the 547 "C" coded samples for 2010, 8 incidents occurred at the laboratory.

1. CA9420100803 – Instrument issues prevented analysis. There was no remaining sample volume for re-analysis. The bottle was received with 17.6 mL of volume, and it was all used in the first aliquot.
2. PA0020100720, PA3020100727, and OR1020100824 – All samples were broken during the transportation from the walk-in refrigerator downstairs up to the MDN Lab. Sample bottles were in a plastic bin that fell off the end of the belt. No volume was salvageable from any of the bottles.
3. PQ1720100914 – Sample bottle was dropped after preservation for methyl Hg while still in its bag. Most of the sample was contained in the bag and was transferred to the new bottle.
4. NC4220100427, ON0720100525, and WI1020100601 – All samples were in the same run, 2010-096, and were unable to be analyzed due to an unplanned power outage on 6/16/10.

The percentage of C-coded samples has increased yearly from 2005 to 2010 from 5.0%, 4.8%, 5.6%, 7.0%, 7.0%, to 8.5%, respectively. This is illustrated in Figure 23. A comparison of the C coded samples has been added in Table 10.



**Figure 22 - Distribution of Quality Rating Codes for Samples Received in 2010**

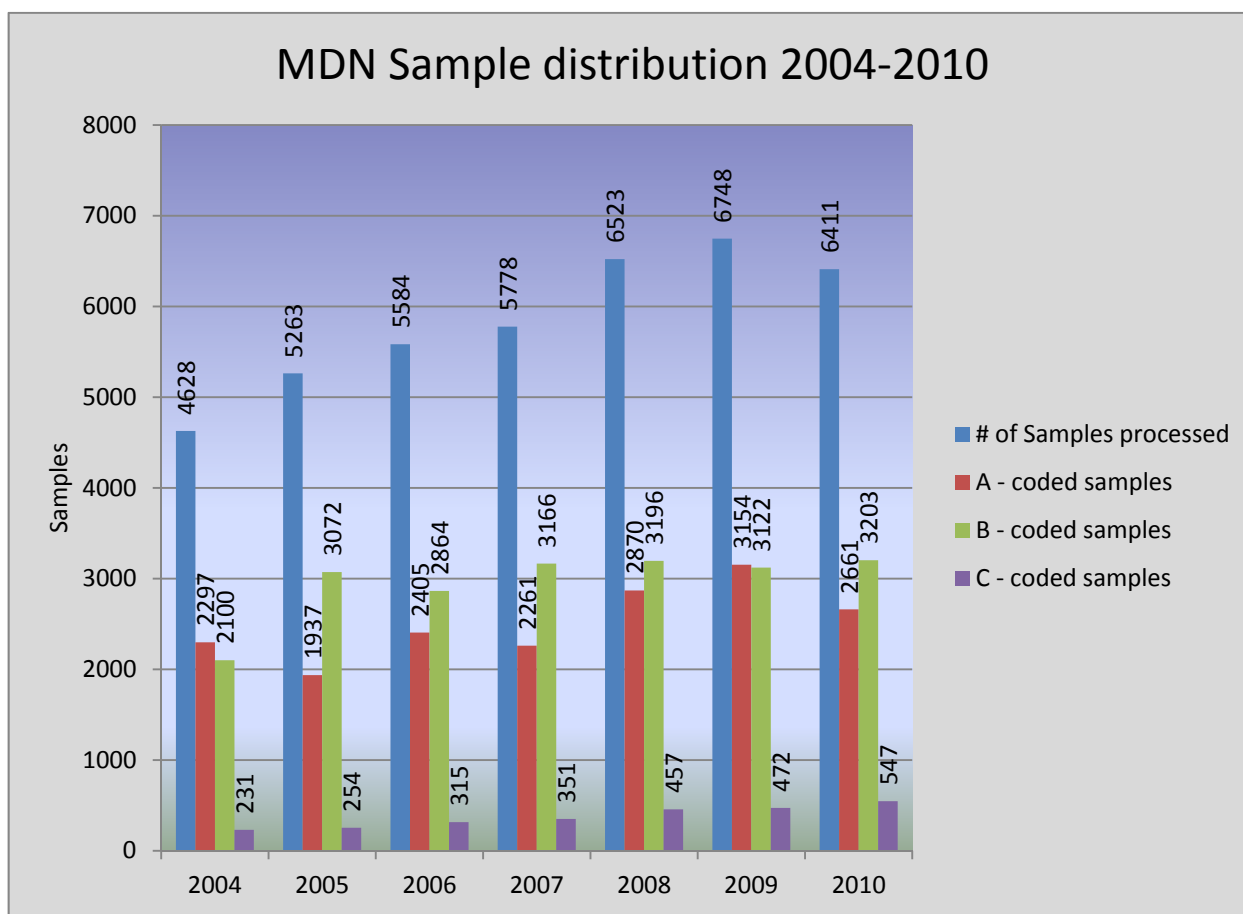


Figure 23 - Distribution of Quality Rating Codes for Samples Received from 2004 to 2010

Error Type	2008	2009	2010
Bulk Sample	51	42	46
Undefined Sample	92	56	108
Site Environment	2	4	0
Sample Condition	20	111	128
Field Protocol	79	13	13
Lab Protocol	5	2	8
Contaminated	2	1	2
Volume Discrepancy	182	193	244
Total	433	422	549

Table 110 - C Coded Samples 2008-2010

## **8. Summary and Conclusions**

The HAL continued to maintain and demonstrate acceptable quality control in 2010. The five DQOs, precision, accuracy, representativeness, comparability, and completeness, were all met. The HAL will continue to look for ways to improve the program to ensure the highest quality. The percentage of C-coded samples has been increasing over the years. HAL will work with the NADP PO to look for ways to decrease the percentage of C-coded samples.

**Table 121 - QC Criteria for EPA 1631E and EPA 1630**

QC Item	EPA Method 1631E Criteria	EPA Method 1630 Criteria
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: 71-125-130% 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

**Table 132 – Qualifiers used by HAL**

Qualifier	Analyte	Text Body
B	THg/MHg	Analyte is found in the associated blank as well as in the sample (CLP B-flag).
E	THg/MHg	The concentration indicated for this analyte is an estimated value above the calibration range of the instrument. This value is considered an estimate (CLP E-flag).
J	THg/MHg	Detected but below the Reporting Limit; therefore, result is an estimated concentration (CLP J-Flag).
QB-01	THg/MHg	The method blank and/or initial/continuing calibration blank contains analyte at a concentration above the MRL. However, the blank concentration(s) are less than 10% of the sample result.
QB-02	THg/MHg	The method blank and/or initial/continuing calibration blank contains analyte at a concentration above the MRL. However, the sample concentrations are less than the MRL.
QB-10	THg/MHg	The method blank and/or initial/continuing calibration blank contains analyte at a concentration above the MRL. Only report sample results greater than 10 times the contamination value (QB-01), or samples less than the MRL (QB-02).
QM-07	THg/MHg	The spike recovery was outside control limits for the MS and/or MSD. The batch was accepted based on LCS and LCSD recoveries within control limits and, when analysis permits, acceptable AS/ASD.
QM-11	MHg	MS and/or MSD recoveries above upper control limits. All reported sample concentrations were below the reporting limit. Batch QC acceptable based on LCS/LCSD recoveries.
QM-12	MHg	Initial or continuing calibration verification and/or blank spike/blank spike duplicate recoveries above upper control limits. All reported sample concentrations were below the reporting limit.
QR-02	THg/MHg	Failing MD is caused by matrix interference. The source sample is not visually homogenous. Acceptable LCS/LCSD show that the preparation of the batch is in control and the failing RPD is due to matrix in-homogeneity.
QR-04	THg/MHg	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 1 time the reporting limit.
QR-06	THg/MHg	The RPD value for the LCS/LCSD was outside of acceptance limits. Batch QC acceptable based on MS/MSD, and where applicable, matrix duplicate RPD value(s) within control limits.
QR-07	THg/MHg	The RPD/RSD value for the matrix duplicate/triplicate was outside of acceptance limits. Batch QC acceptable based on MS/MSD and/or LCS/LCSD RPD values within control limits.
QR-08	THg/MHg	The RPD value for the MS/MSD was outside of acceptance limits. Batch QC acceptable based on matrix duplicate and/or LCS/LCSD RPD values within control limits.
QR-09	THg/MHg	MS/MSD and/or MD/MT RPD or RSD greater than the control limits due to a non-homogenous sample matrix. Batch QC acceptable based on LCS/LCSD RPD.

## Appendix A: MDL Studies 2010



## Matrix Specific MDL Study: Total Mercury in Water CV-AFS # 1

Analyzed by Jeanne Faverman: \_\_\_\_\_

Mercury Laboratory Manager, Gerard Van Der Jagt: \_\_\_\_\_

Report Prepared by Kristina Spadafora: \_\_\_\_\_

### Objective

On an annual basis to determine the Method Detection Limit (MDL) for instrument CV-AFS#1 which is used for the analysis of Mercury Deposition Network (MDN) samples and to verify the already established Practical Quantitation Limit (PQL) for total mercury in water. This is done according to preparation method FGS MDN-04.1 (FGS-012), and analysis method FGS MDN-05.1 (FGS-069), and following the protocols outlined in 40 CFR 136, Appendix B. As detailed below, the MDL for Total Mercury in water samples was determined to be **0.101** ng/L THg for CV-AFS#1.

### Analytical Method

A calibration was performed according to FGS MDN-05.1 (FGS-069). Briefly, this method incorporates oxidation with the addition of BrCl, reduction of Mercury in the sample aliquot with SnCl<sub>2</sub>, analysis by purge and trap and dual amalgamation CV-AFS.

The MDL study consisted of the oxidation and analysis of ten water replicates of a 0.50 ng/L solution. The solution was prepared as follows: 67.5 µL of a 10 ng/mL Hg standard (LIMS# 1001048) was pipette into 1350 grams of reagent water in a 2000 mL volumetric flask. 13.5 mL of BrCl was then added and the solution was brought up to a final volume of 1363.50 mL, resulting in a concentration of 0.50 ng/L of THg oxidized to 1% (v/v) BrCl. The results of these measurements are found in the table on the page 3, as well in the raw data sheets ID # THG011-101006.

All results are reported corrected for the method blanks and corrected the instrument 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,  $\sigma$  is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\text{MDL} = t \cdot \sigma = (2.821) * (0.0358) = \underline{0.101 \text{ ng/L}}.$$

Dataset THg011-101006 was used for the MDL study. All ten replicates showed a percent recovery between 70-130% ( $114.4\% \pm 7.2\%$ ), making this dataset eligible for determining an MDL and to verify the PQL value. The PQL value for this study is 0.50 ng/L which is the same as the spiking level.

## Matrix Specific MDL Study: Total Mercury in Water by CV-AFS# 1

### Total Mercury for Water samples MDL Study Data for CV.AFS #1

**Dataset**

**ID: THG011-101006**

Sample	[THg], ng/L		
BrCl-1	0.080		
BrCl-2	0.090		
BrCl-3	0.050		
<b>Mean</b>	<b>0.073</b>		
<b>SD</b>	<b>0.021</b>		
	Result [THg], ng/L	Spike Level, [TV], ng/L	[%Rec]
MDL-Rep1	0.51	0.50	102.0%
MDL-Rep2	0.58	0.50	116.0%
MDL-Rep3	0.53	0.50	106.0%
MDL-Rep4	0.55	0.50	110.0%
MDL-Rep5	0.55	0.50	110.0%
MDL-Rep6	0.59	0.50	118.0%
MDL-Rep7	0.58	0.50	116.0%
MDL-Rep8	0.60	0.50	120.0%
MDL-Rep9	0.61	0.50	122.0%
MDL-Rep10	0.62	0.50	124.0%
<b>Mean</b>	<b>0.572</b>	<b>0.50</b>	<b>114.4%</b>
<b>SD</b>	<b>0.0358</b>	<b>0.00</b>	<b>7.2%</b>
	[THg], ng/L	Certified Value	[%Rec]
NIST 1641d	7660	7840	<b>97.7%</b>
<b>MDL</b>	0.101		
<b>PQL/MDL</b>	4.95		



## Matrix Specific MDL Study: Total Mercury in Water CV-AFS #9

Analyzed by Adela Blaga: *AB*

Mercury Laboratory Manager, Gerard Van Der Jagt: *GV*

Report Prepared by Kristina Spadafora: *Kristina Spadafora*

### Objective

On an annual basis to determine the Method Detection Limit (MDL) for instrument CV-AFS#9 which is used for the analysis of Mercury Deposition Network (MDN) samples and to verify the already established Practical Quantitation Limit (PQL) for total mercury in water. This is done according to preparation method FGS MDN-04.1 (FGS-012), and analysis method FGS MDN-05.1 (FGS-069), and following the protocols outlined in 40 CFR 136, Appendix B. As detailed below, the MDL for Total Mercury in water samples was determined to be **0.062** ng/L THg for CV-AFS#9.

### Analytical Method

A calibration was performed according to FGS MDN-05.1 (FGS-069). Briefly, this method incorporates oxidation with the addition of BrCl, reduction of Mercury in the sample aliquot with SnCl<sub>2</sub>, analysis by purge and trap and dual amalgamation CV-AFS.

The MDL study consisted of the oxidation and analysis of ten water replicates of a 0.50 ng/L solution. The solution was prepared as follows: 50 µL of a 10 ng/mL Hg standard (LIMS# 1000549) was pipette into reagent water in a 1000 mL volumetric flask. 10 mL of BrCl was then added and the solution was brought up to a final volume of 1010 mL, resulting in a concentration of 0.50 ng/L of THg oxidized to 1% (v/v) BrCl. The results of these measurements are found in the table on the page 3, as well in the raw data sheets ID # THg091-100528.

All results are reported corrected for the method blanks and corrected the instrument 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,  $\sigma$  is the standard deviation of the results obtained on samples spiked at a level near the MDL.

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

Dataset THg091-100528 was used for the MDL study. All ten replicates showed a percent recovery between 70-130% ( $104.4\% \pm 4.4\%$ ), making this dataset eligible for determining an MDL and to verify the PQL value. The PQL value for this study is 0.50 ng/L which is the same as the spiking level.

## Matrix Specific MDL Study: Total Mercury in Water by CV-AFS #9

### MDL Study Data for CV.AFS #9

Dataset ID: THg091-100528

Sample	[THg], ng/L		
BrCl-1	0.050		
BrCl-2	0.010		
BrCl-3	0.010		
<b>Mean</b>	<b>0.023</b>		
<b>SD</b>	<b>0.023</b>		
	Result ng/L	Spike Level, [TV], ng/L	[%Rec]
MDL-Rep1	0.520	0.500	104.0%
MDL-Rep2	0.490	0.500	98.0%
MDL-Rep3	0.480	0.500	96.0%
MDL-Rep4	0.540	0.500	108.0%
MDL-Rep5	0.540	0.500	108.0%
MDL-Rep6	0.540	0.500	108.0%
MDL-Rep7	0.540	0.500	108.0%
MDL-Rep8	0.530	0.500	106.0%
MDL-Rep9	0.530	0.500	106.0%
MDL-Rep10	0.510	0.500	102.0%
<b>Mean</b>	<b>0.522</b>	<b>0.500</b>	<b>104.4%</b>
<b>SD</b>	<b>0.022</b>	<b>0.000</b>	<b>4.4%</b>
	[THg], ng/L	Certified Value	[%Rec]
NIST 1641d	8020	7840	102.3%
<b>MDL</b>	0.062		
<b>PQL/MDL</b>	8.053		



$$\text{MDL} = t^* \sigma = (2.821) * (0.021) = \underline{0.060 \text{ ng/L.}}$$

Dataset THg101-100528 was used for the MDL study. All ten replicates showed a percent recovery between 70-130% ( $116.2\% \pm 4.3\%$ ), making this dataset eligible for determining an MDL and to verify the PQL value. The PQL value for this study is 0.50 ng/L which is the same as the spiking level.

## Matrix Specific MDL Study: Total Mercury in Water by CV-AFS #10

### MDL Study Data for CV.AFS#10

**Dataset ID: THg101-100528**

Sample	[THg], ng/L
BrCl-1	0.040
BrCl-2	0.050
BrCl-3	0.030
<b>Mean</b>	<b>0.040</b>
<b>SD</b>	<b>0.010</b>

	Result ng/L	Spike Level, [TV], ng/L	[%Rec]
MDL-Rep1	0.560	0.500	112.0%
MDL-Rep2	0.560	0.500	112.0%
MDL-Rep3	0.550	0.500	110.0%
MDL-Rep4	0.600	0.500	120.0%
MDL-Rep5	0.570	0.500	114.0%
MDL-Rep6	0.610	0.500	122.0%
MDL-Rep7	0.580	0.500	116.0%
MDL-Rep8	0.590	0.500	118.0%
MDL-Rep9	0.580	0.500	116.0%
MDL-Rep10	0.610	0.500	122.0%
<b>Mean</b>	<b>0.581</b>	<b>0.500</b>	<b>116.2%</b>
<b>SD</b>	<b>0.021</b>	<b>0.000</b>	<b>4.3%</b>

	[THg], ng/L	Certified Value	[%Rec]
NIST 1641d	7970	7840	<b>101.7%</b>

<b>MDL</b>	0.060
<b>PQL/MDL</b>	8.314





## MDL/PQL Study for Methyl Mercury in Water (FGS-070) CV.GC.AFS #7

Analyzed by Adela Blaga: \_\_\_\_\_  
Mercury Supervisor Ryan Nelson: \_\_\_\_\_  
Report Prepared by Lucas Knowles: \_\_\_\_\_  
Report Reviewed by Kristina Spadafora: \_\_\_\_\_

MDL Study Data for Methyl Mercury in Water (FGS-070)  
Sequence# 1C03009 (MMHg07-110303-1)  
Batch# F103033  
WO# 1012134

**Objective.** Determine the method detection limit (MDL) for methyl mercury in water, using the Distillation of Aqueous Samples for Methyl Mercury method FGS-013, and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for Methyl Mercury in Water was determined to be **0.018 ng/L MHg.**

**Analytical Method.** A calibration was performed according to FGS-070. Briefly, this method incorporates the digestion and extraction followed by analysis utilizing aqueous phase ethylation, CV purge and trap, thermal desorption, GC separation, pyrolytic decomposition, and detection using CV-AFS. An efficiency factor of 0.8064 was used.

The MDL study consisted of the distillation and analysis of ten water replicates spiked with 0.050 ng/L of MHg (25  $\mu$ L @ 1.00 ng/mL spiked into 0.50 g distillation vials – LIMS # 1001915). The results of these measurements are found in the table on the next page, as well in the raw data sheets (ID # MHg07-110303-1, 1C03009). All results reported are **corrected** for the instrument blanks and the method blanks.

**MDL Calculation.** Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked samples, with  $n = 9$  replicates (8 degrees of freedom). Ten replicates were originally run, however sample 1012134-10 recovered significantly out of control and was removed as an outlier. In this case, the  $t$  value of 2.896 was used in the following equation, where  $\sigma$  is the standard deviation of the results obtained on samples spiked at a level near the MDL.

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

The MDL calculated from these data is  $(2.896) * (0.0062)$ , or 0.018 ng/L.

**MDL Validation.** The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, R-value, etc.) passed. All 9 replicates for each passing analyte showed a percent recovery between 70-130% and the PQL/MDL was less than 10 make the results eligible to determine both an MDL and a PQL value.

# MDL/ PQL Study for Methyl Mercury in Water (FGS-070) CV.GC.AFS #7

## MHg in waters

**Sequence**            **1C03009**  
**Batch**                **F103033**  
**WO#**                  **1012134**

**% Recovery**  
**Limits:**  
**70-130%**

### 0.050 ng/L, MHg

Sample	[MHg], µg/L			
F103033-BLK1	0.012			
F103033-BLK2	0.010			
F103033-BLK3	0.008			
	[MHg], ng/L	[TV], ng/L	[%Rec]	
1012134-01	0.046	0.050	91.4%	
1012134-02	0.042	0.050	83.9%	
1012134-03	0.047	0.050	94.4%	
1012134-04	0.046	0.050	92.9%	
1012134-05	0.043	0.050	85.4%	
1012134-06	0.055	0.050	111%	
1012134-07	0.059	0.050	118%	
1012134-08	0.053	0.050	106%	
1012134-09	0.043	0.050	85.4%	
<b>Mean</b>	<b>0.048</b>	<b>0.050</b>	<b>96.6%</b>	
<b>SD</b>	<b>0.0062</b>	<b>0.000</b>	<b>12.4%</b>	
<b>F103033-BS1</b>	<b>4.646</b>	<b>5.380</b>	<b>86.4%</b>	<b>%RPD</b>
<b>F103033-BSD1</b>	<b>4.744</b>	<b>5.380</b>	<b>88.2%</b>	<b>2.10%</b>

**MDL**                    0.018  
**PQL (TV)/MDL**        2.78



## MDL/PQL Study for Methyl Mercury in Water (FGS-070) CV.GC.AFS #15

Analyzed by Adela Blaga: Asfa  
Mercury Supervisor Ryan Nelson: Ryan Nelson  
Report Prepared by Lucas Knowles: Lucas Knowles  
Report Reviewed by Kristina Spadafora: Kristina Spadafora

MDL Study Data for Methyl Mercury in Water (FGS-070)  
Sequence# 1B03010 (MMHg15-110203-1)  
Batch# F102012  
WO# 1010242

**Objective.** Determine the method detection limit (MDL) for methyl mercury in water, using the Distillation of Aqueous Samples for Methyl Mercury method FGS-013, and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for Methyl Mercury in Water was determined to be **0.020 ng/L MHg**.

**Analytical Method.** A calibration was performed according to FGS-070. Briefly, this method incorporates the digestion and extraction followed by analysis utilizing aqueous phase ethylation, CV purge and trap, thermal desorption, GC separation, pyrolytic decomposition, and detection using CV-AFS. An efficiency factor of 0.8064 was used.

The MDL study consisted of the distillation and analysis of ten water replicates spiked with 0.056 ng/L of MHg (45  $\mu$ L @ 0.05 ng/mL spiked into 45 mL distillation vials – LIMS # 1001916). The results of these measurements are found in the table on the next page, as well in the raw data sheets (ID # MHg15-110203-1, 1B03010). All results reported are **corrected** for the instrument blanks and the method blanks.

**MDL Calculation.** Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked samples, with  $n = 10$  replicates (9 degrees of freedom). In this case, the  $t$  value of 2.821 was used in the following equation, where  $\sigma$  is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\text{MDL} = t \cdot \sigma$$

The MDL calculated from these data is  $(2.821) \cdot (0.0070)$ , or 0.020 ng/L.

**MDL Validation.** The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, R-value, etc.) passed. All 10 replicates for each passing analyte showed a percent recovery between 70-130% and the PQL/MDL was less than 10 make the results eligible to determine both an MDL and a PQL value.

# MDL/ PQL Study for Methyl Mercury in Water (FGS-070) CV.GC.AFS #15

## MHg in waters

**Sequence**                    **1B03010**  
**Batch**                        **F102012**  
**WO#**                         **1010242**

**%  
Recovery  
Limits:  
70-130%**

### 0.050 ng/L, MHg

Sample	[MHg], µg/L			
F102012-BLK1	0.000			
F102012-BLK2	0.000			
F102012-BLK3	0.000			
	[MHg], ng/L	[TV], ng/L	[%Rec]	
1010242-01	0.047	0.050	93.0%	
1010242-02	0.049	0.050	97.9%	
1010242-03	0.049	0.050	97.9%	
1010242-04	0.055	0.050	110%	
1010242-05	0.037	0.050	73.4%	
1010242-06	0.061	0.050	122%	
1010242-07	0.044	0.050	88.1%	
1010242-08	0.043	0.050	85.7%	
1010242-09	0.045	0.050	90.6%	
1010242-10	0.042	0.050	83.2%	
<b>Mean</b>	<b>0.047</b>	<b>0.050</b>	<b>94.2%</b>	
<b>SD</b>	<b>0.0070</b>	<b>0.00</b>	<b>14.0%</b>	
<b>F102012-BS1</b>	<b>1.649</b>	<b>2.000</b>	<b>82.4%</b>	<b>%RPD</b>
<b>F102012-BSD1</b>	<b>2.040</b>	<b>2.000</b>	<b>102%</b>	<b>21.2%</b>

**MDL**                            0.020  
**PQL (TV)/MDL**            2.54