# National Atmospheric Deposition Program

# Mercury Deposition Network

Mercury Analytical Laboratory

2011 Annual Quality Assurance Report

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# Introduction

Frontier Global Sciences Inc. (FGS) 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 (Figure 1) at the end of 2011, compared to 113 active sites at the end of 2010.

The HAL analyzes weekly precipitation samples for total mercury from all active MDN sites and for methyl mercury from 23 sites. At the end of 2010, MDN had 25 active sites for methyl mercury. 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.
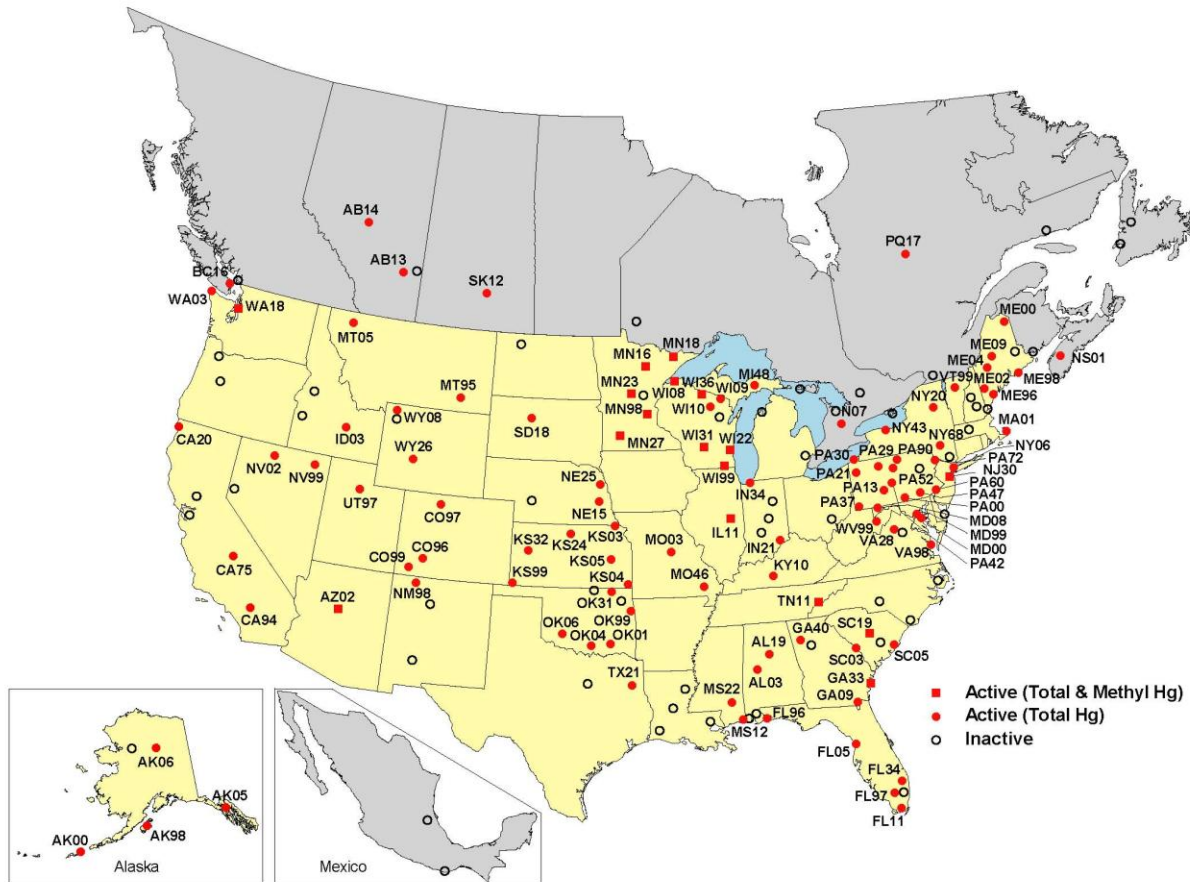


**Figure 1 - Locations of MDN Sites During 2011**

FGS continued to maintain and demonstrate acceptable quality control in 2011. FGS demonstrated consistency and reproducibility in bottle blanks, preparation blanks, certified reference materials, matrix duplicates, and matrix spikes. Results for all of these quality-control (QC) samples are plotted in control charts and summarized in this report.

The following changes occurred between 2010 and 2011.

- During 2011 the Mercury Deposition Network lost a total of four sites, and at the end of 2011, the MDN network included 110 sites, compare to 113 sites at the end of 2010.
- Frontier changed their primary National Environmental Laboratory Accreditation Program (NELAP) accreditation body from the Florida Department of Health to the State of Louisiana Department of Environmental Quality, starting July 1, 2011.
- The MDN network hired Richard Hedelund as a laboratory Technician on September 26, 2011.
- By the end of September, Jeanne Harrell replaced Adela Blaga as primary analyst for total mercury for MDN samples. Adela is the primary methyl mercury analyst of MDN samples and also back-up analyst for total mercury analysis when needed.
- Frontier Global Sciences moved from the previous location at 414 Pontius Avenue North, Seattle, WA 98109 on December 16, 2011 and was back in operation at its new facility at 11720 North Creek Pkwy North, Suite 400, Bothell, WA 98011 on December 19, 2011.

# 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 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 is 75-125% recovery.
- **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 ($\sigma$) 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 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 PQL and the MDL shall be less than or equal to 10 for a MDL to be valid. A PQL/MDL ratio greater than 10 indicates that the study was performed at a too high concentration. The standard deviation was low at the analyzed level and this does not produce enough variability to establish a realistic MDL. The study shall be reanalyzed at a lower concentration.

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 2011. All MDL and PQL studies are on file with the Quality Assurance department and are available upon request.

Two MDL and two IDL studies were completed for the instrumentation used for analysis of MDN samples for total mercury collected during 2011. The IDL studies were performed after the move to the new location in Bothell, before any samples were analyzed on the instruments. The IDL studies were performed to verify that no damage was caused to the instrument during the move and that the instruments would have the same sensitivity, and also to verify that no contamination had been introduced into the system as a result of the move.

The MDL studies for total mercury for instrument #1 and #9 (datasets THg01-111227-1 and THg09-111227-1), were performed at a PQL of 0.50 ng/L and had PQL/MDL ratios greater than 10 at 15.86 and 10.88. Since it is the policy that the PQL/MDL<10 for the MDLs to be acceptable, none of these values have been used in this report. Instead a MDL of 0.074 ng/L has been used. This value was established for the IDL study for instrument #9, and will be used to evaluate data.

Two MDL studies were performed for methyl mercury at a PQL of 0.05 ng/L. A MDL study was performed on instrument 7 after the move to the new building and can be found in dataset MMHg07-111229-1, and a MDL study was performed on instrument 15 in dataset MMHg15-120320-1. The analyzed MDL for methyl mercury for 2011 was 0.019ng/L.

**Table 1 - MDL Studies for 2011 Summary Table**

| Instrument | Dataset | MDL (ng/L) | PQL (ng/L) | PQL/MDL |
|---|---|---|---|---|
| CV-AFS#1 | MDN IDL THg01-111219-1 | 0.056 | 0.50 | 8.94 |
| CV-AFS#9 | MDN IDL THg09-111219-1 | 0.074 | 0.50 | 6.81 |
| CV-AFS#1 | THg01-111227-1 | 0.032 | 0.50 | 15.9 |
| CV-AFS#9 | THg09-111227-1 | 0.046 | 0.50 | 10.9 |
| CV-GC-AFS #7 | MMHg07-111229-1 | 0.01877 | 0.050 | 2.66 |
| CV-GC-AFS #15 | MMHg15-120320-1 | 0.01235 | 0.050 | 4.05 |

## 1.3 Accreditations

Frontier Global Sciences 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. Since July 1, 2011, the State of Louisiana Department of Environmental Quality is Frontier Global Sciences' primary accreditation body for the National Environmental Laboratory Accreditation Program (NELAP). Frontier is also ISO/IEC 17025:2005 accreditation 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 comes in 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 must 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

In 2011, no laboratory bottle blank was higher than the MDL for total mercury performed for 2011 of 0.074 ng/L.

In 2011, there was no laboratory bottle blank above the MDL for methyl mercury. No bottle blanks were taken during the months of September-December and BB2020110428 analyzed in dataset MHg7-110810-1 was excluded due to failing QC. The reason for the missing bottle blanks will be documented with an Incident Report (QA2012-052), which will serve as additional training and reminder of the process. Therefore only six bottle blanks are included in the graph for 2011. . Laboratory bottle blanks are expected to be at, or near, the MDL (0.019ng/L, Table 2). Cases where blanks are higher are 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 because the 20 mL of the 1% HCl added to the sample bottles is diluted to final volume of water collected at the site.  Therefore, the blank values are more meaningful in mass per bottle units.

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

| 2011 Laboratory Bottle Blanks | n | Average (ng/bottle) | Standard Deviation | MDL (ng/L) | PQL (ng/L) |
|---|---|---|---|---|---|
| Total Mercury | 123 | 0.022 | 0.010 | 0.074 | 0.50 |
| Methyl Mercury | 6 | 0.00042 | 0.0004 | 0.019 | 0.050 |

**MDN 2011 Total Mercury**
**Laboratory Bottle Blanks**
**n = 121, average = 0.022 ng/bottle, stdev = 0.010**

Average 0.022 ng/bottle

January - December 2011
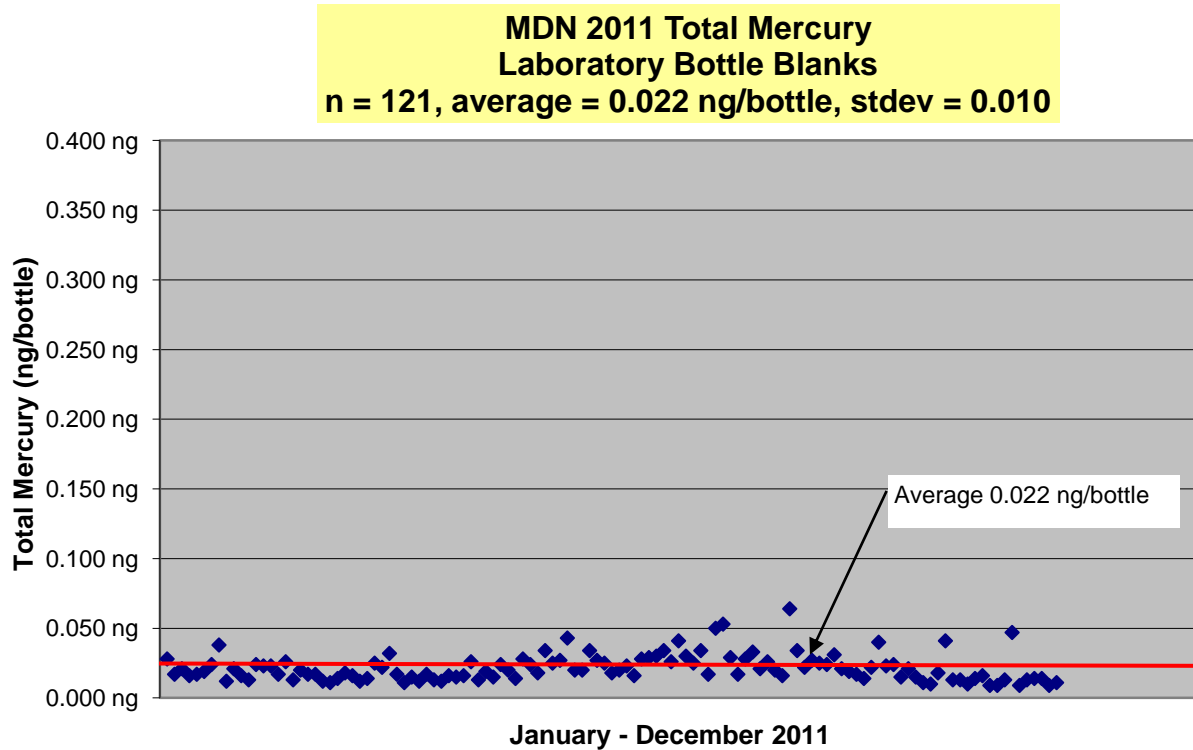
**Figure 2 - 2011 Plot of Total Mercury Mass in Laboratory Bottle Blanks for 121 Samples**



**MDN 2011 Methyl Mercury**
**Laboratory Bottle Blanks**
**n = 6, average = 0.00042 ng/bottle, stdev = 0.00045**

Average 0.00042 ng/bottle

January - December 2011
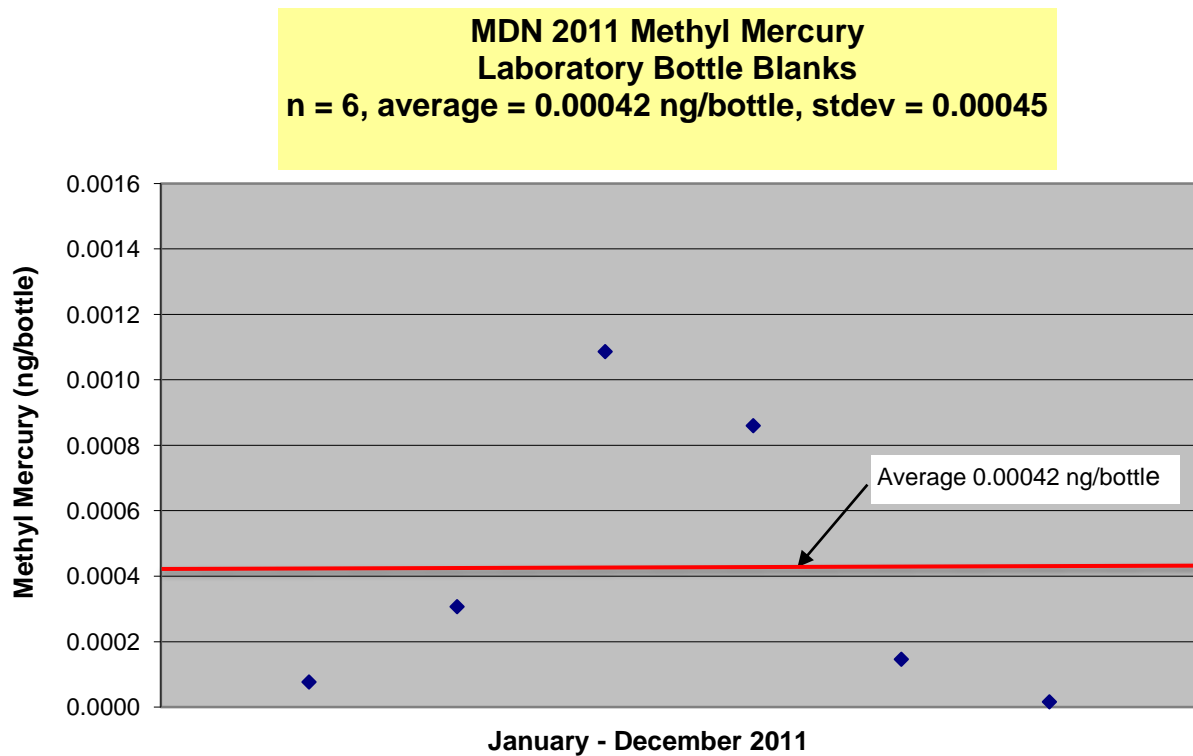
**Figure 3 - 2011 Plot of Methyl Mercury Mass in Laboratory Bottle Blanks for 6 Samples**

# 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 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 100 mL 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 µL), 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 0.25 ng/L. This control limit is lower than the US EPA method 1631E method blank, which individually must be less than 0.50 ng/L, which is the 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. During 2011, HAL did not have control criteria on the standard deviation; see Table 11 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

In 2011, 13 preparation blanks for total mercury were above the calculated $\bar{x}+3\sigma$ limit of 0.143 ng/L. All the preparation blanks analyzed during 2011 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.

In 2011, two preparation blanks for methyl mercury were at the newly established control limit of 0.040 ng/L ($\bar{x}+3\sigma$). None of the preparation blanks was higher than the control limit of 0.045 ng/L. The standard deviation for 2011 of 0.012 ng/L is less than the EPA requirement of <0.015 ng/L.

**Table 3 - Preparation Blanks Summary Table**

| 2011 Preparation Blanks | n | Average (ng/L) | Stdev (ng/L) | MDL (ng/L) | Mean +3σ Control Limit (ng/L) | HAL Control Limit (ng/L) | EPA 1631E/1630 |
|---|---|---|---|---|---|---|---|
| Total Mercury | 674 | 0.030 | 0.038 | 0.101 | 0.143 | 0.25 | < 0.50 |
| Methyl Mercury | 132 | 0.005 | 0.012 | 0.019 | 0.040 | 0.045 | Mean <0.045 σ<0.015 |

**MDN 2011 Total Mercury in Preparation Blanks**
**n = 674, average = 0.030 ng/L, StDev = 0.038**

Warning Limit +2σ (0.106 ng/L)
Control Limit + 3σ (0.143 ng/L)
Average (0.030 ng/L)

Concentration (ng/L)

January - December 2011
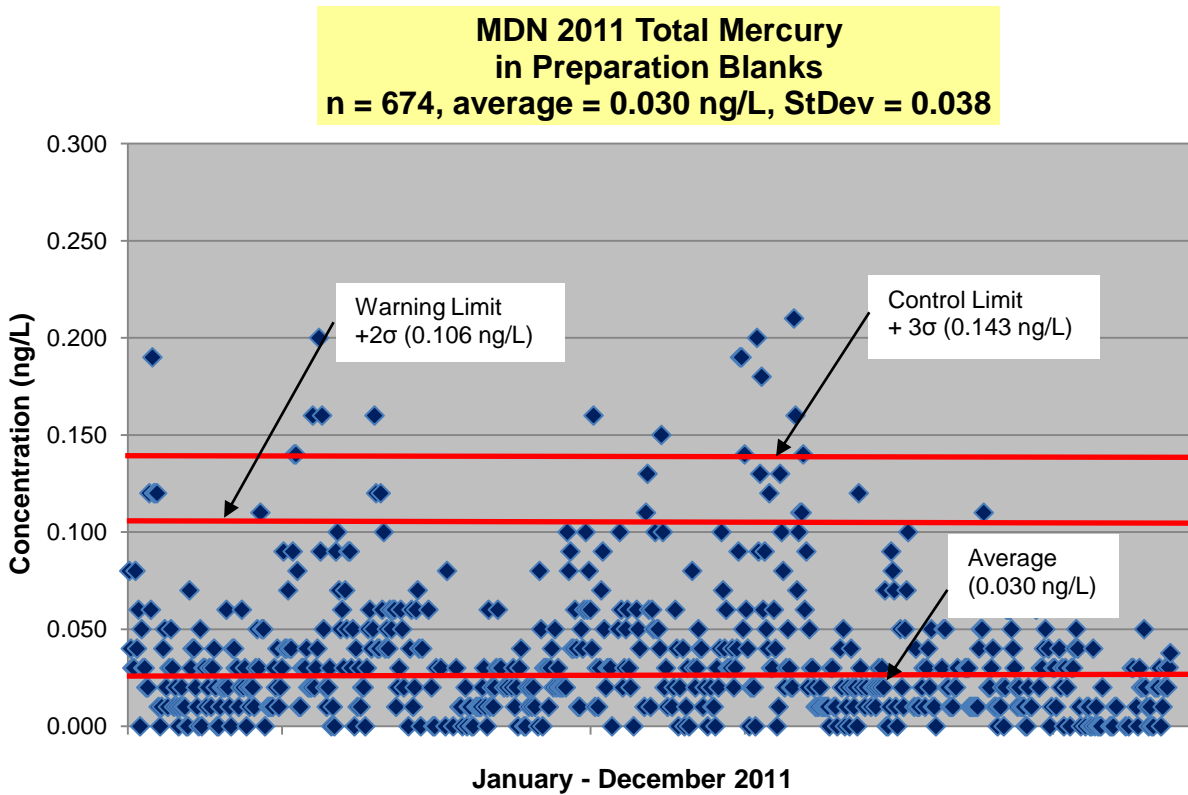
**Figure 4 - 2011 Control Chart for Total Mercury Concentration in Reagent Preparation Blanks**



**MDN 2011 Methyl Mercury Preparation Blanks**
**n = 132, average = 0.0048 ng/L, stdev = 0.0119**

Control Limit + 3σ (0.0405 ng/L)
Warning Limit + 2σ (0.0286 ng/L)
Average (0.0048 ng/L)

Methyl Mercury (ng/L)

January - December 2011
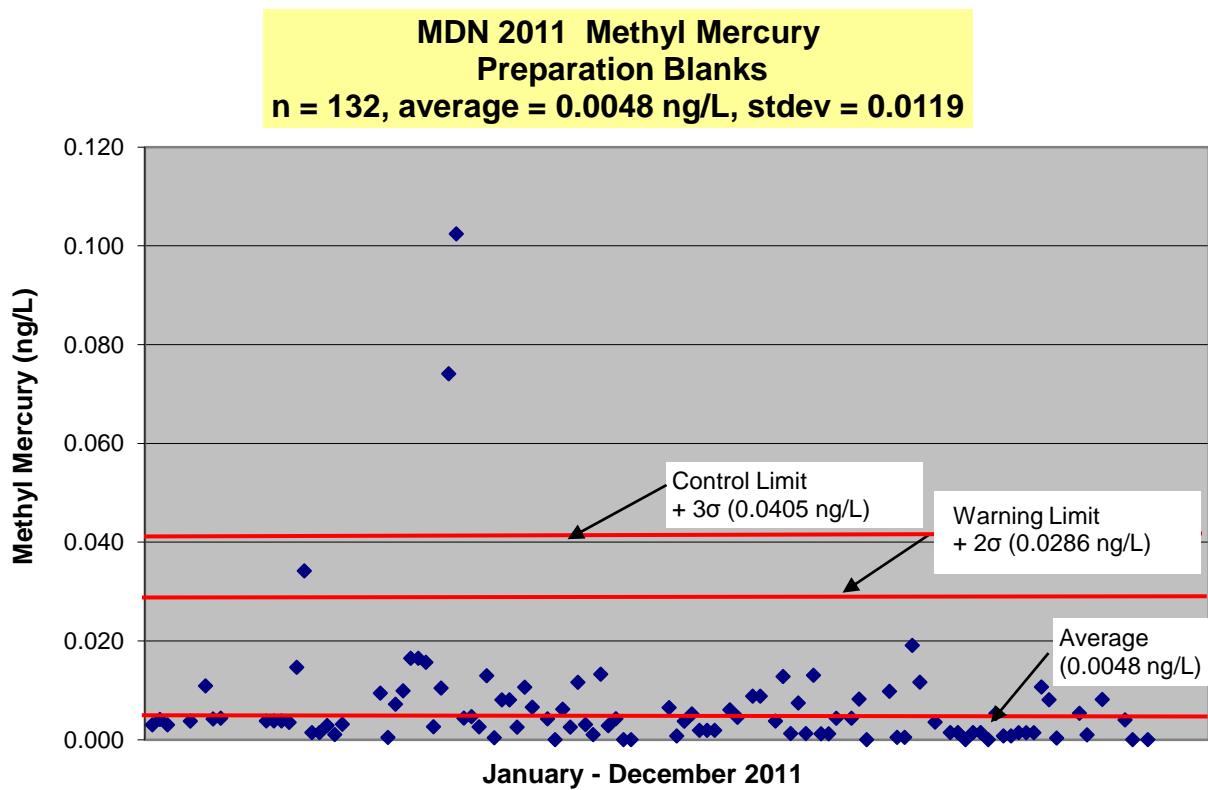
**Figure 5 - 2011 Control Chart for Methyl Mercury Concentration in Reagent Preparation Blanks**

## 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 2 ng/L standard for methyl mercury are analyzed as ongoing calibration standards. 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%.

### 2.2.2 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

Control limits are calculated using the mean value plus/minus three times the standard deviation. For 2011, the range was between 88.0-108.9% for total mercury CCV. Three samples were above the calculated control limit of 108.9% ($\bar{x}$+3σ), and five samples were below the $\bar{x}$-3σ of 88.0%. These values were all within the control limit of 80-120% used at HAL.

No reportable CCV recoveries were outside the $\bar{x}$±3σ control limit of 72.3-126.4% for methyl mercury.

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

| 2011 Continuing Calibration Standard | n | Average recovery (%) | Stdev of recovery (%) | ±3σ Control Limit (%) | EPA 1631E/1630 Control Limits (%) |
|---|---|---|---|---|---|
| Total Mercury | 806 | 98.5 | 3.5 | 88.0-109 | 77-123 |
| Methyl Mercury | 141 | 98.7 | 11.7 | 72.3-126 | 67-133 |

**MDN 2011 Total Mercury
Ongoing Calibration Standard
n = 806, average = 98.5 %, stdev = 3.5 %**

Upper Warning Limit
+ 2σ (105%)

Upper Control Limit
+ 3σ (109%)

Average
(98.5%)

Lower Warning Limit
-2σ (91.5%)

Lower Control Limit
- 3σ (88.0%)

% Recovery

January - December 2011
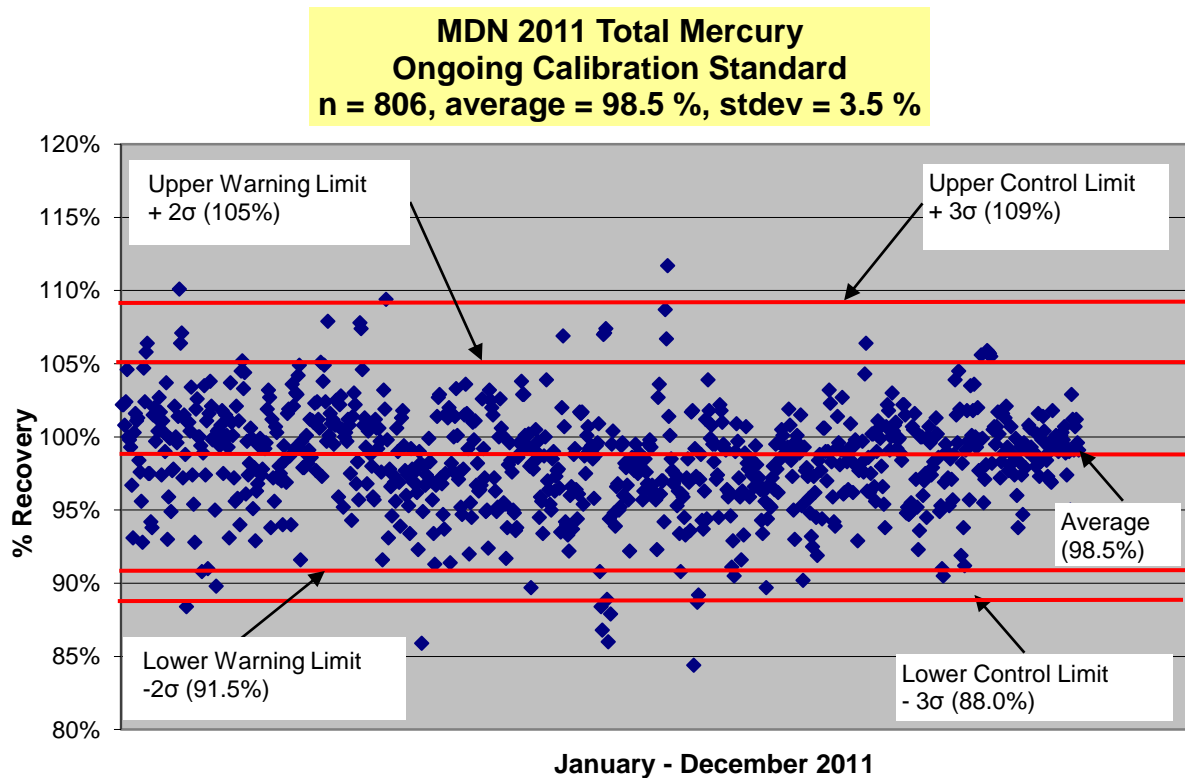
**Figure 6 - 2011 Control Chart for Total Mercury Continuing Calibration Standard Percent Recovery**



**MDN 2011  Methyl Mercury
Ongoing Calibration Standard
n = 132, average = 99.3%, stdev = 9.0%**

Upper Control Limit
+ 3σ (126%)

Upper Warning Limit
+ 2σ (117%)

Average
(99.3%)

Lower Control Limit
- 3σ (72.3%)

Lower  Warning Limit
- 2σ (81.3%)

% Recovery

January - December 2011
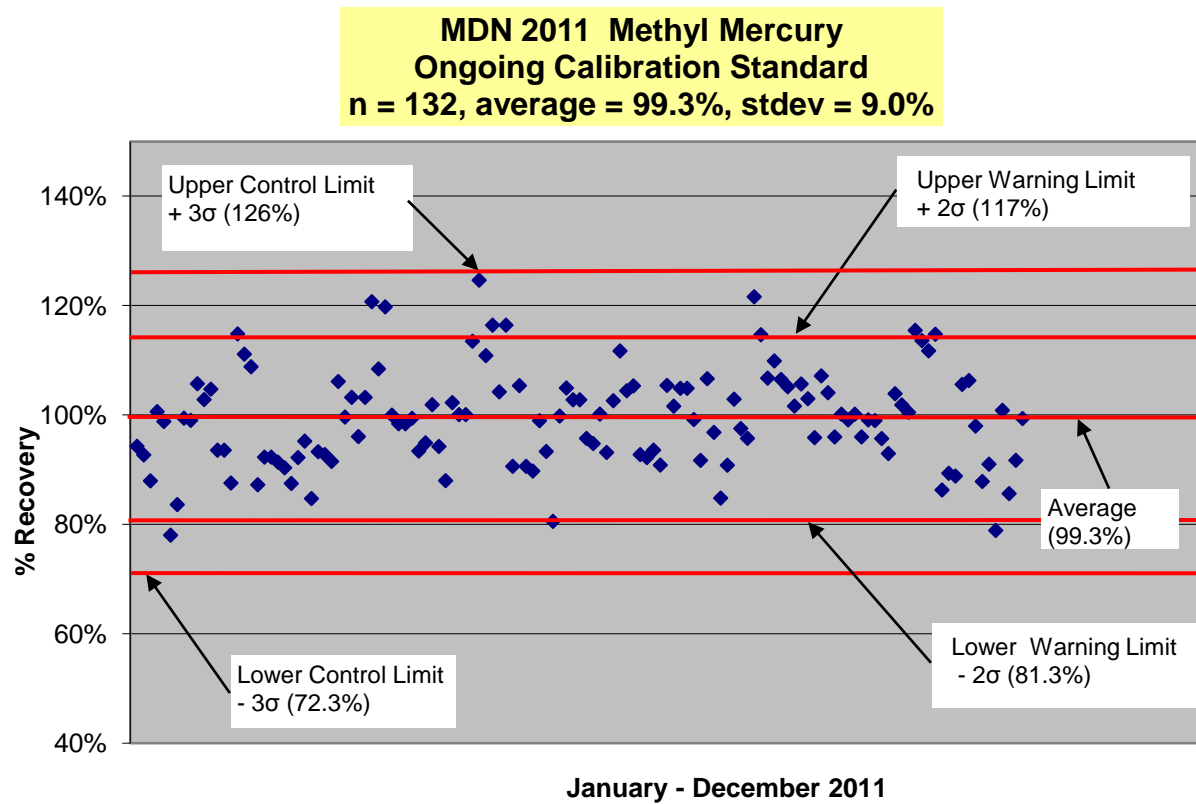
**Figure 7 - 2011 Control Chart for Methyl Mercury Ongoing Calibration Standard Percent Recovery**

## 2.3 Continuing Calibration Blanks

### 2.3.1 Description

Continuing Calibration Blanks (CCBs) are analyzed during the course of sample analysis, 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

There were several ongoing CCBs for the MDN project in 2011 for total mercury that were outside the calculated control limit of -0.093 to 0.098 ng/L ($\bar{x}\pm3\sigma$). No CCBs exceeded 0.25 ng/L, which is the control limit that is used for MDN analysis at HAL.

For 2011, a control limit for methyl mercury based on ($\bar{x}\pm3\sigma$) is -0.002 to 0.009 ng/L, and only two CCBs were above the upper control limit at 0.010 ng/L.

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

| 2011 Ongoing Calibration Blanks | n | Average (ng/L) | Stdev (ng/L) | MDL (ng/L) | Control Limits (ng/L) | EPA 1631E/1630 Control Limits |
|---|---|---|---|---|---|---|
| Total Mercury | 1703 | 0.003 | 0.032 | 0.074 | -0.093-0.098 | Individually <0.50 ng/L, mean <0.25 ng/L with a standard deviation <0.10 ng/L |
| Methyl Mercury | 136 | 0.004 | 0.002 | 0.019 | -0.002-0.009 | NA |

**MDN 2011 Total Mercury**
**Ongoing Calibration Blanks**
**n = 1703, average = 0.003 ng/L, stdev = 0.032**

Upper Control Limit
+ 3σ (0.098 ng/L)

Upper Warning Limit
+ 2σ (0.066 ng/L)

Average
(0.003 ng/L)

Lower Warning Limit
-2σ (-0.061 ng/L)

Lower Control Limit
- 2σ (-0.093 ng/L)
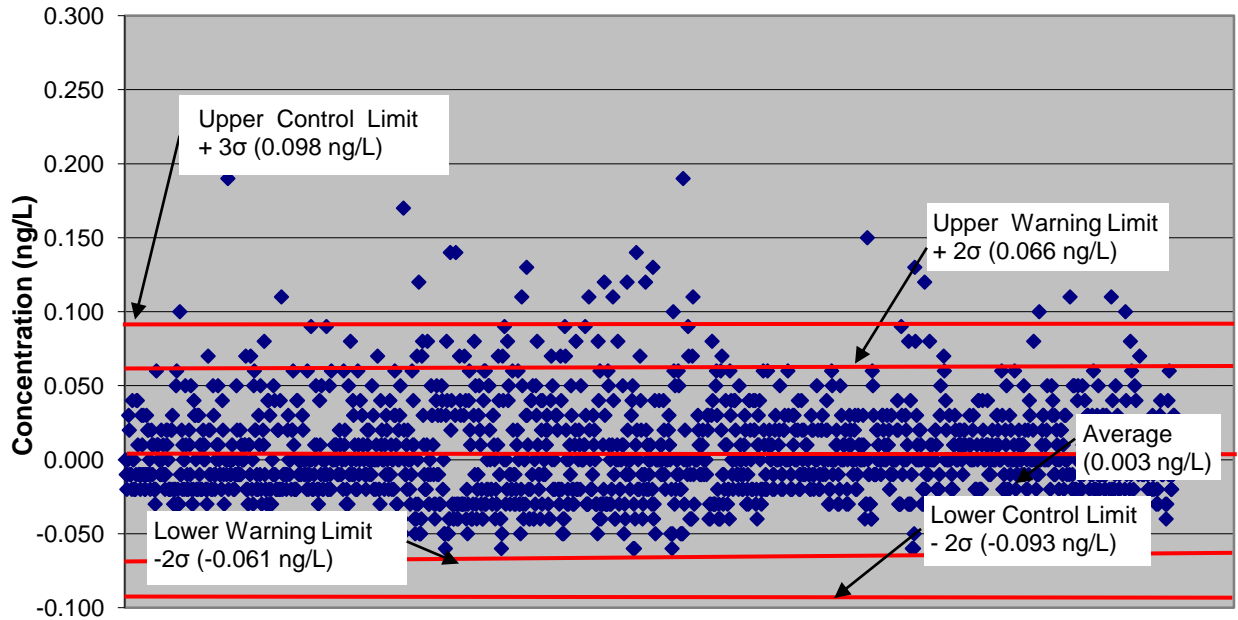
**Figure 8 - 2011 Control Chart for Total Mercury Continuing Calibration Blanks**

**MDN 2011 Methyl Mercury**
**Ongoing Calibration Blanks**
**n = 136, average = 0.004 ng/L, stdev = 0.002**

Upper Control Limit
+ 3σ (0.009 ng/L)

Upper Warning Limit
+2σ (0.007 ng/L)

Average
(0.004 ng/L)

Lower Control Limit
-3σ (-0.002 ng/L)

Lower Warning Limit
-2σ (-0.0001 ng/L)
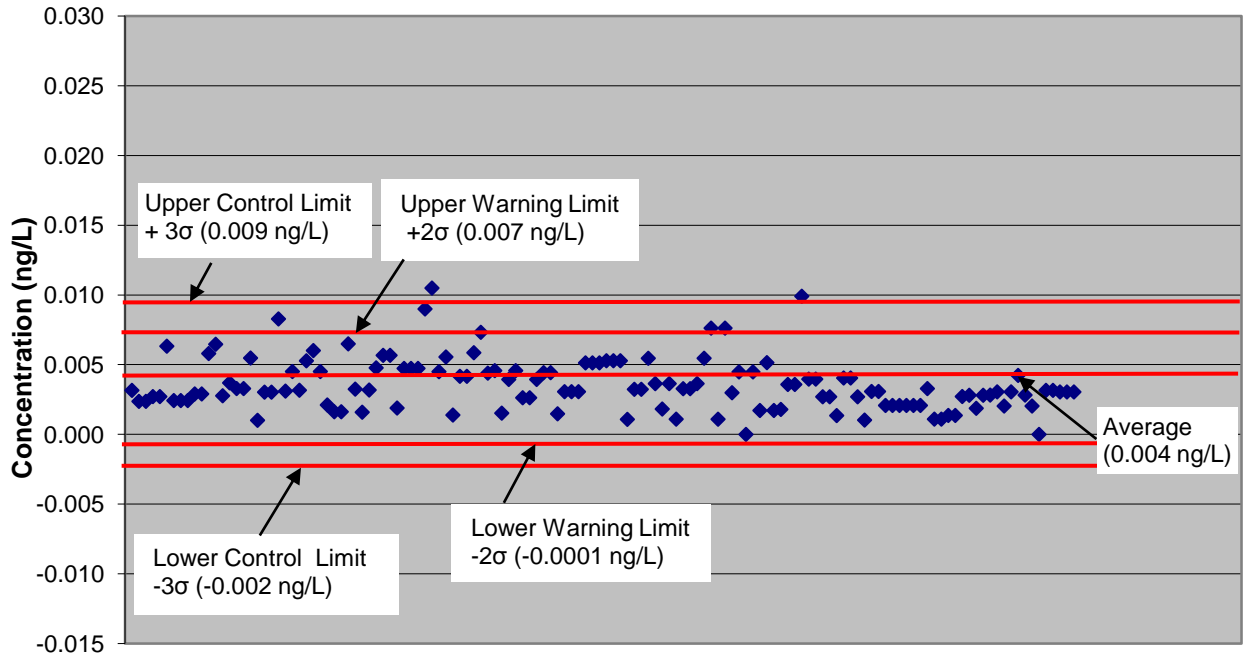
**January - December 2011**

**Figure 9 - 2011 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 an inhomogeneous sample matrix and/or poor analytical precision.

### 2.4.3 Discussion

For 2011, the calculated control limit for total mercury based on $\bar{x}+3\sigma$ was 14.2% 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 84.3% 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 0.050 ng/L and can result in high RPD. As an example, 99PR20111207 was analyzed in duplicate on 3/21/2012 with results below the lowest calibration point at 0.000 ng/L and 0.001 ng/L, which results in a RPD of 600.0% (this data point has been removed from the chart). 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 as according to 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 12 for qualifiers used at HAL.

Values for QC samples that were qualified for known problems were excluded from the control charts to avoid misrepresentation of actual precision.

**Table 6 - Matrix Duplicates Summary Table 2011**

| 2011 Matrix Duplicates | n | Average RPD (%) | Stdev (%) | Upper control Limit +3σ (%) | EPA 1631E/1630 Control Limits |
|---|---|---|---|---|---|
| Total Mercury | 667 | 3.3 | 3.6 | 14.2 | NA |
| Methyl Mercury | 20 | 20.1 | 21.4 | 84.3 | NA |

**MDN 2011 Total Mercury
Matrix Duplicate RPD
n = 667, average = 3.3%, stdev = 3.6%**

Control Limit
+ 3σ (14.2% )

Warning Limit
+ 2σ (10.5%)

Average
(3.3%)

January - December 2011
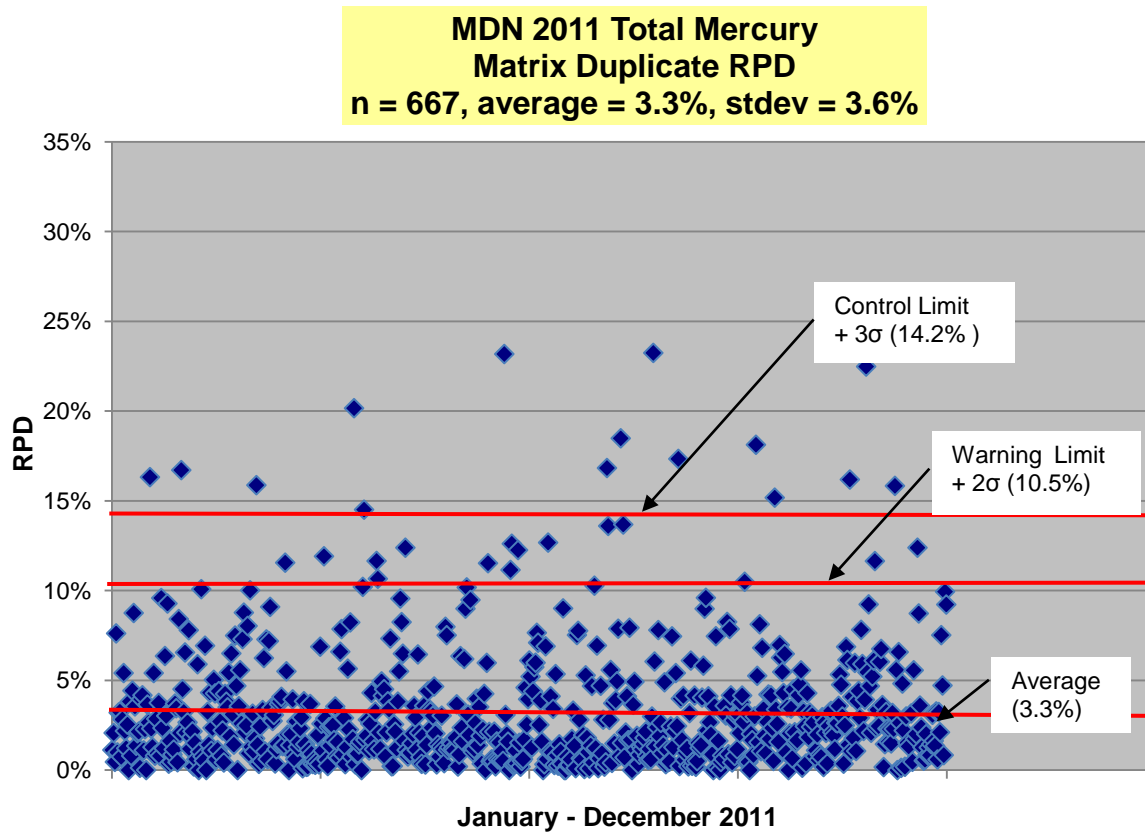
**Figure 10 - 2011 Control Chart of the Relative Percent Differences for Total Mercury Concentrations in Matrix Duplicates**



**MDN 2011 Methyl Mercury
Matrix Duplicate RPD
n = 20, average = 20.1%, stdev = 21.4%**

Control Limit
+ 3σ (84.3%)

Warning Limit
+ 2σ (62.9%)

Average
(20.1%)

January - December 2011
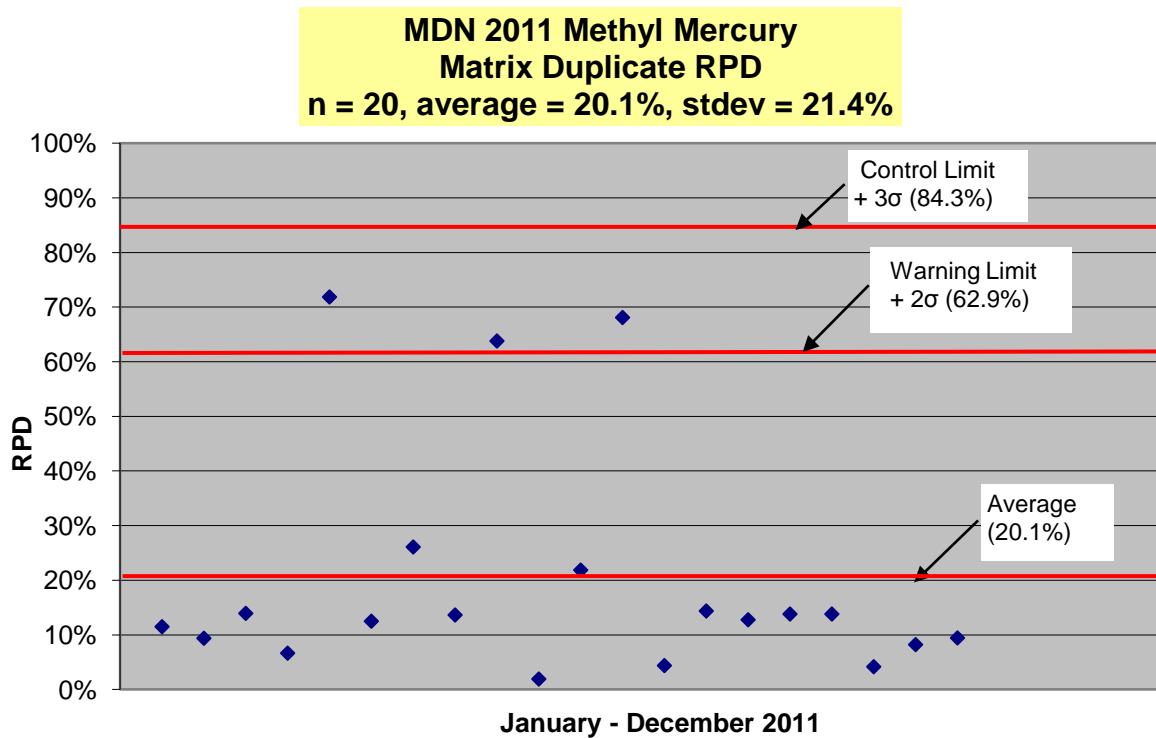
**Figure 11 - 2011 Control Chart of the Relative Percent Differences for Methyl Mercury Concentrations in Matrix Duplicates**

## 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 and during a normal analytical run three matrix spikes are analyzed. The source samples are selected depending on available volume as 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 $\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 is a sign of matrix interference, after investigation by trap and bubbler testing, the samples 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 size.

### 2.5.3 Discussion

The control limit for the recovery of the matrix spike for THg based on $\bar{x}\pm3\sigma$ is 79.9%-113%. For 2011, only two values were greater than 113%, these were both analyzed on the same dataset 2011-127. All values are within the 75-125% control limit used at HAL.

For methyl mercury, a control limit 62.5%-147% was calculated based on $\bar{x}\pm3\sigma$ for the recovery of the matrix spike and the matrix spike duplicate. During 2011, MS % recovery was greater than the 130% (control limit in the laboratory) for four samples, and one of these values was also above the calculated low control limit of 147% at 156.9% recovery. The high recovery at 156.9% was analyzed in dataset MHg7-110804-1, which had acceptable recoveries for the BS/BSD at 107.8% and 118.7%, and could therefore be qualified with QM-07 (table 12). No values were below the laboratory control limit of 65% recovery.

The relative percent difference (RPD) of the matrix spike/matrix spike duplicates had a calculated control limit of 25.7% ($\bar{x}+3\sigma$) for 2011. No RPD exceeded 25%.

**Table 7 - Matrix Spike Recoveries for 2011 Samples**

| 2011 Matrix Spikes | n | Average Recovery (%) | Stdev of Recovery (%) | Control Limits ±3σ (%) | HAL Control Limits | EPA 1631E/1630 Control Limits (%) |
|---|---|---|---|---|---|---|
| Total Mercury | 667 | 96.4 | 5.5 | 79.9-113 | 75-125 | 71-125 |
| Methyl Mercury | 76 | 105 | 14.1 | 62.5-147 | 65-135 | 65-135 |

**Table 8 - Matrix Spike/Matrix Spike RPD for 2011 Samples**

| 2011 Matrix Spikes | n | Average RPD (%) | Stdev (%) | +3σ (%) | EPA 1630 Control limits RPD (%) |
|---|---|---|---|---|---|
| Methyl Mercury | 38 | 7.3 | 6.2 | 25.7 | <35% |

**MDN 2011 Total Mercury
Matrix Spike Percent Recoveries
n = 667, average = 96.4%, std=5.5%**
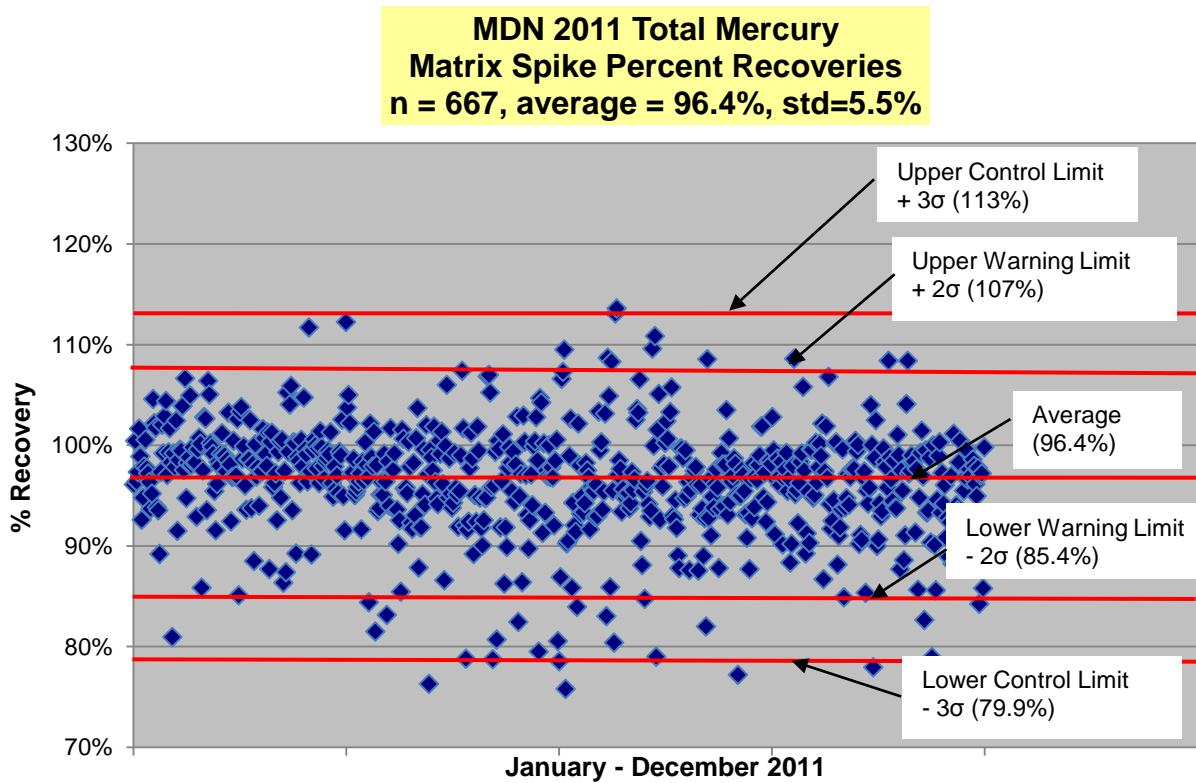
**Figure 12 - Control Chart for Total Mercury Percent Recovery in Matrix Spikes During 2011**



**MDN 2011 Methyl Mercury
Matrix Spikes/Matrix Spike Duplicates, % Recovery
n = 76, average = 104.8%, stdev = 14.1**
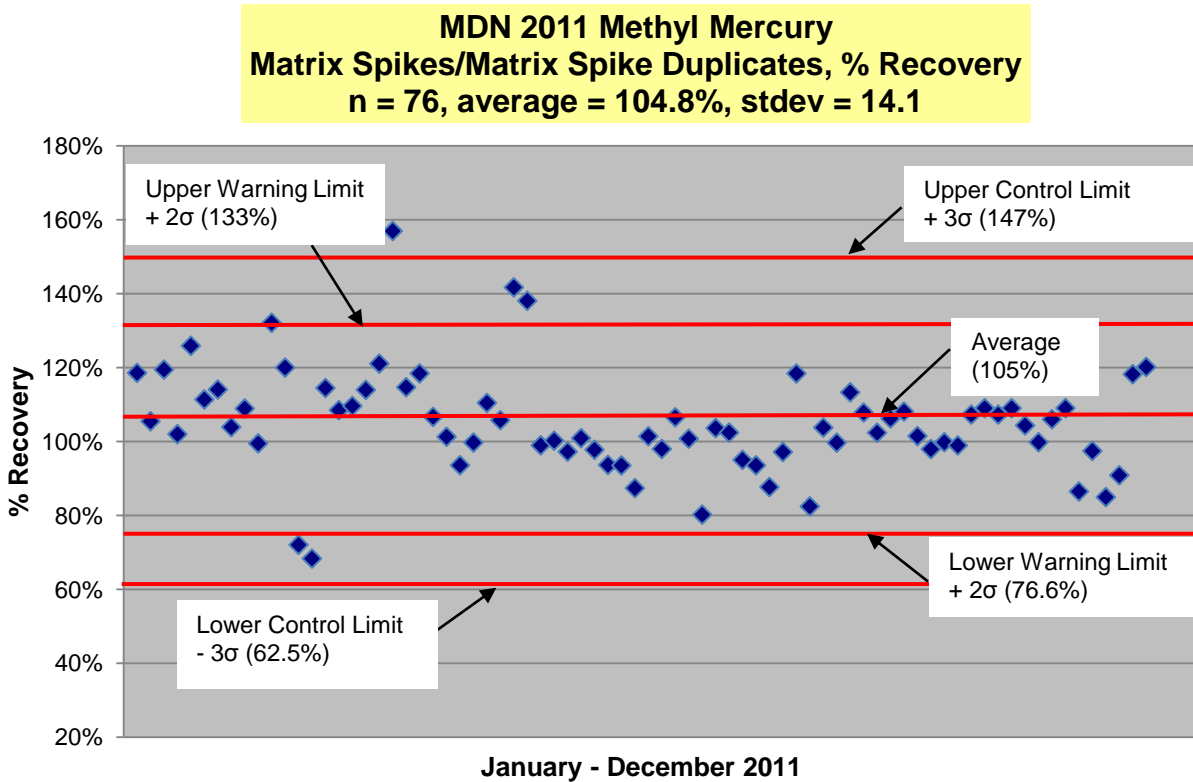
**Figure 13 - Control Chart for Methyl Mercury Percent Recovery in Matrix Spikes During 2011**

**MDN 2011 Methyl Mercury
Matrix Spikes/Matrix Spike Duplicates, RPD
n = 38, average = 7.3%, stdev = 6.2%**
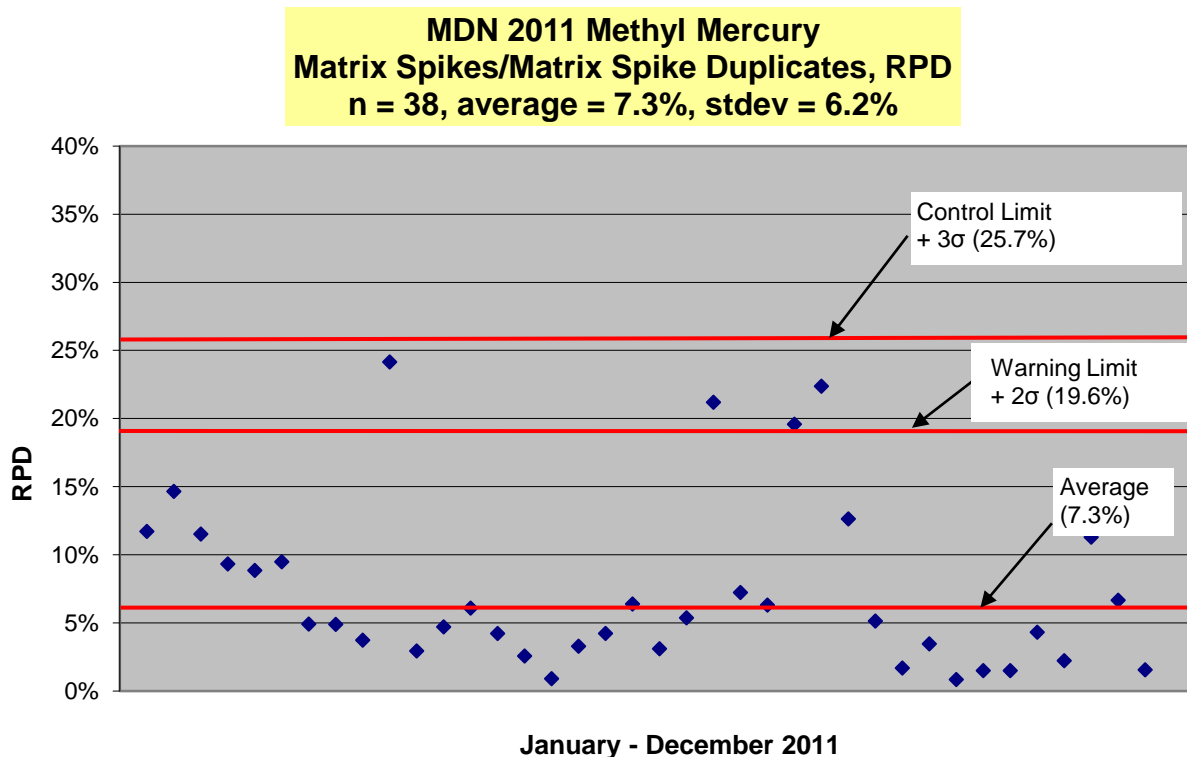
**Figure 14 - Control Chart of the Relative Percent Differences for Methyl Mercury Matrix Spike/Matrix Spike Duplicate Pairs during 2011.**

## 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. 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 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 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.

### 2.6.2 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

In 2011, the mean of 446 certified reference material recoveries for total mercury was 96.0% with a standard deviation of 2.9%. There was one certified reference material recovery above the upper control limit of 105% ($\bar{x}+3\sigma$) and two below the lower control limit of 87.3% ($\bar{x}-3\sigma$). 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 3.1% (n=223), with a standard deviation of 2.5%. Three RPD values were above the upper control limit calculated by $\bar{x}\pm3\sigma$ of 10.5%. All the RPD values were below the 25% used in the laboratory and shows high precision between the samples.

In 2011, the mean recovery of 90 blank spikes and blank spike duplicates for methyl mercury was 105% with a standard deviation of 10.3%. There was one blank spike with recovery outside the control limit of 74.1-136% based on $\bar{x}\pm3\sigma$ for 2011 at 140.6%. This was for dataset MHg7-120119-1 where 8 samples were qualified by QM-12 (table 12) and reported.  All other samples were flagged as non-reportable. The average RPD value for the BS/BSD was 9.3% (n=45) with a standard deviation of 7.4%. Three RPD values were above the actual control limit used in the laboratory of 25%, but below the upper control limit based on $\bar{x}\pm3\sigma$ of 31.6%.  These high RPDs were on datasets MHg15-120321-1 at 26.8%, MHg7-120104-1 at 30.7%, and in dataset MHg7-120119-1 at 28.5%. These RPD values were qualified with QR-06 (table 12).

**MDN 2011Total Mercury
CRM Recovery
n = 446 average = 96.0%, Stdev = 2.9%**

Upper Warning Limit + 2σ (102%)

Upper Control Limit + 3 σ (105%)

Average (96.0%)

Lower Warning Limit - 2σ (90.2%)

Lower Control Limit - 3σ (87.3%)

January - December 2011
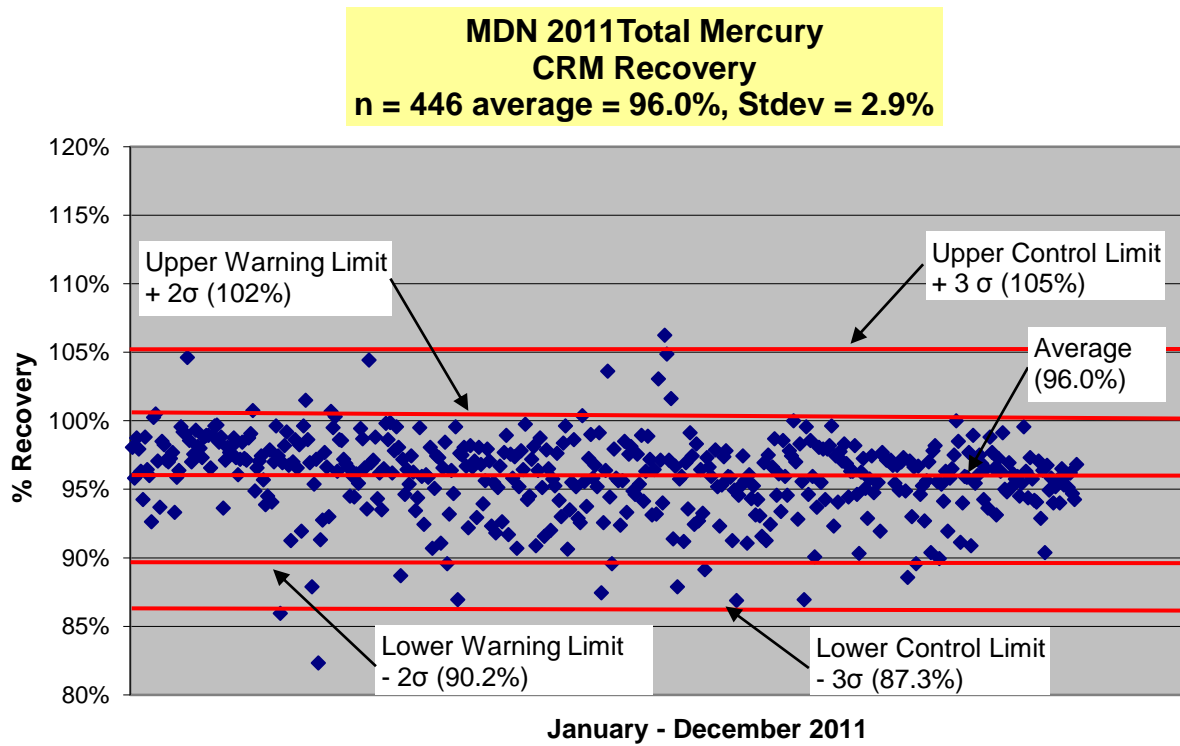
**Figure 15 - Control Chart for Total Mercury Percent Recovery in Certified Reference Material Samples During 2011**



**MDN 2011 Total Mercury
CRM RPD
n = 223 average = 3.1%, Stdev = 2.5%**

Warning Limit + 2σ (8.1%)

Control Limit + 3σ (10.5%)

Average (3.1%)

January - December 2011
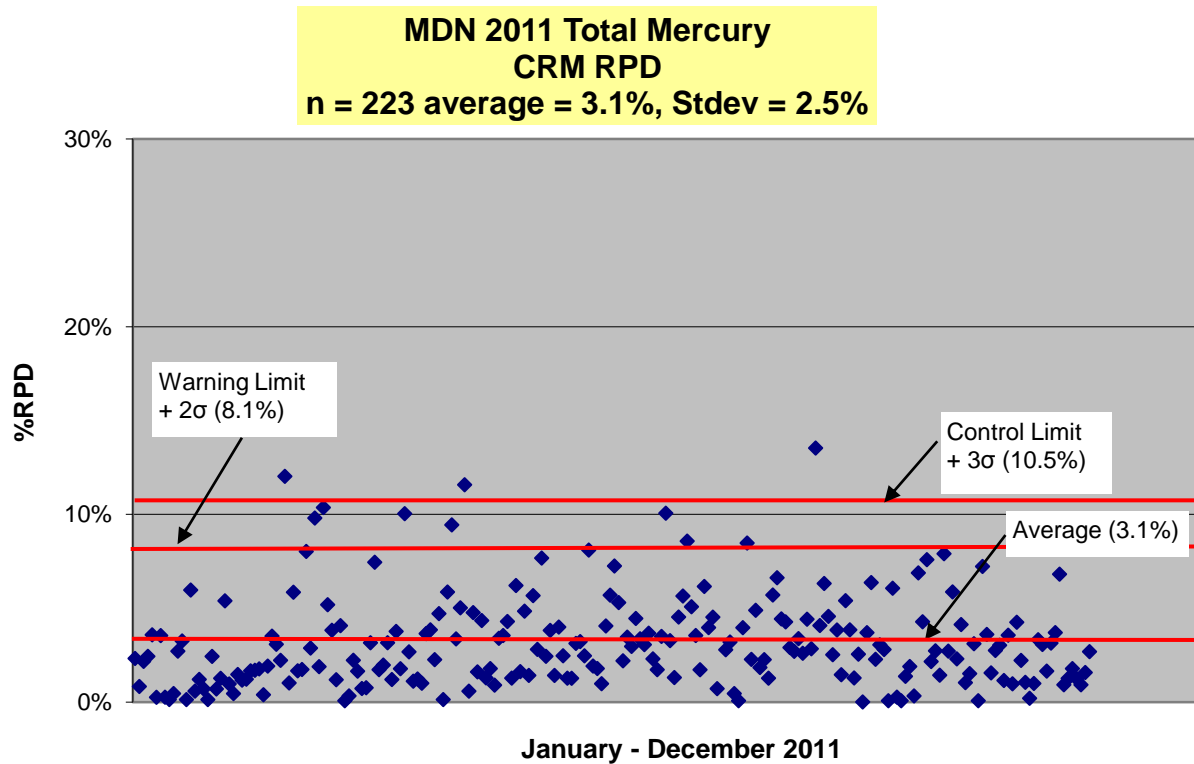
**Figure 16 - Control Chart for Total Mercury Relative Percent Difference (%RPD) in CRM /CRM Duplicates Samples During 2011**
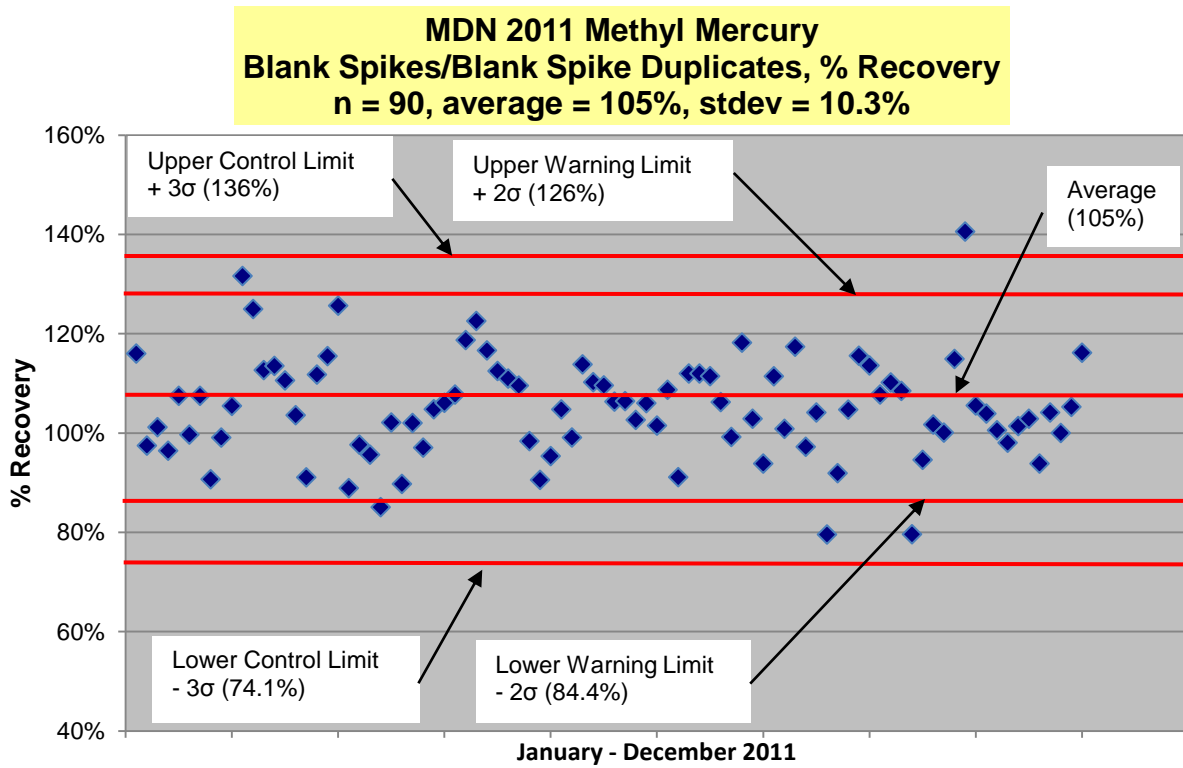
**Figure 17 - Control Chart for Methyl Mercury Percent Recovery in Blank Spikes/Blank Spikes Duplicates Samples During 2011**
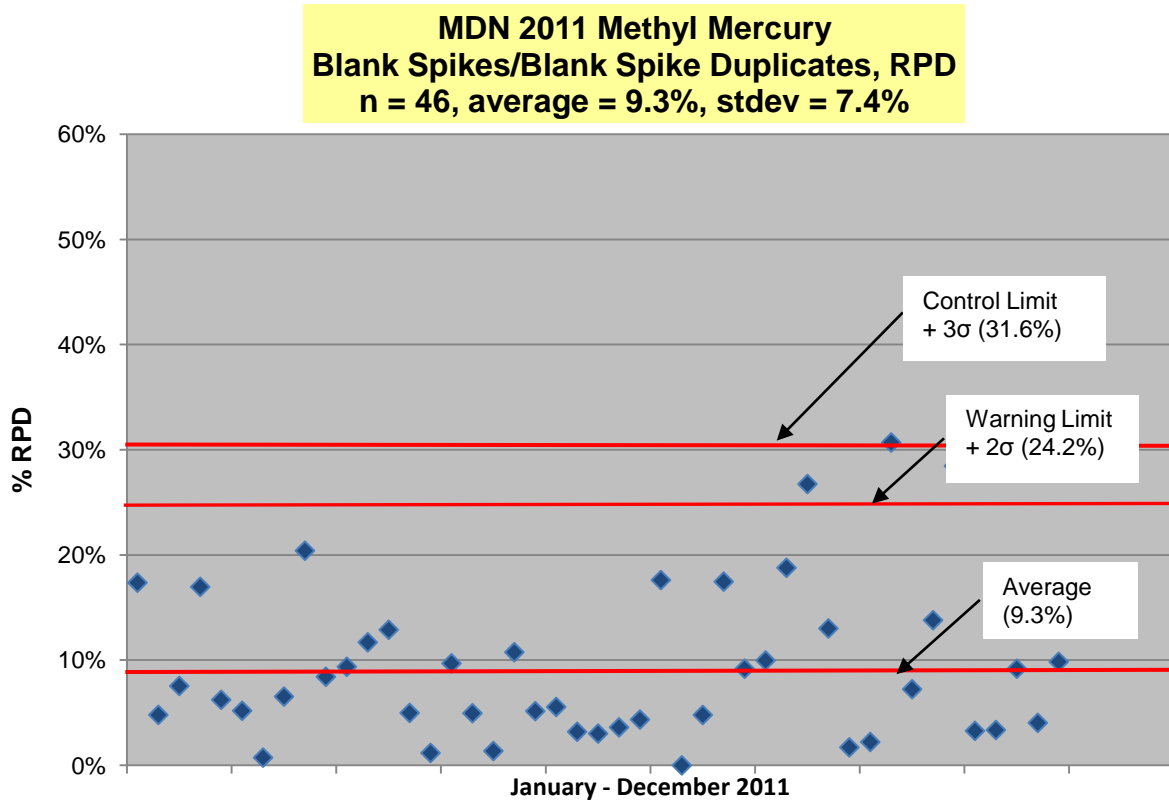


**Figure 18 - Control Chart for Methyl Mercury Relative Percent Difference (%RPD) in Blank Spikes/Blank Spikes Duplicates Samples During 2011**

# 3. Calculations

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

## 3.1 Calculation: Gross MDN Sample Concentration

Calc 1){(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 = Subppt * Concentration ($ng/m^2$)

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 – EmtyMass – 20 (20 mL preservative)

SampleHgMass = AliqotHg * (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**

FGS DATA SET ID:
MDN LAB DATA SET CODE:
Analysis Date:
Analyzer:
Analyst:
REVIEWER:
DATE:

Analytical Run
D=Duplicate Analysis
Trap Set:
S=Sample Spike @ 1.00ng

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

**Key**
- Reference Materials
- Preparation Blanks
- Matrix Duplicates
- Matrix Spikes
- CCVs
- CCBs

**Figure 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 DMR-QA (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 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 below were completed by FGS during 2011, in addition to the monthly USGS that are not included in the table. Results for any tests are available upon request.

**Table 9 - Proficiency Tests**

| Proficiency Test | Organization | Open-close date |
|---|---|---|
| 111411D | ERA-Environmental Resource Associates | (11/14/2011 - 2/29/2011) |
| 082511B | ERA-Environmental Resource Associates | (8/25/2011 - 10/9/2011) |
| WP-199 | ERA-Environmental Resource Associates | (8/15/2011 - 9/29/2011) |
| WP-198 | ERA-Environmental Resource Associates | (7/11/2011 - 8/25/2011) |
| QTA | Absolute Standards | (6/14/2011-6/27/2011) |
| 032511E | ERA-Environmental Resource Associates | (3/25/2011 - 5/9/2011) |
| 031811A | ERA-Environmental Resource Associates | (3/18/2011 - 5/2/2011) |
| DMR-QA 31 | ERA-Environmental Resource Associates | (3/14/2011 - 7/1/2011) |
| SOIL-73 | ERA-Environmental Resource Associates | (1/24/2011 - 3/10/2011) |
| WP-192 | ERA-Environmental Resource Associates | (1/17/2011 - 3/3/2011) |

# 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) that at least 15 mL can be measured out as aliquot size, are analyzed for total mercury as a field bottle blank sample and are "A" coded and receive "Q" as a sample type. Field blanks with a measured aliquot size less than 15 mL are still analyzed and are "A" coded, but receive "D" (Dry week) as sample type. The analysis is based on mass of sample added to the bubbler and therefore no dilution is needed. There were 79 samples in 2011 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.

### 6.1.3 Discussion

In 2011, the mean of 167 Field Bottle Blanks was 0.048 ng/bottle with a standard deviation of 0.037 ng/bottle. Figure 20 shows sample AZ0220110118 with elevated mercury value in the field blank of 0.425 ng.  All six field blank samples collected from the AZ02 site had levels higher than the national average of 0.048 ng/bottle. The average from the Arizona site was 0.137 ng/bottle.
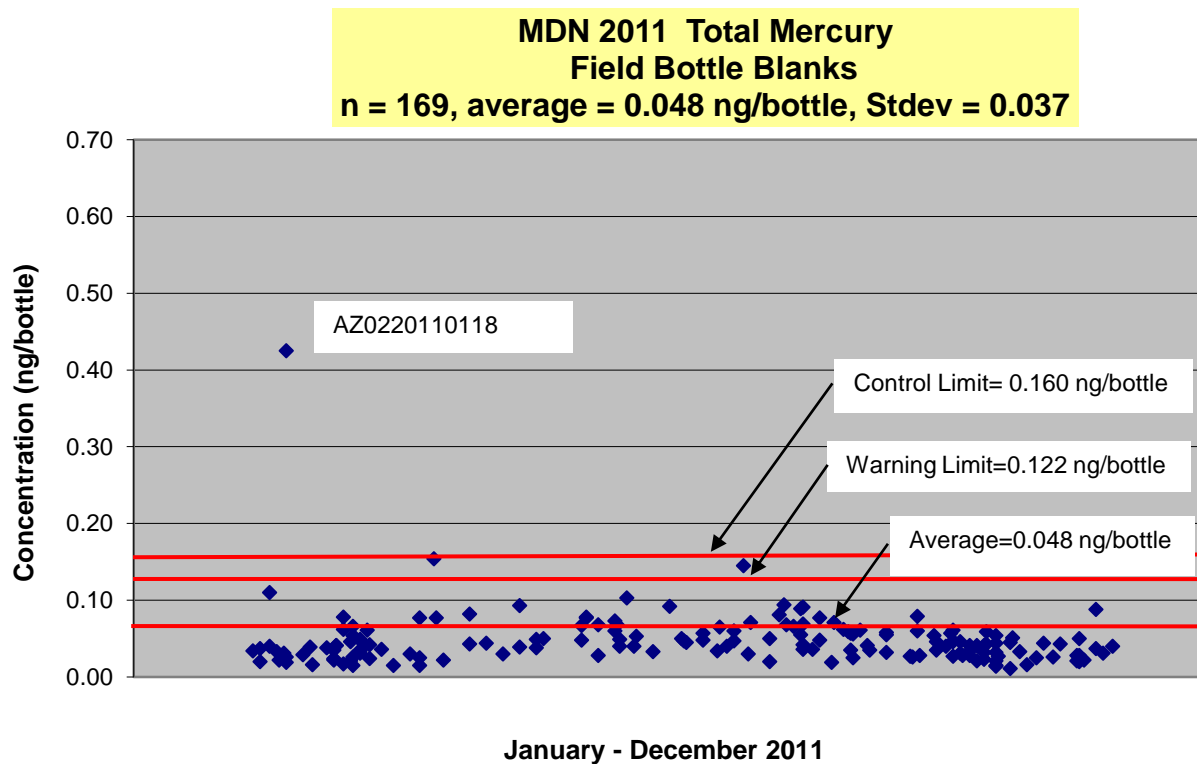
**Figure 20 - Time Series Plot of Total Mercury Concentrations in Field Bottle Blanks During 2011**

## 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 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 2011, the mean of 54 system blanks was 0.051 ng/aliquot with a standard deviation of 0.037 ng/aliquot compared to the control sample with a mean of 0.013 ng/aliquot and a standard deviation of 0.011 ng/aliquot. During 2011, four locations had higher levels of mercury in their control sample compare to in the system blank. Theses locations are OK0420110607, ON0720110712, PA4220110719, and VA2820111011. A system blank processed at PA72 (sample PA7220111108) had a mercury concentration of 0.229 ng/aliquot. The site operator had noted on the MOF under the remark section 10 "Possible contamination during installation of digital rain gauge." The raingage was installed on November 4, 2011, and the electronic raingage record shows 2 openings on 2011-11-04.

**2011 MDN Total Mercury System Blanks**
**n = 54**
**Control Average = 0.013 ng/aliquot, Stdev = 0.011**
**System Blank Average = 0.051 ng/aliquot, Stdev = 0.037**
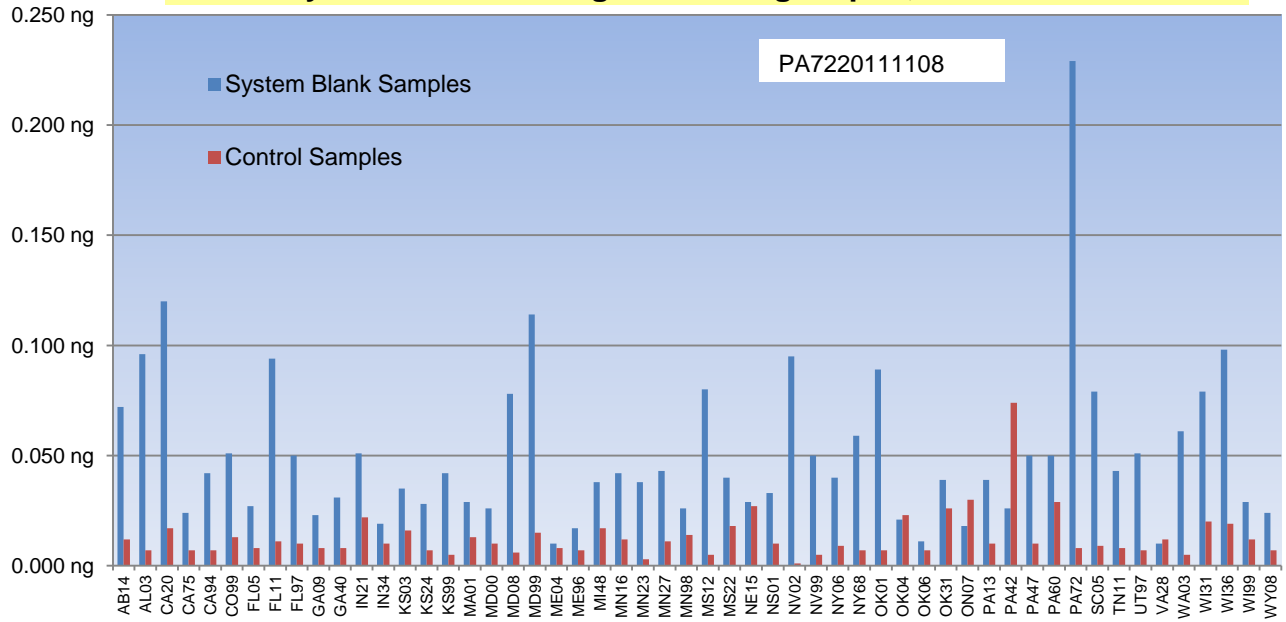
**Figure 21 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2011**

# 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 6259 samples in 2011, which is a decrease of 2.4% compare to the 6411 samples that were processed during 2010. 1931 samples received a QR code of "A", 3864 received a "B" QR code, and 464 received a "C" QR code. HAL continued to maintain and demonstrate acceptable quality control in 2011. This comparison is based on HAL assessing the QR codes. These codes can later be changed by the NADP Program Office (PO).

Of the 464 "C" coded samples for 2011, 7 incidents occurred at the laboratory.

1. Samples CO9720111116, GA0920111115, NE1520111115, OK0620111115, SC0520111115, and SC1920111115 were in the analytical run 2011-186, which was unable to be closed out due to matrix duplicate failures.

2. KY1020111122 was contaminated during preservation. The pipette tip fell into the sample.

From 2005 to 2010 the percentage of "C"-coded samples increased steadily from 5.0 to 8.5%. The percentage of C-coded samples decreased during 2011 to 7.4%. This is illustrated in Figure 23. A comparison of "C"-coded sample error types is shown in Table 10.

The number of "B"-coded samples increased during 2011 to 61.7% compared to 50.0% during 2010. The number of "A"-coded samples decreased o 30.9%, compared to 41.5% for 2010.

To investigate the increase of "B"-coded samples during 2011, the note codes for the "B"-coded samples were reviewed. The total number of "d" note-coded samples (d=debris in sample) increased from 1685 during 2010 to 2419 during 2011. During 2010, samples with debris were noted by the laboratory 430 times compared to 1050 times during 2011.. The total number of "h" note-coded samples (h=sample handling problems) increased from 375 in 2010 to 584 in 2011 (56% increase), whereof samples that leaked increased from 262 to 438 (67% increase). The total number of "m" note-coded samples (m=missing information) increased from 915 to 970, which is a 6% increase. These results indicate that the increase of "B"-coded samples, is

due to problems with sample integrity, not missing digital raingage data or missing temperature recordings as initially suspected.



**2011 Distribution of MDN Quality Rating Codes**

7.4% C coded samples

30.9% A coded samples

61.7% B coded samples
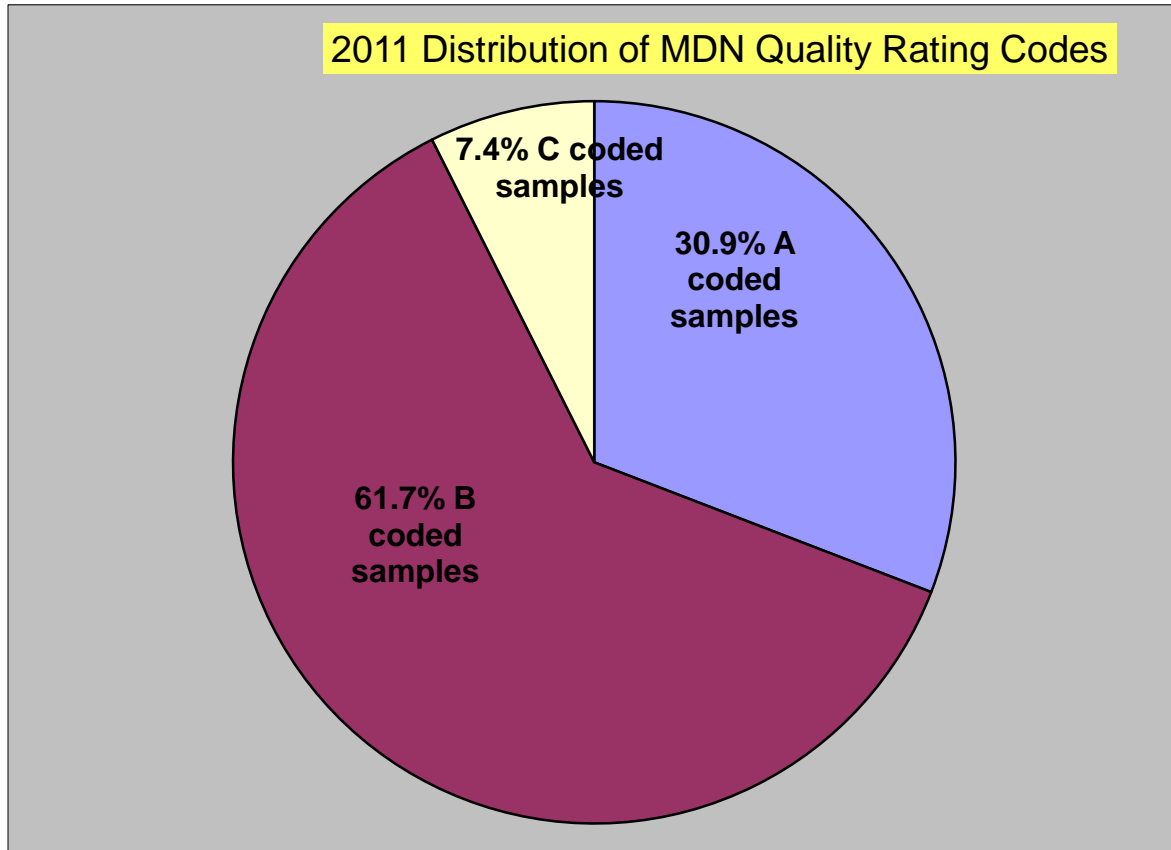
**Figure 22 - Distribution of Quality Rating Codes for Samples Received in 2011**

## MDN Sample distribution 2004-2011

| Year | # of Samples processed | A - coded samples | B - coded samples | C - coded samples |
|------|------------------------|-------------------|-------------------|-------------------|
| 2004 | 4628 | 2297 | 2100 | 231 |
| 2005 | 5263 | 1937 | 3072 | 254 |
| 2006 | 5584 | 2405 | 2864 | 315 |
| 2007 | 5778 | 2261 | 3166 | 351 |
| 2008 | 6523 | 2870 | 3196 | 457 |
| 2009 | 6748 | 3154 | 3122 | 472 |
| 2010 | 6411 | 2661 | 3203 | 547 |
| 2011 | 6259 | 1931 | 3864 | 464 |
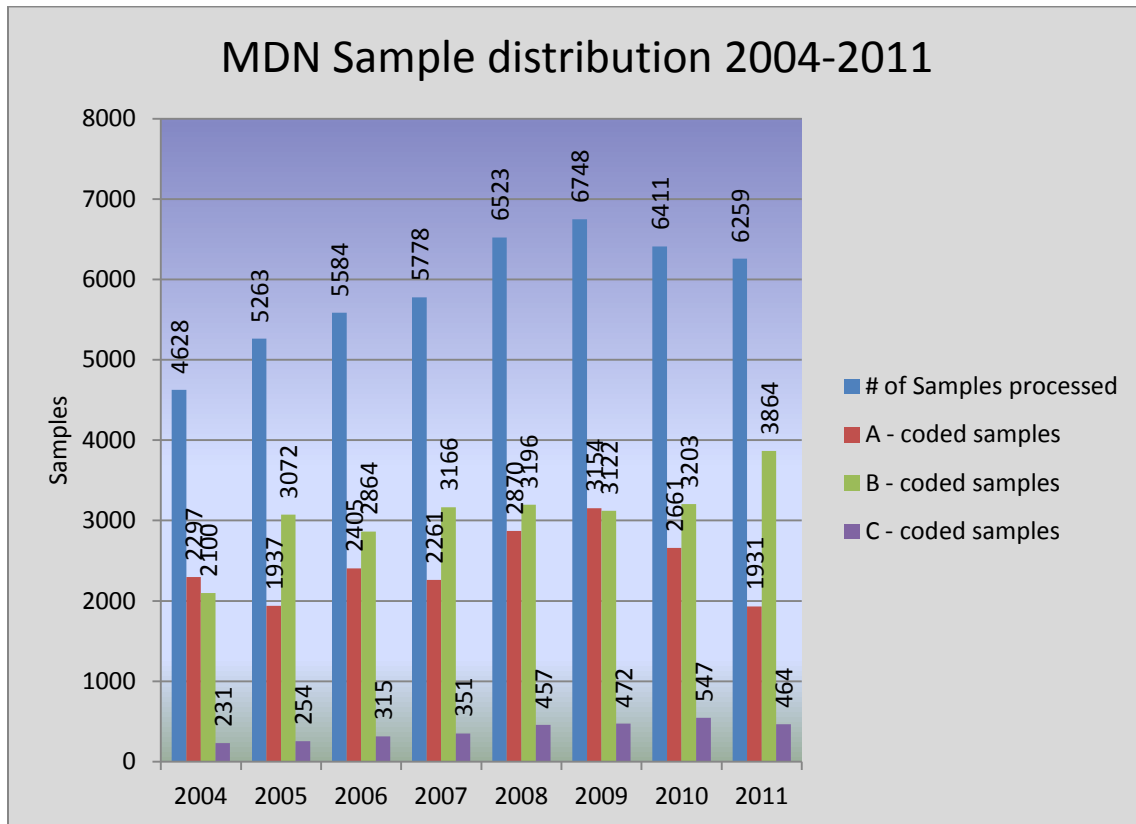
**Figure 23 - Distribution of Quality Rating Codes for Samples Received from 2004 to 2011**

| Error Type | 2008 | 2009 | 2010 | 2011 |
|------------|------|------|------|------|
| Bulk Sample | 51 | 42 | 46 | 49 |
| Undefined Sample | 92 | 56 | 108 | 71 |
| Site Environment | 2 | 4 | 0 | 1 |
| Sample Condition | 20 | 111 | 128 | 119 |
| Field Protocol | 79 | 13 | 13 | 10 |
| Lab Protocol | 5 | 2 | 8 | 7 |
| Contaminated | 2 | 1 | 2 | 0 |
| Volume Discrepancy | 182 | 193 | 244 | 238 |
| Total | 433 | 422 | 549 | 464 |

**Table 10 - C-Coded Samples by Error Type, 2008-2011**

# 8. Summary and Conclusions

The HAL continued to maintain and demonstrate acceptable quality control in 2011. The five DQOs, precision, accuracy, representativeness, comparability, and completeness, were all met. The MDL for total Hg was 0.074 ng/L at a PQL of 0.50 ng/L, and the MDL for MMHg was 0.019 ng/L at a PQL of 0.05 ng/L. Average bottle blank Hg and MMHg content was quantified at 0.022 ng Hg/bottle and 0.00042 ng MMHg/bottle, respectively.  Preparation and calibration blank total Hg and MHg contents were acceptably low and within control limits.  QC sample recoveries for ICVs, CCVs, MS/MSDs, BS/BSDs, and CRMs were within control limits. RPDs for MDs, MSDs, and BSDs were less than $\pm25\%$. External proficiency testing by ERA, Absolute Standards, and USGS yielded acceptable results.

Field bottle blanks (n=169) and system blanks (n=54) indicated that field contamination levels continue to be low with two samples that had unusually high total Hg contamination, the maximum of which was 0.229 ng/sample.

The percentage of C-coded samples decreased from 8.5% (2010) to 7.4% during 2011 compared to a steady increase from 2005 to 2010. During 2011 the percentage of A coded samples decreased from 41.5% (2010) to 30.9% during 2011. The number of B coded samples has increased from 50.0% (2010) to 61.7% for 2011.

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

**Table 11 - 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% Rec. RPD $\leq$ 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 $\leq$ 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 12 - 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 homogeneous. 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 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. |

## 9. Definitions of Abbreviations and Acronyms
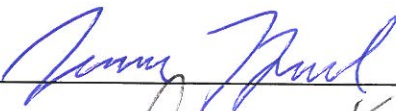
| | |
|---|---|
| **AIRMoN** | Atmospheric Integrated Research Monitoring Network |
| **APDC** | Ammonium PyrrolidineDithioCarbamate |
| **AS/ASD** | Analytical Spike/ Analytical Spike Duplicate |
| **BS/BSD** | Blank Spike/ Blank Spike Duplicate |
| **CCB** | Continued Calibration Blank |
| **CCV** | Continued Calibration Verification |
| **CFR** | Code of Federal Regulations |
| **CRM** | Certified Reference Material |
| **CVAFS** | Cold Vapor Atomic Fluorescence Spectrometry |
| **DMR-QA** | Discharge Monitoring Report-Quality Assurance |
| **DQO** | Data Quality Objectives |
| **EPA** | Environmental Protection Agency |
| **FGS** | 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 |
| **NPDES** | National Pollutant Discharge Elimination System |

| | |
|---|---|
| **NRCC** | National Research Council Canada |
| **OPR** | Ongoing Precision and Recovery |
| **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 |
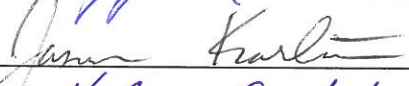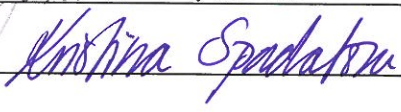
# 10. Appendix A: MDL Studies 2011

# IDL Study:
# Total Mercury in Water CV-AFS #1

Analyzed by Jeanne Harrel: _____

MDN Site Liaison, Jason Karlstrom: _____

Report Prepared by Kristina Spadafora: _____

## Objective

To perform an IDL study as an initial verification of instrument THg-01 after the move to the new facility on December 16-18, 2011 before the analysis of any Mercury Deposition Network (MDN) samples on the instrument.

## Analytical Method

The IDL study consisted of ten direct spikes into the bubblers with 5µL of THG Calibration STD 10 ng/mL LIMS# 1102754 and addition of $SnCl_2$. The IDL samples have not been oxidized with the addition of BrCl. The samples were then analyzed following the regular analysis method FGS MDN-05.1 (FGS-069). The IDL was calculated by following the protocols outlined in 40 CFR 136, Appendix B. As detailed below, the IDL for Total Mercury in water samples was determined to be **0.056** ng/L for THg for CV-AFS#01.

The results of these measurements are found in the table on the page 3, as well in the raw data sheets ID # THg01-111219-1.

The results are <u>not corrected</u> for the method blanks since no BrCl method blanks were performed, but <u>corrected</u> by the instrument blanks.

## IDL Calculation

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

$$IDL = t*\sigma = (2.821) * (0.020) = \underline{0.056 \text{ ng/L}}.$$

\\Cuprum\gen_admin\Quality Assurance\MDLs PQLs & RLs\Complete Reports of MDL Studies by Analyte and Matrix\Current\MDL Study (THg)\MDN IDL THg 01-111219-1

Dataset THg01-111219-1 was used for the IDL study. All ten replicates showed a percent recovery between 70-130% (99.4% ± 3.8%), making this dataset eligible for determining an IDL and to verify that the instrument sensitivity has not been compromised during the transport to the new facility.

At the old facility the 4.00ng calibration point had a PA of 12377.416 (THg01-111114) compared to 12222.45. The THg peak appears on the chromatogram at 3.29 min after relocation verses 3.14 min before the move.

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**Total Mercury for Water samples**
**IDL Study Data for CV.AFS #01**

12/20/2011
**Dataset**
**ID:** **THg01-111219-1**

| Sample | [THg], ng/L |
|--------|-------------|
| BrCl-1 | NA |
| BrCl-2 | NA |
| BrCl-3 | NA |
| **Mean** | **NA** |
| **SD** | **NA** |

| | Result [THg], ng/L | Spike Level, [TV], ng/L | [%Rec] |
|--------|--------------------|-----------------------|--------|
| IDL-Rep1 | 0.510 | 0.50 | 102% |
| IDL-Rep2 | 0.535 | 0.50 | 107% |
| IDL-Rep3 | 0.503 | 0.50 | 101% |
| IDL-Rep4 | 0.479 | 0.50 | 95.8% |
| IDL-Rep5 | 0.505 | 0.50 | 101% |
| IDL-Rep6 | 0.509 | 0.50 | 102% |
| IDL-Rep7 | 0.473 | 0.50 | 94.6% |
| IDL-Rep8 | 0.470 | 0.50 | 94.0% |
| IDL-Rep9 | 0.490 | 0.50 | 98.0% |
| IDL-Rep10 | 0.498 | 0.50 | 99.6% |
| **Mean** | **0.497** | **0.50** | **99.4%** |
| **SD** | **0.020** | **0.00** | **4.0%** |

| | [THg], ng/L | Certified Value | [%Rec] |
|--------|-------------|-----------------|--------|
| NIST 1641d | 7419 | 7840 | **94.6%** |

| IDL | 0.056 |
|---------|-------|
| PQL/IDL | 8.94 |

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## IDL Study:
## Total Mercury in Water CV-AFS #09

Analyzed by Jeanne Harrel: _____

MDN Site Liaison, Jason Karlstrom: _____

Report Prepared by Kristina Spadafora: _____

## Objective

To perform an IDL study as an initial verification of instrument THg-09 after the move to the new facility on December 16-18, 2011 before the analysis of any Mercury Deposition Network (MDN) samples on the instrument.

## Analytical Method

The IDL study consisted of ten direct spikes into the bubblers with 5µL of THg Calibration Std 10 ng/mL LIMS# 1102754 and addition of $SnCl_2$. The IDL samples have not been oxidized with the addition of BrCl. The samples were analyzed following the regular analysis method FGS MDN-05.1 (FGS-069). The IDL was calculated by following the protocols outlined in 40 CFR 136, Appendix B. As detailed below, the IDL for Total Mercury in water samples was determined to be **0.074** ng/L for THg for CV-AFS#09.

The results of these measurements are found in the table on the page 3, as well in the raw data sheets ID # THg09-111219-1.

The results are <u>not corrected</u> for the method blanks since no BrCl method blanks were performed, but <u>corrected</u> by the instrument blanks.

## IDL Calculation

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

IDL = t*σ = (2.821) * (0.020) = <u>0.074 ng/L</u>.

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Dataset THg09-111219-1 was used for the IDL study. All ten replicates showed a percent recovery between 70-130% (102.3% ± 5.0%), making this dataset eligible for determining an IDL and to verify that the instrument sensitivity has not been compromised during the transport to the new facility.

At the old facility the 4.00ng calibration point had a PA of 3133.710 (THg091-111114) compared to 3955.03. The THg peak appears on the chromatogram at 2.86 min after relocation verses 2.83 min before the move.

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**Total Mercury for Water samples**
**IDL Study Data for CV.AFS #09**

12/20/2011
**Dataset**
**ID:**          **THg09-111219-1**

| Sample | [THg], ng/L | | |
|---|---|---|---|
| BrCl-1 | NA | | |
| BrCl-2 | NA | | |
| BrCl-3 | NA | | |
| **Mean** | **NA** | | |
| **SD** | **NA** | | |
| | **Result [THg], ng/L** | **Spike Level, [TV], ng/L** | **[%Rec]** |
| IDL-Rep1 | 0.520 | 0.50 | 104% |
| IDL-Rep2 | 0.509 | 0.50 | 102% |
| IDL-Rep3 | 0.512 | 0.50 | 102% |
| IDL-Rep4 | 0.508 | 0.50 | 102% |
| IDL-Rep5 | 0.457 | 0.50 | 91.4% |
| IDL-Rep6 | 0.502 | 0.50 | 100% |
| IDL-Rep7 | 0.559 | 0.50 | 112% |
| IDL-Rep8 | 0.536 | 0.50 | 107% |
| IDL-Rep9 | 0.502 | 0.50 | 100% |
| IDL-Rep10 | 0.511 | 0.50 | 102% |
| **Mean** | **0.512** | **0.50** | **102.3%** |
| **SD** | **0.026** | **0.00** | **5.2%** |

| | [THg], ng/L | Certified Value | [%Rec] |
|---|---|---|---|
| NIST 1641d | 7535 | 7839.5 | **96.1%** |

| | |
|---|---|
| **IDL** | 0.073 |
| **PQL/IDL** | 6.81 |

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Analyzed by: <u>Adela Blaga</u>     07/17/12
MDN Laboratory Manager: <u>Gerard van der Jagt</u>     7-17-12
Report Prepared by: <u>Kristine Teffeau</u>   KTeffeau 7/16/12
Report Reviewed by: <u>Kristina Spadafora</u>   Krishna Spadafora 7/16/2012

MDL Study Data for Mercury in Precipitation Samples
Preparation Method: FGS-MDN-04
Analysis Method: FGS-MDN-05
Dataset: THg01-111227-1

**Objective**  To verify the existing Method Detection Limit (MDL).  This MDL verification study applies to Total Mercury in precipitation samples as prepared by method FGS-MDN-04 and analyzed by method FGS-MDN-05. The MDL verification was calculated and evaluated in accordance with 40 CFR 136.  As detailed below, the MDL for Total Mercury in Water was determined to be **0.032 ng/L Hg.**

**Analytical Method**  Briefly, the Hg in an aliquot of sample is oxidized with BrCl, reduced with $SnCl_2$ and analyzed by purge and trap and dual amalgamation CV-AFS.  A calibration was performed in accordance with FGS-MDN-05.

The MDL study consisted of a 0.50 ng/L Hg solution divided into ten replicates.  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 (2.43 units).  All final concentrations were **corrected** for the preparation blanks (0.029 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.

$$MDL = t*σ$$

The MDL calculated from these data is (2.821)*(0.011), or **0.032 ng/L Hg**.

**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 PQL/MDL ratio which does not exceed 10 (PQL or spike level).  This MDL study was not valid as it did not meet the criteria with a PQL/MDL ratio of 15.860.

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Total Mercury in Waters (FGS-MDN-05)

12/27/2011
THg01-111227-1

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

| Sample | [THg], ng/L | [TV], ng/L | [%Rec] |
|---|---|---|---|
| BrCl-1 | 0.023 | | |
| BrCl-2 | 0.028 | | |
| BrCl-3 | 0.035 | | |
| Mean | 0.029 | | |
| SD | 0.006 | | 70-130% |
| | [THg], ng/L | [TV], ng/L | [%Rec] |
| MDL-1 | 0.597 | 0.500 | 119% |
| MDL-2 | 0.594 | 0.500 | 119% |
| MDL-3 | 0.596 | 0.500 | 119% |
| MDL-4 | 0.612 | 0.500 | 122% |
| MDL-5 | 0.610 | 0.500 | 122% |
| MDL-6 | 0.630 | 0.500 | 126% |
| MDL-7 | 0.599 | 0.500 | 120% |
| MDL-8 | 0.614 | 0.500 | 123% |
| MDL-9 | 0.614 | 0.500 | 123% |
| MDL-10 | 0.604 | 0.500 | 121% |
| Mean | 0.60700 | 0.500 | 121% |
| SD | 0.01118 | 0.000 | 2.24% |

| NIST 1641d | 7632.786 | 7839.50 | 97.4% |
|---|---|---|---|

**MDL**      0.03153
**TV/MDL**     *15.860*

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Matrix\Current\MDL Study (THg)\MDL THg MDL #1 12.27.2011

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Analyzed by: Adela Blaga    _07/17/12_

MDN Laboratory Manager: Gerard van der Jagt    _7-17-12_

Report Prepared by: Kristine Teffeau    _KETeffeau, 7/16/12_

Report Reviewed by: Kristina Spadafora    _Kristina Spadafora 7/16/2012_

MDL Study Data for Mercury in Precipitation Samples
Preparation Method: FGS-MDN-04
Analysis Method: FGS-MDN-05
Dataset: THg09-111227-1

**Objective**  To verify the existing Method Detection Limit (MDL).  This MDL verification study applies to Total Mercury in precipitation samples as prepared by method FGS-MDN-04 and analyzed by method FGS-MDN-05. The MDL verification was calculated and evaluated in accordance with 40 CFR 136.  As detailed below, the MDL for Total Mercury in Water was determined to be **0.046 ng/L Hg.**

**Analytical Method**  Briefly, the Hg in an aliquot of sample is oxidized with BrCl, reduced with $SnCl_2$ and analyzed by purge and trap and dual amalgamation CV-AFS.  A calibration was performed in accordance with FGS-MDN-05.

The MDL study consisted of a 0.50 ng/L Hg solution divided into ten replicates.  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 (2.43 units).  All final concentrations were **corrected** for the preparation blanks (0.028 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)*(0.016), or **0.046 ng/L Hg**.

**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 PQL/MDL ratio which does not exceed 10 (PQL or spike level).  This MDL study was not valid as it did not meet the criteria with a PQL/MDL ratio of 10.881.

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Total Mercury in Waters (FGS-MDN-05)

12/27/2011
THg09-111227-1

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

| Sample | [THg], ng/L | | |
|---|---|---|---|
| BrCl-1 | 0.031 | | |
| BrCl-2 | 0.042 | | |
| BrCl-3 | 0.011 | | |
| Mean | 0.028 | | |
| SD | 0.016 | | 70-130% |
| | [THg], ng/L | [TV], ng/L | [%Rec] |
| MDL-1 | 0.635 | 0.500 | 127% |
| MDL-2 | 0.612 | 0.500 | 122% |
| MDL-3 | 0.626 | 0.500 | 125% |
| MDL-4 | 0.626 | 0.500 | 125% |
| MDL-5 | 0.632 | 0.500 | 126% |
| MDL-6 | 0.672 | 0.500 | 134% |
| MDL-7 | 0.627 | 0.500 | 125% |
| MDL-8 | 0.649 | 0.500 | 130% |
| MDL-9 | 0.635 | 0.500 | 127% |
| MDL-10 | 0.643 | 0.500 | 129% |
| Mean | 0.63570 | 0.500 | 127% |
| SD | 0.01629 | 0.000 | 3.26% |

| NIST 1641d | 7691.083 | 7839.50 | 98.1% |
|---|---|---|---|

**MDL**      0.04595
**TV/MDL**      *10.881*

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Matrix\Current\MDL Study (THg)\MDN THg MDL #9 12.27.2011

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# MDL/ PQL Study for Methyl Mercury in Precipitation Samples (FGS-MDN-08) CV-GC-AFS #7

Analyzed by: <u>Adela Blaga</u>    *MA*    07/09/12

Mercury Supervisor: <u>Gerard van der Jagt</u>    7/9/17

Report Prepared by: <u>Kristine Teffeau</u>    *K5 Teffeau*  7/6/12

Report Reviewed by: <u>Kristina Spadafora</u>    *Kristina Spadafora* 7/9/12

MDL Study Data for Methyl Mercury in Precipitation Samples
Preparation Method: FGS-MDN-07
Analysis Method: FGS-MDN-08
Dataset: MHG7-111229-1

**Objective**  Verify the existing CV-GC-AFS #7 Method Detection Limit (MDL) is still valid after the instrument was moved from one facility to another. This MDL verification study applies to Methyl Mercury in precipitation samples as prepared by method FGS-MDN-07 and analyzed by method FGS-MDN-08. 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 **0.01877 ng/L MHg.**

**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 FGS-MDN-08.

The MDL study consisted of a 0.050 ng/L solution of MHg 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 (0.002 units).

$$MDL = t*\sigma$$

The MDL calculated from these data is (2.821)*(0.00665), or **0.01877 ng/L MHg**.

**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 PQL/MDL ratio which does not exceed 10. The existing Methyl Mercury MDL of 0.026 ng/L was verified and the MDL did not require updating in the LIMS. See table below.

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 (70-130%). All 10 replicates were spiked at the current PQL (0.050 ng/L) and recovered between 70-130%.

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**MHg in Precipitation Samples**
**CV-GC-AFS #7**
**12/29/2011**
**MMHg07-111229-1 MDN**

**0.050 ng/L, MHg**

| Sample | [MHg], ng/L | | | |
|---|---|---|---|---|
| PBW1 | 0.002 | | **% R** | |
| PBW2 | 0.002 | | **Limits:** | |
| PBW3 | 0.002 | | **70-130** | |
| | **[MHg], ng/L** | **[TV], ng/L** | **[%Rec]** | |
| PQL Rep1 | 0.062 | 0.050 | 124% | |
| PQL Rep2 | 0.046 | 0.050 | 92.0% | |
| PQL Rep3 | 0.046 | 0.050 | 92.0% | |
| PQL Rep4 | 0.058 | 0.050 | 116% | |
| PQL Rep5 | 0.050 | 0.050 | 100% | |
| PQL Rep6 | 0.050 | 0.050 | 100% | |
| PQL Rep7 | 0.058 | 0.050 | 116% | |
| PQL Rep8 | 0.062 | 0.050 | 124% | |
| PQL Rep9 | 0.058 | 0.050 | 116% | |
| PQL Rep10 | 0.046 | 0.050 | 92.0% | |
| **Mean** | **0.05360** | **0.050** | **107%** | |
| **SD** | **0.00665** | **0.00** | **13.3%** | |
| | | | | |
| **BS1** | **2.131** | **2.000** | **107%** | **%RPD** |
| **BSD1** | **1.474** | **2.000** | **73.7%** | **36.4%** |

| | |
|---|---|
| **MDL** | 0.01877 |
| **PQL (TV)/MDL** | 2.66 |
| **FMDL** | 0.026 |
| **2x FMDL** | 0.052 |
| **FPQL** | 0.050 |

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Analyzed by: Adela Blaga _____ 07/09/12 _____
Mercury Supervisor: Gerard van der Jagt _____ 7/8/12
Report Prepared by: Kristine Teffeau _KS Teffeau 7/6/12_
Report Reviewed by: Kristina Spadafora _Kristina Spadafora 7/9/12_

MDL Study Data for Methyl Mercury in Precipitation Samples
Preparation Method: FGS-MDN-07
Analysis Method: FGS-MDN-08
Dataset: MHG15-120320-1

**Objective**   To verify the existing Method Detection Limit (MDL).  This MDL verification study applies to Methyl Mercury in precipitation samples as prepared by method FGS-MDN-07 and analyzed by method FGS-MDN-08. 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 **0.01235 ng/L MHg.**

**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 FGS-MDN-08.

The MDL study consisted of a 0.050 ng/L solution of MHg 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 (0.27 units).  All final concentrations were **corrected** for the preparation blanks (0.001 units).

**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 **0.01235 ng/L MHg**.

**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 PQL/MDL ratio which does not exceed 10.  The existing Methyl Mercury MDL of 0.026 ng/L was verified and the MDL did not require updating in the LIMS.  See table below.

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 (70-130%).  All 10 replicates were spiked at the current PQL (0.050 ng/L) and recovered between 70-130%.

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**MHg in Precipitation Samples**
**CVAFS 15**
**3/20/2012**
**MHg15-120320-1 MDN**

**0.050 ng/L, MHg**

| Sample | [MHg], ng/L | | |
|---|---|---|---|
| F203241-BLK1 | -0.001 | | **% Rec** |
| F203241-BLK2 | 0.006 | | **Limits:** |
| F203241-BLK3 | 0.000 | | **70-130** |

| | [MHg], ng/L | [TV], ng/L | [% Rec] |
|---|---|---|---|
| F203241-BS2 | 0.058 | 0.050 | 116% |
| F203241-BS3 | 0.045 | 0.050 | 90.0% |
| F203241-BS4 | 0.047 | 0.050 | 94.0% |
| F203241-BS5 | 0.051 | 0.050 | 102% |
| F203241-BS6 | 0.051 | 0.050 | 102% |
| F203241-BS7 | 0.051 | 0.050 | 102% |
| F203241-BS8 | 0.048 | 0.050 | 96.0% |
| F203241-BS9 | 0.043 | 0.050 | 86.0% |
| F203241-BSA | 0.048 | 0.050 | 96.0% |
| F203241-BSB | 0.054 | 0.050 | 108% |
| **Mean** | **0.04960** | **0.050** | **99.2%** |
| **SD** | **0.00438** | **0.000** | **8.75%** |

| | | | | %RPD |
|---|---|---|---|---|
| **F203241-BS1** | **2.031** | **2.000** | **102%** | |
| **F203241-BSD1** | **1.902** | **2.000** | **95.1%** | **6.56%** |

| | |
|---|---|
| **MDL** | 0.01235 |
| **PQL (TV)/MDL** | 4.05 |
| **FMDL** | 0.026 |
| **2x FMDL** | 0.052 |
| **FPQL** | 0.050 |

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Matrix\Current\MDL Study (MHg)\MDL Verfication Study (MHg in Water) - MDN 03.20.2012