National Atmospheric Deposition Program

Mercury Deposition Network

Mercury Analytical Laboratory

2009 Annual Quality Assurance Report

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Table of Contents

List of Figures

List of Tables

Definitions of Abbreviations and Acronyms

AIRMoN	Atmospheric Integrated Research Monitoring Network
AS	Analytical Spike
ASD	Analytical Spike Duplicate
CAL	Central Analytical Lab
CCB	Continued Calibration Blank
CCV	Continued Calibration Verification
COC	Chain of Custody
CRM	Certified Reference Material
CVAFS	Cold Vapor Atomic Fluorescence Spectrometry
DQO	Data Quality Objectives
EMOF	Electronic Mercury Observer Form
HAL	Mercury (Hg) Analytical Lab
ICB	Initial Calibration Blank
ICV	Initial Calibration Verification
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MD	Matrix Duplicate
MDL	Method Detection Limit
MDN	Mercury Deposition Network
MHg	Methyl Mercury
MOF	Mercury Observer Form
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NADP	National Atmospheric Deposition Program
NED	Network Equipment Depot
OPR	Ongoing Precision and Recovery
PB	Preparation Blanks
PE	Performance Evaluation
PQL	Practical Quantitation Limit
PT	Proficiency Test
QA/QC	Quality Assurance/Quality Control
QAP	Quality Assurance Plan
QR	Quality Rating Code
QCS	Quality Control Sample
RL	Reporting Limit
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
SRM	Standard Reference Material
THg	Total Mercury (Hg)
TV	True Value
USGS	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. MDN has grown to incorporate 119 official MDN sites at the end of 2009 in the United States and Canada (Figure 1).

As the HAL, FGS receives weekly precipitation samples to be analyzed for total mercury. HAL also analyzes samples for methyl mercury from 25 official MDN sites participating in the methyl mercury program. The analytical technique, a modified EPA Method 1631 Revision B, was developed by Nicolas S. Bloom, one of FGS' founders. FGS also served as the referee lab for the Method 1631 final validation study.
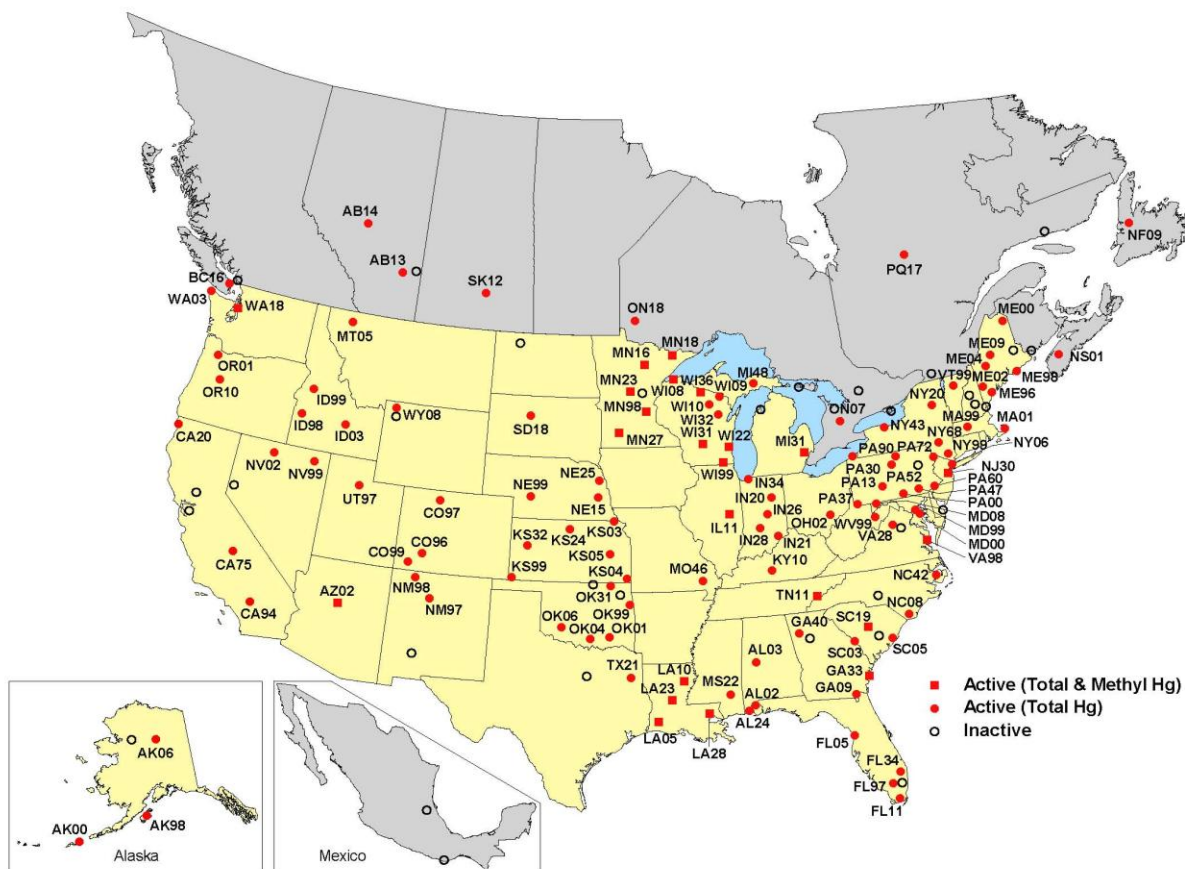
Figure 1 - Locations of MDN Sites During 2009

FGS continued to maintain and demonstrate acceptable quality control in 2009. Due to the addition of new MDN sites, the number of quality control points increased from about 1,900 in 2008, to more than 2000 quality control measurements in 2009. 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.

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 ≤ 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 achieved 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 Detections 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 3-10 times the expected MDL are analyzed. The standard deviation (σ) is taken from the resulting data and the MDL is determined as t * σ of the replicates. For ten replicates, the MDL is calculated as follows: MDL=2.821 * σ. This value should not be interpreted as the method reporting limit.

The Practical Quantitation Limit (PQL) is the reporting limit for the method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is determined by running ten replicate samples with a concentration that must meet a recovery of 70-130%.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 for the MDL study results analyzed during 2009 for the instruments that are used to analyze the MDN samples for total and methyl mercury.

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 acts as FGS' primary accreditation body for the National Environmental Laboratory Accreditation Program (NELAP). 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. At least one bottle blank should be collected per month and analyzed for methyl mercury. Only 9 bottle blanks were collected for methyl mercury during 2009.

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 objectively subtracted from final sample results.

1.4.3 Discussion

In 2009, three laboratory bottle blanks were higher than the total mercury MDL. The current MDL for total mercury is 0.052ng/L. None of the bottle blanks were above the reporting limit of 0.5ng/L. In 2009 there was no laboratory bottle blank above the MDL for methyl mercury. The current MDL for methyl mercury is 0.023ng/L (See Table 1). 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.

Figure 2 shows a slight bias in the middle and at the end of the year with an average of 0.026ng/L. The MDL is at 0.023ng/L and analytical variability at this low level can cause the bias effect.

Table 1 - Laboratory Bottle blank Summary Table

2009 Laboratory Bottle Blanks	n	Average (ng/bottle)	Standard Deviation	MDL (ng/L)	PQL (ng/L)
Total Mercury	122	0.026	0.041	0.052	0.50
Methyl Mercury	9	0.001	0.0009	0.023	0.050

Total Mercury
Laboratory Bottle Blanks
n = 122, average = 0.026 ng/bottle, stdev = 0.041
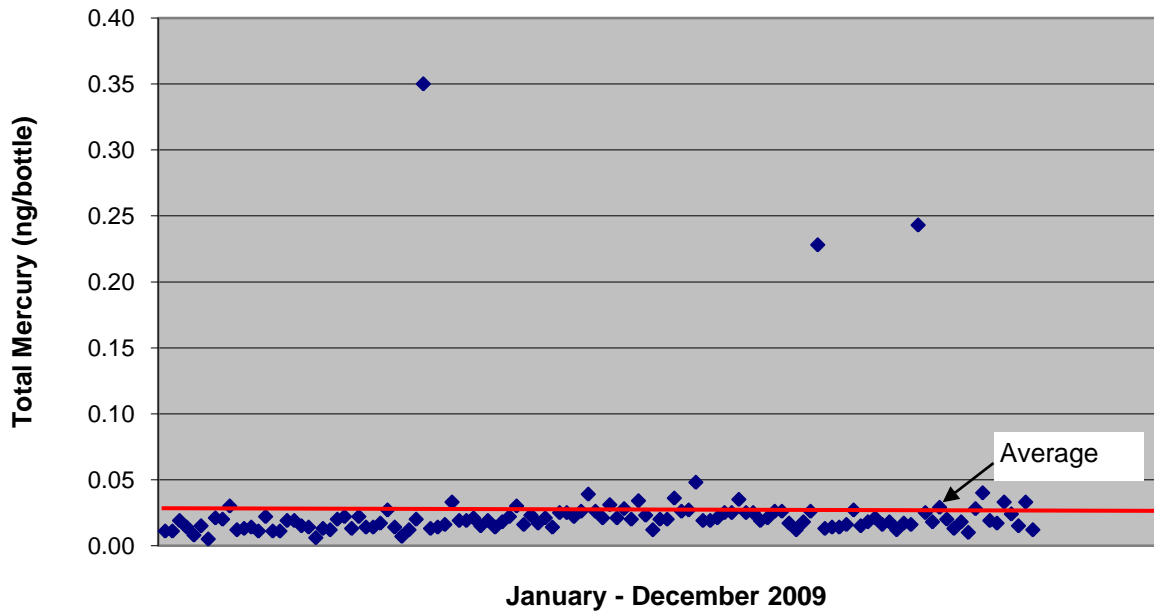
Figure 2 - Plot of Total Mercury Mass in Laboratory Bottle Blanks for 122 Samples Analyzed in 2009.

Methyl Mercury
Laboratory Bottle Blanks
n = 9, average = 0.001 ng/bottle, stdev = 0.0009
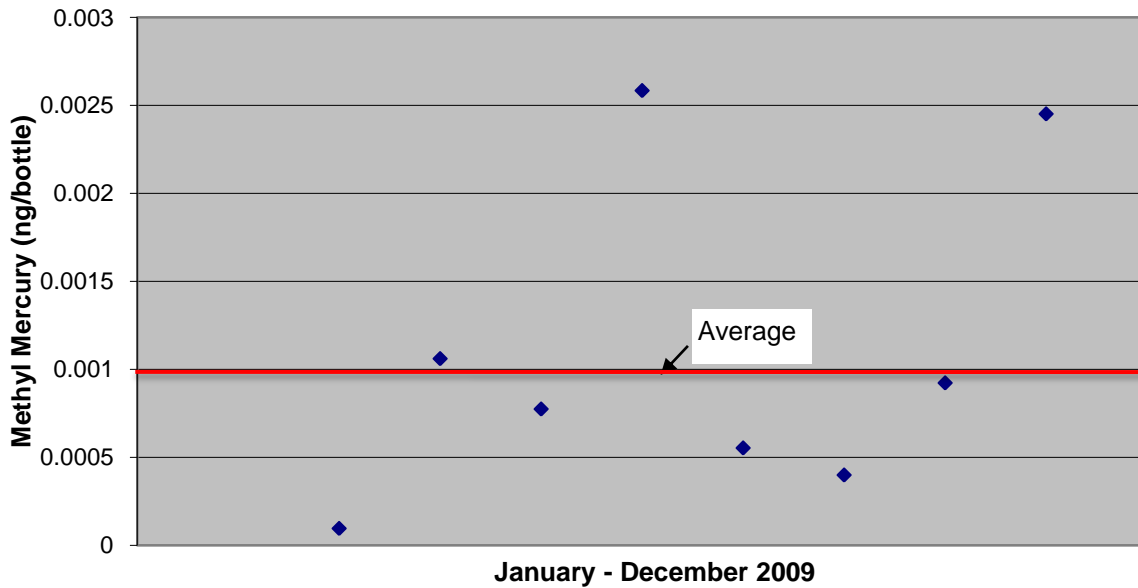
Figure 3 - Plot of Methyl Mercury Mass in Laboratory Bottle Blanks for 9 Samples Analyzed in 2009

2. Quality Control

Quality Control (QC) samples each 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 (0.200mL), and stannous chloride (0.300mL) in 100mL of reagent water. Preparation blanks for methyl mercury consist of 45 mL reagent water, hydrochloric acid (0.4%), ammonium pyrrolidine dithiocarbamate (0.200mL of APDC) solution, ethylating agent (38.5μL), acetate buffer (0.300mL), and reagent water. Currently, the HAL control limit for total mercury in the preparation blank is 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 0.5ng/L, see Table 10 for a summary of QC Criteria for EPA 1631E and 1630.

The HAL control limit for methyl mercury is currently set at 0.025 ng/L. HAL does not have control criteria on the standard deviation.

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 2009, 24 preparation blanks for total mercury were above the newly established control limit of 0.093 ng/L based on 3σ. One preparation blank was right at 0.25ng/L. All the preparation blanks analyzed during 2009 were less than the EPA criteria of 0.5ng/L.

In 2009, one preparation blank for methyl mercury was at the newly established control limit of 0.038 ng/L (3σ). No preparation blank exceeded the previous control limit of 0.040ng/L. (See Table 2). The standard deviation for 2009 of 0.0109 ng/L is less than the EPA requirement of <0.015 ng/L.

Dataset MHg15-090707-1 had preparation blank contamination (PB1=0.224ng/L, PB3=0.229 ng/L) and all samples with remaining sample volume were redistilled and were reanalyzed. Only two MDN samples were impacted: LA1020090505 and WA1820090526. These samples could not be redistilled due to insufficient sample volume. Sample LA1020090505 was analyzed in duplicate. Both the source sample and the duplicate sample had no detectable MHg. Sample WA1820090526 (ND) was used as source sample for the matrix spike and the matrix spike duplicate and both recovered at 102.4% and 106.2%. No reported data was affected.

Table 2 - Preparation Blanks Summary Table

2009 Preparation Blanks	n	Average (ng/L)	Stdev (ng/L)	MDL (ng/L)	3σ Control Limit (ng/L)	HAL Control Limit (ng/L)	EPA 1631E/1630
Total Mercury	714	0.024	0.031	0.052	0.093	0.25	< 0.50
Methyl Mercury	126	0.005	0.0109	0.023	0.038	0.025	Mean <0.045 σ<0.015

Total Mercury in Preparation Blanks
n = 714, average = 0.024ng/L, StDev = 0.031
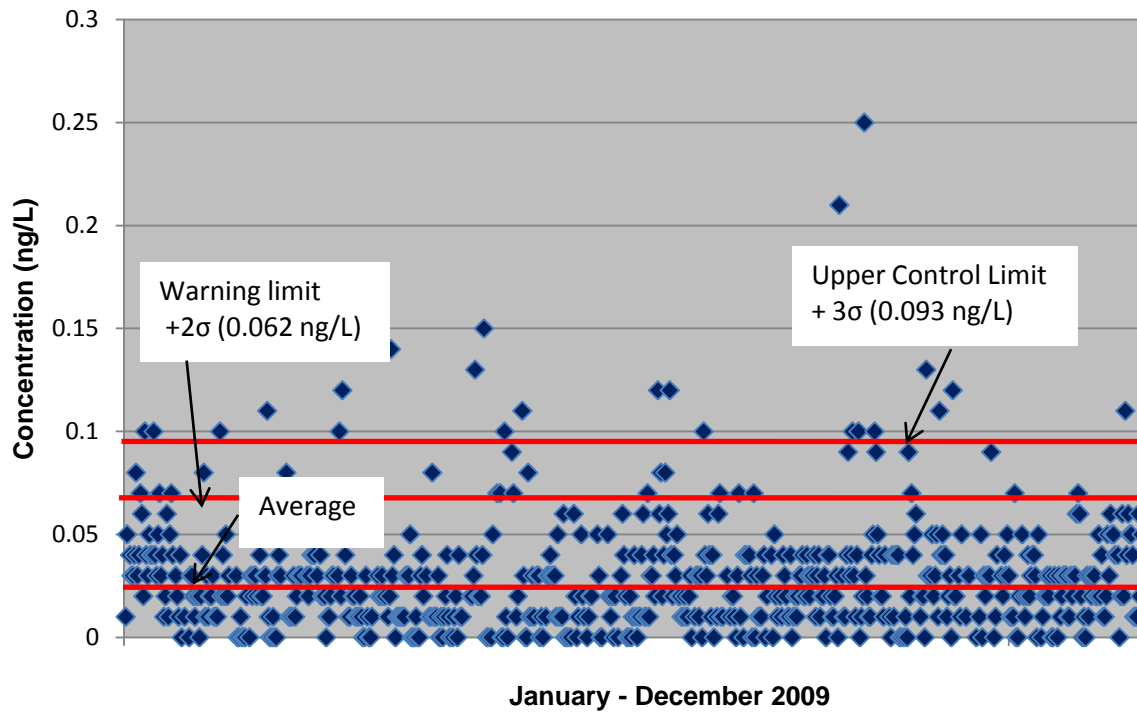
Figure 4 - Control Chart for Total Mercury Concentration in Reagent Preparation Blanks During 2009

**Methyl Mercury
Preparation Blanks
n = 126, average = 0.0052 ng/L, stdev = 0.0109**

Upper control limit
+ 3σ (0.038ng/L)

Warning limit
+ 2σ (0.027ng/L)

Average

January - December 2009
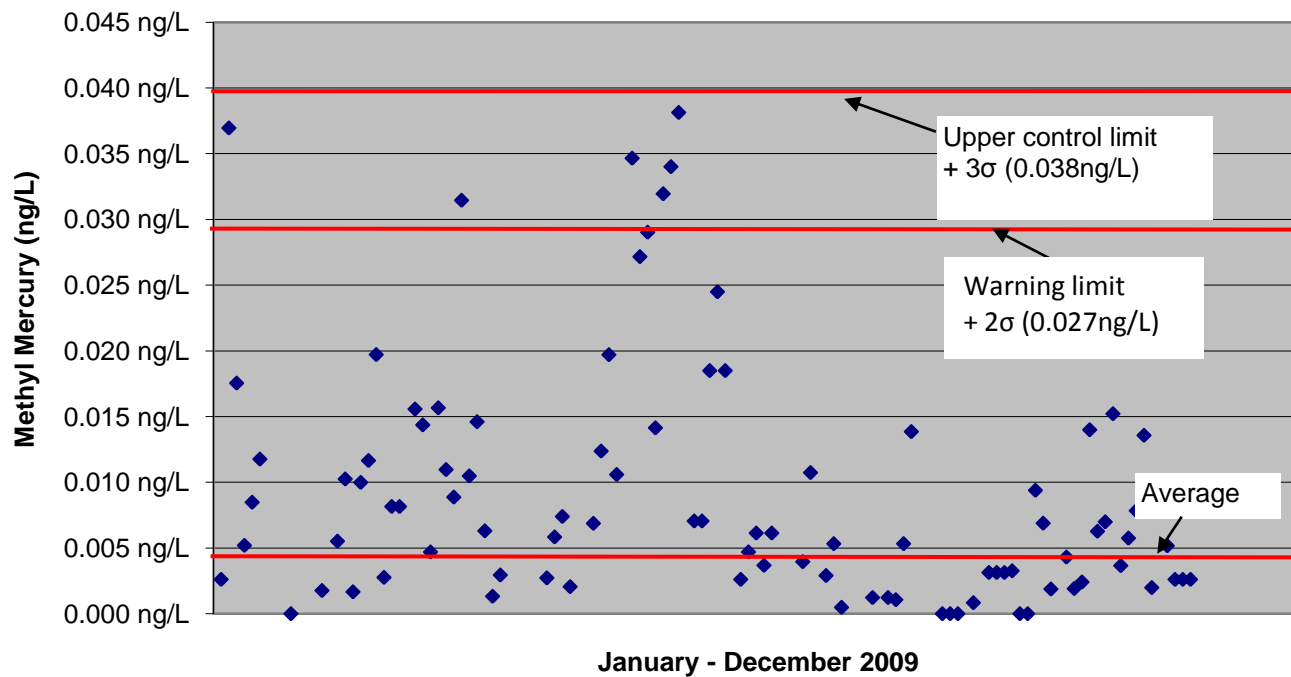
Figure 5 - Control Chart for Methyl Mercury Concentration in Reagent Preparation Blanks During 2009

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 that used in the primary standard solution. 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, typically 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). Typically, a 10ng/L standard for total mercury and a 2ng/L standard for methyl mercury are analyzed as an ongoing calibration standard. The MDN control limits for CCVs for total mercury are currently set to 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 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.

2.2.3   Discussion

Control limits are defined as 3 times the standard deviation. These values are determined once per year and are used throughout the entire year. In 2009, 4 samples for total mercury were above the newly established control limit of 108.1% (+3σ), no samples were below the newly established control limit of 84.7% (-3σ). There were no ongoing calibration standard recoveries for the MDN project for methyl mercury in 2009 that were above or below the newly established control limits of 130.3% (+3σ) and 58.8% (-3σ) (See Table 3).

Table 3 - Ongoing Calibration Standard Summary Table

2009 Ongoing Calibration Standard	n	Average (%)	Stdev (%)	±3σ Control Limit (%)	EPA 1631E/1630 Control Limits (%)
Total Mercury	738	96.4	3.9	84.7-108.1	77-123
Methyl Mercury	140	94.5	11.9	58.9-130.3	67-133

Total Mercury
Ongoing Calibration Standard
n = 738, average = 96.4 %, stdev = 3.9 %

Upper Warning Limit + 2σ (104.1%)

Upper Control Limit + 3σ (108.1%)

Lower Warning Limit -2σ (88.6%)

Average

Lower Control Limit - 3σ (84.7%)

% Recovery

January - December 2009
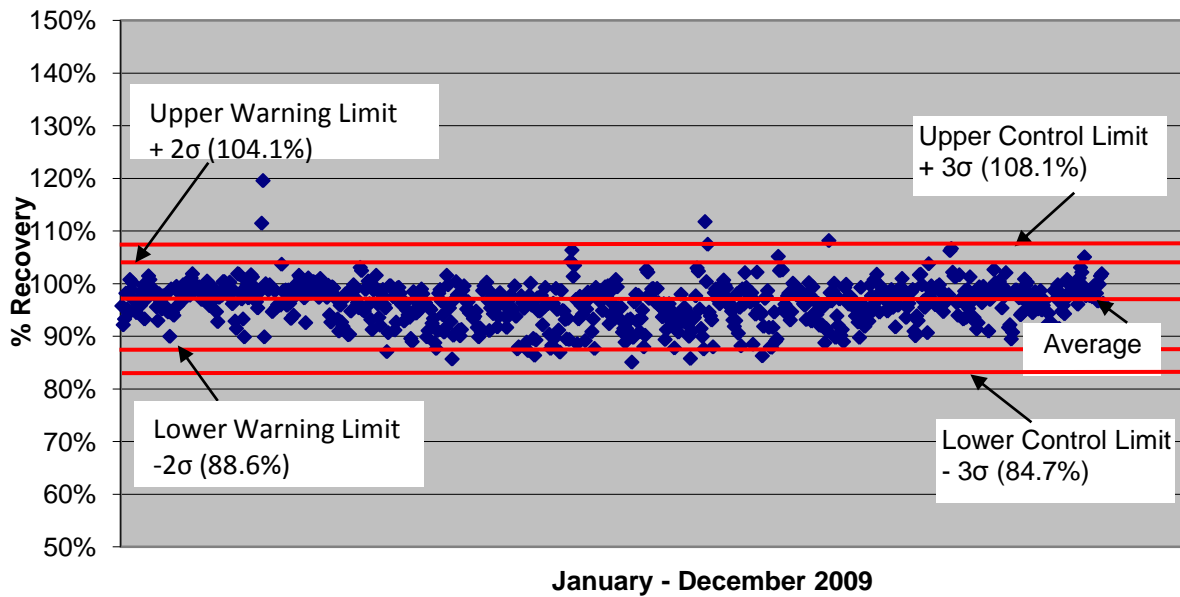
Figure 6 - Control Chart for Total Mercury Continuing Calibration Standard Percent Recovery

Methyl Mercury
Ongoing Calibration Standard
n = 140, average = 94.5%, stdev = 11.9%

Upper Control Limit + 3σ (130.3%)

Upper Warning Limit + 2σ (118.4%)

Average

Lower Warning Limit - 2σ (70.7%)

Lower Control Limit - 3σ (58.8%)

% Recovery

January - December 2009
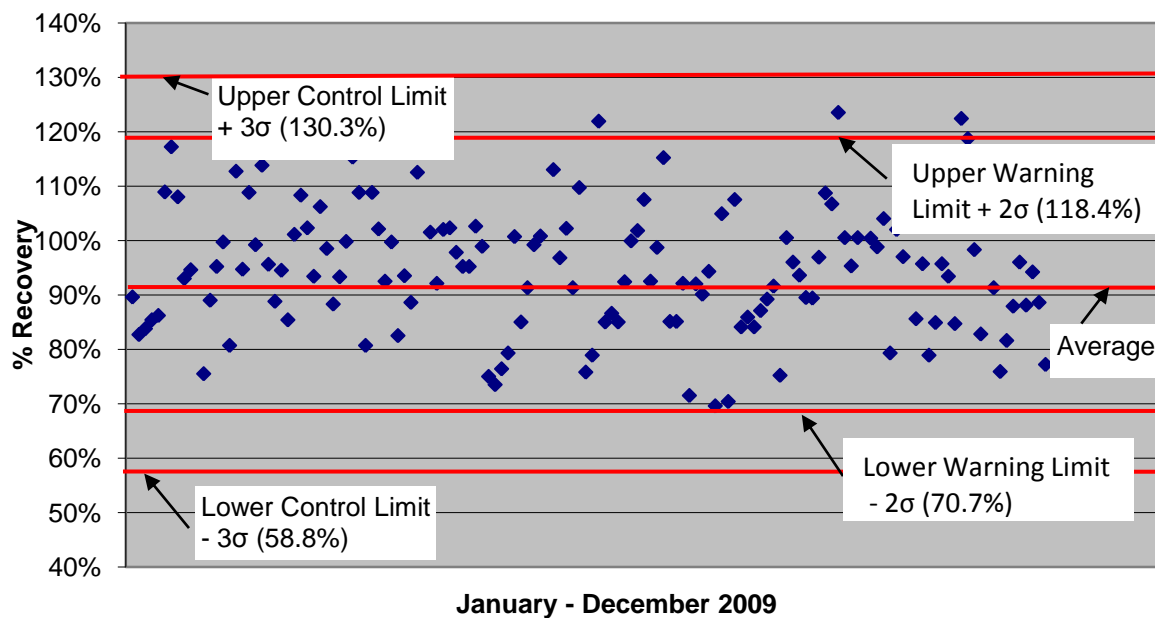
Figure 7 - Control Chart for Methyl Mercury Ongoing Calibration Standard Percent Recovery

2.3 Continuing Calibration Blanks

2.3.1 Description

Continuing calibration blanks (CCBs) are analyzed during the course of sample analysis, after ten or fewer samples and at the end of each analytical run. The MDN control limit for total mercury, the mean of the initial calibration blank (ICB) and CCB shall be less or equal to 0.25ng/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 calibration blanks for the MDN project in 2009 for total mercury that were above the newly established control limit of 0.098 ng/L (+3σ). No calibration blanks were above 0.25ng/L, which is the control limit that is used during analysis at HAL.

For 2009, a control limit for methyl mercury based on (+3σ) is 0.055ng/L. The control limit used in the laboratory is 0.025ng/L.

Ongoing calibration blanks are expected to be at or near MDL. In cases where the blanks are significantly higher, the situation is investigated. Possible contamination sources are researched and identified. Once the contamination has been isolated and corrected, the run is continued.

From review of the methyl mercury control chart, the spread of CCB values is greater during the beginning of the year and low and stable during the end of the year. The true reason for this is undetermined, but together, the following actions resolved the problem and lowered the CCBs:

-The split bottle used for the acetate buffer was changed.

-Thorough maintenance was performed on both instruments.

Table 4 - Ongoing Calibration Blanks Summary Table

2009 Ongoing Calibration Blanks	n	Average (ng/L)	Stdev (ng/L)	MDL (ng/L)	Control limit (ng/L)	EPA 1631E/1630 Control limits
Total Mercury	1669	0.005	0.031	0.052	0.098	Individually <0.5ng/L, mean <0.25ng/L with a standard deviation <0.10ng/L
Methyl Mercury	149	0.012	0.014	0.023	0.055	NA

**Total Mercury
Continuing Calibration Blanks
n = 1669, average = 0.005 ng/L, stdev = 0.031**
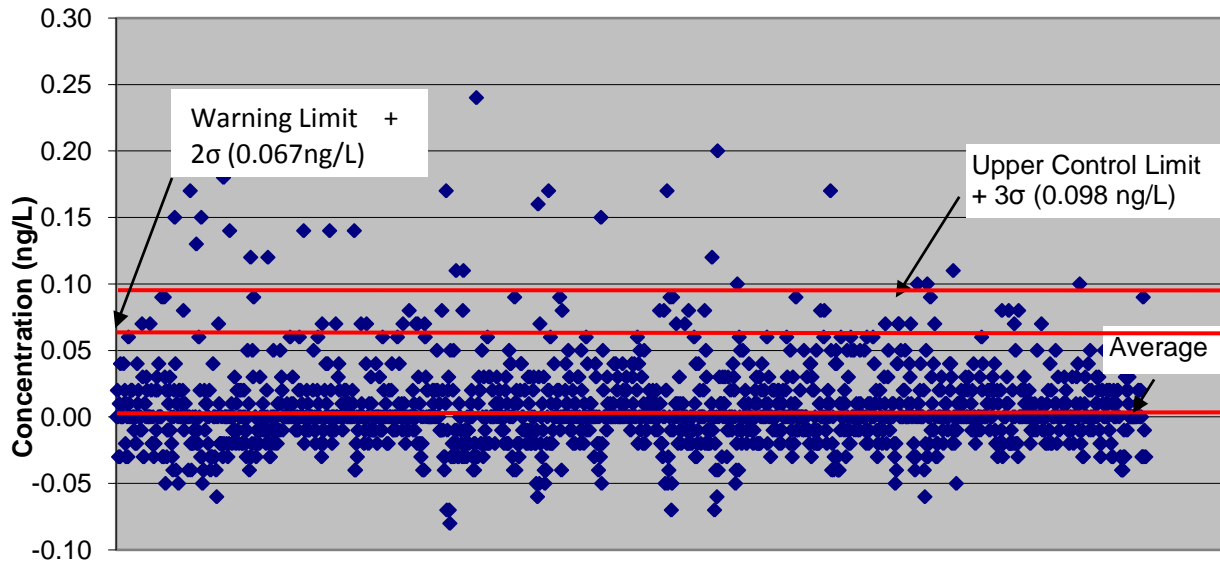
Figure 8 - Control Chart for Total Mercury Continuing Calibration Blanks During 2009

**Methyl Mercury
Continuing Calibration Blanks
n = 149, average = 0.012ng/L, stdev = 0.014**
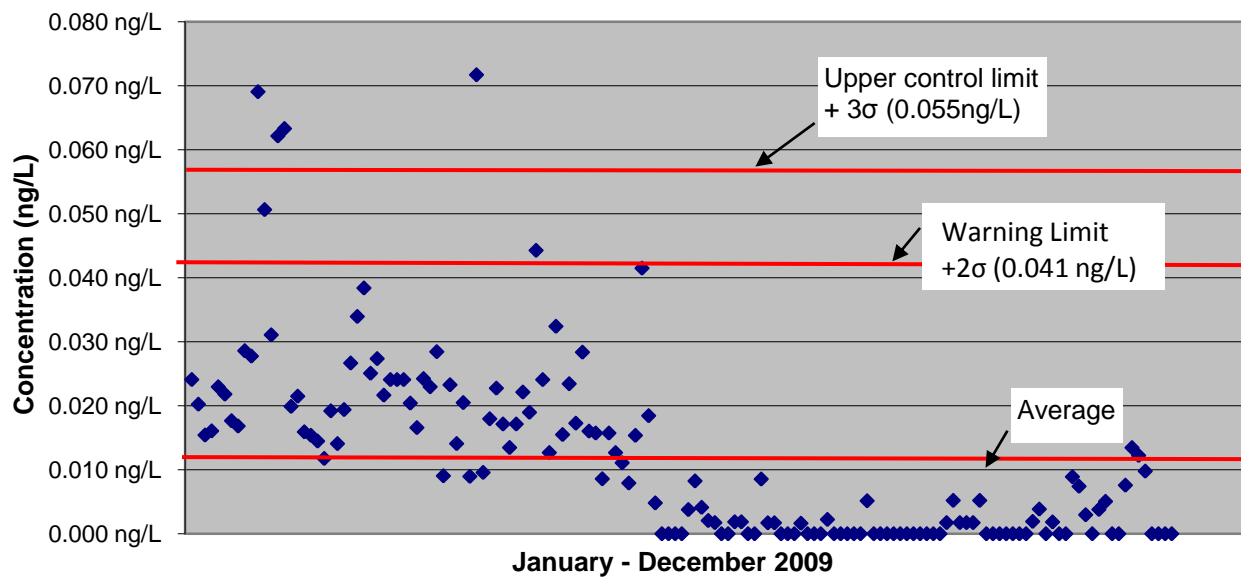
Figure 9 - Control Chart for Methyl Mercury Continuing Calibration Blanks During 2009

2.4 Matrix Duplicates

2.4.1 Description

Matrix duplicates 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 currently set at 25%. 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 normal analytical run three matrix duplicates 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.

2.4.2 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.

2.4.3 Discussion

For 2009, a control limit based on 3σ is 17.12% RPD. No duplicate pairs were above the upper control limit of 25%, which is control limit used at HAL.

For 2009, a control limit based on 3σ is 75.2% RPD and no duplicate pairs for methyl mercury were above the control limit. The actual upper control limit used in the lab is 25%. For many of the samples, the methyl mercury concentration is lower than, or equal to, the reporting limit of 0.05ng/L. As an example, the recovery criteria for the calibration point at the PQL level is 70-130%, and analytical values of 0.05ng/L and 0.65ng/L, which are within the control criteria, produce a RPD of 26.1%. MDN samples of low concentration that produce high RPD values can often be qualified with QR-04 "This 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."

Table 5 - Matrix Duplicates Summary Table 2009

2009 Matrix Duplicates	n	Average RPD (%)	Stdev (%)	Upper control limit 3σ (%)	EPA 1631E/1630 Control limits
Total Mercury	706	3.69	4.47	17.12	NA
Methyl Mercury	19	25.1	16.7	75.2	NA

**Total Mercury
Matrix Duplicate RPD
n = 706, average = 3.69%, stdev = 4.47%**
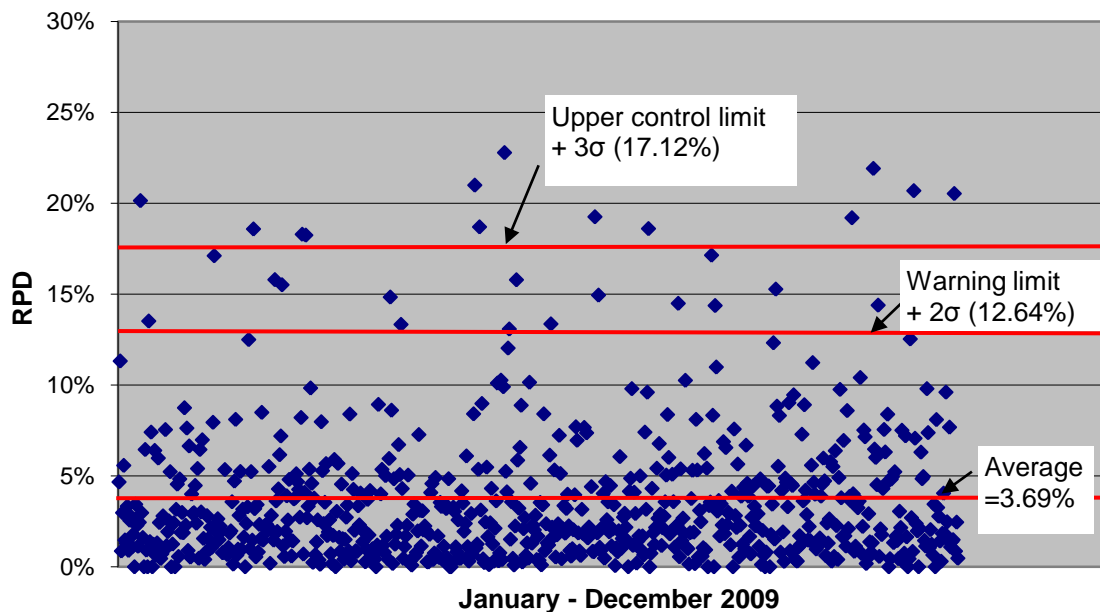
Figure 10 - Control Chart of the Relative Percent Differences for Total Mercury Concentrations in Matrix Duplicates During 2009

**Methyl Mercury
Matrix Duplicate RPD
n = 19, average = 25.1%, stdev = 16.7%**
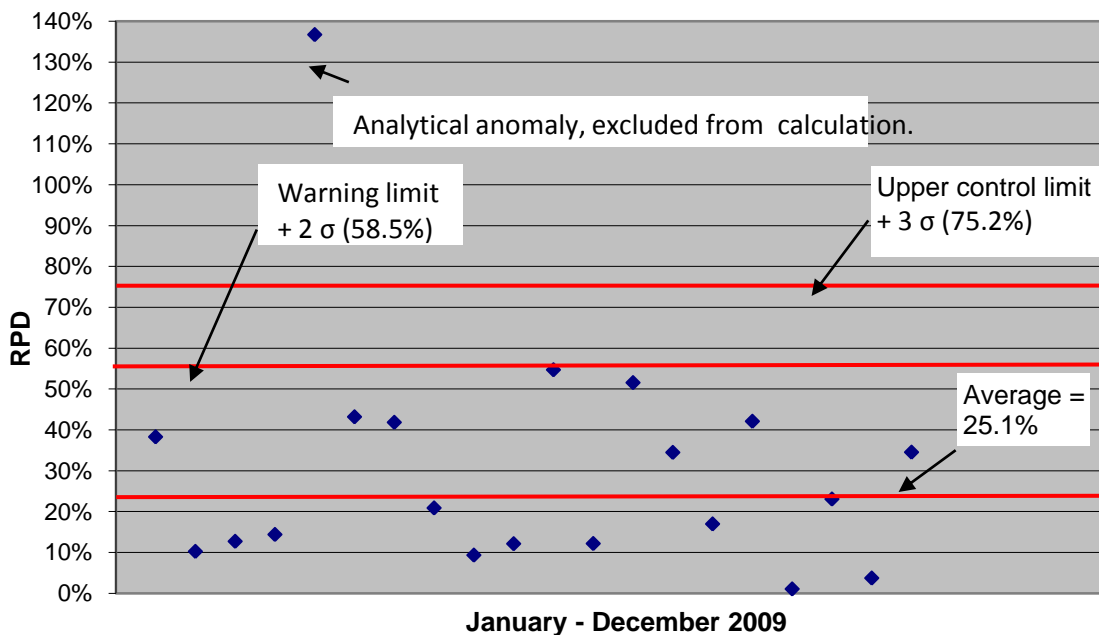
Figure 11 - Control Chart of the Relative Percent Differences for Methyl Mercury Concentrations in Matrix Duplicates During 2009

2.5 Matrix Spikes

2.5.1 Description

A matrix spike (MS) is created when an MDN sample with known mercury content is split in two portions and then 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 0.06ng/L for MHg), whichever is greater. One matrix spike 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.

2.5.2 Purpose

The purpose of analyzing MS and MSD is to demonstrate the performance of the analytical method in a particular sample matrix, and to recognize matrix interference. In this type of analysis, 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 analyzed 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.

2.5.3 Discussion

The control limit based on ±3σ is 81.4%-110%. For 2009, 5 values were greater, and 2 values were below these limits. All values are within the 75-125% control limit used at HAL.

For methyl mercury for 2009, a control limit based on ±3σ is 59.0%-147.8%. During 2009, one set of MS/MSD failed low at 50.4% and 45.2%. This dataset was qualified with QM-07 following Frontier's internal QC standards, since the RPD for the LCS/LCSD was in control. QM-7 = 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. No AS/ASD is possible for methyl mercury samples, since the entire sample volume is being analyzed.

No matrix spike/matrix spike duplicate RPD was above the newly established control limit of 24.3% (+3σ) (See Figure 14). The previous control limit for matrix spike/matrix spike duplicate pairs was 25% RPD.

Table 6 - Matrix Spike Recoveries for 2009 Samples

2009 Matrix Spikes	n	Average (%)	Stdev (%)	Control limits ±3σ (%)	HAL Control limits	EPA 1631E/1630 Control limits (%)
Total Mercury	706	95.7	4.8	81.4-110.0	75-125	71-125
Methyl Mercury	70	103.4	14.8	59.0-147.8	65-135	65-135

Table 7 - Matrix Spike/Matrix Spike % RPD for 2009 Samples

2009 Matrix Spikes	n	RPD Average (%)	Stdev (%)	+3σ (%)	EPA 1630 Control limits % RPD
Methyl Mercury	35	7.3	5.7	24.3	<35%
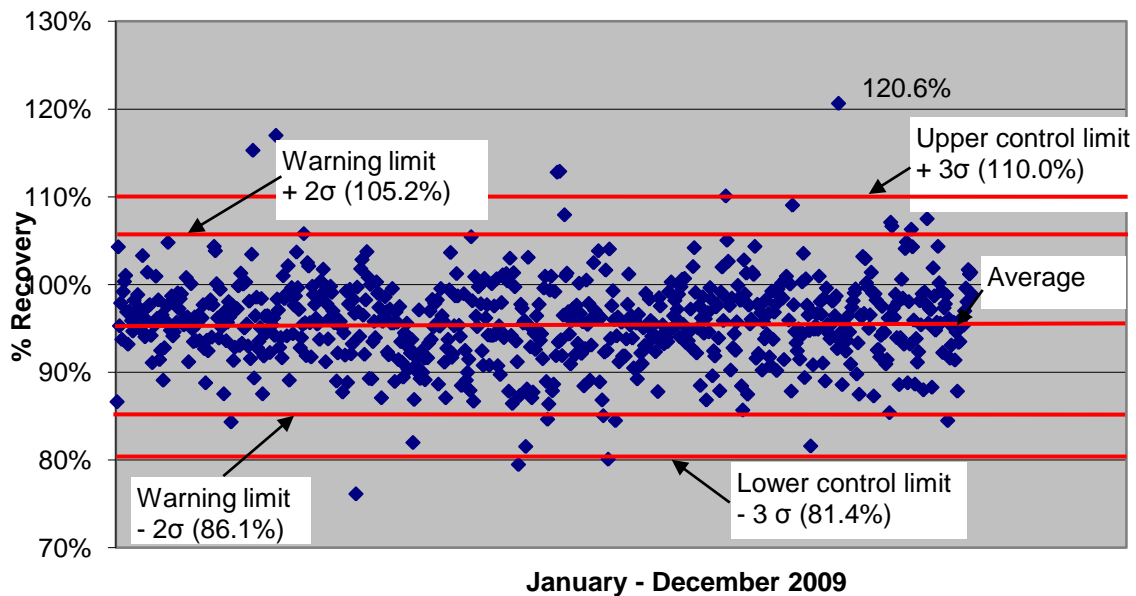
Figure 12 - Control Chart for Total Mercury Percent Recovery in Matrix Spikes During 2009

Figure 13 - Control Chart for Methyl Mercury Percent Recovery in Matrix Spikes During 2009

**Methyl Mercury
Matrix Spikes/Matrix Spike Duplicates, RPD
n = 35, average = 7.3%, stdev = 5.7%**
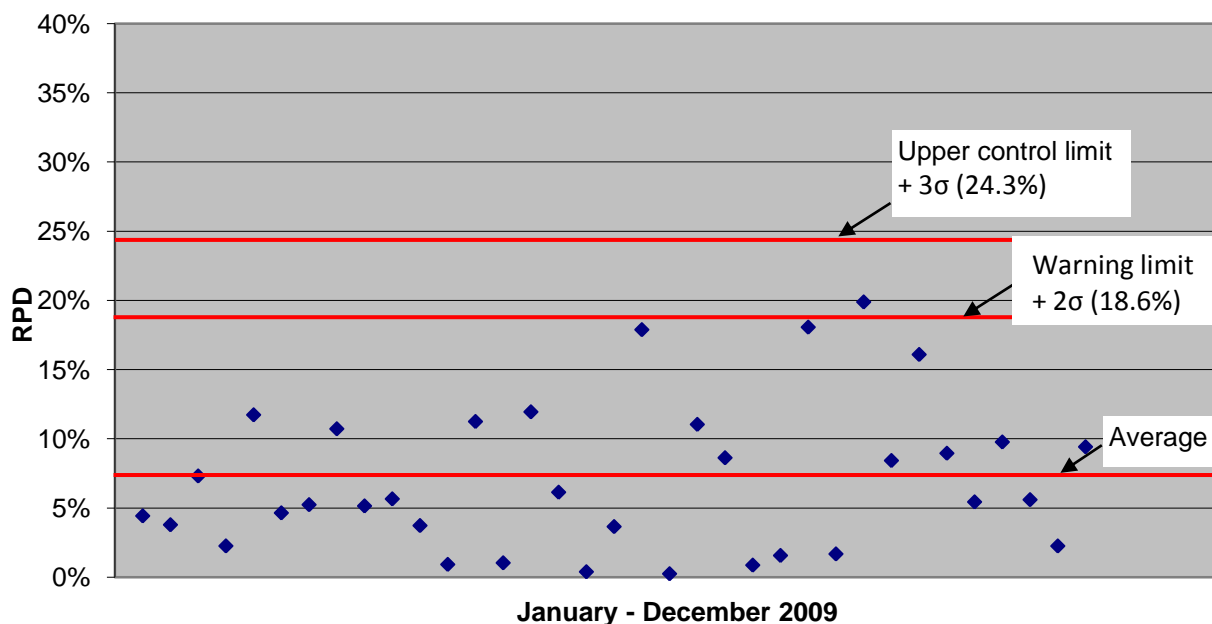
Figure 14 - Control Chart of the Relative Percent Differences for Methyl Mercury Matrix Spike/Matrix Spike Duplicate Pairs during 2009.

2.6 Certified Reference Materials

2.6.1 Description

Reference materials 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 Reference Material matching the MDN rainwater matrix. Instead, HAL uses National Institute of Standards and Technology (NIST) reference Material 1641d ""Mercury in Water." The MDN control limits for total mercury are currently set at 75-125% with a RPD of 25%, and for methyl mercury to 70-130%, with a RPD of 25%. The US EPA methods 1630 and 1631 do not require a certified reference material. There is no CRM available for methyl mercury, therefore a Blank Spike and a Blank Spike Duplicate (BS/BSD) are analyzed.

2.6.2 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.

2.6.3 Discussion

In 2009, the mean of 454 certified reference material recoveries for total mercury was 94.4% with a standard deviation of 3.4%. There was one certified reference material recovery above the upper control limit of 105.1% (+3σ) and nine below the lower control limit of 86.5% (-3σ) established for 2008. The new control limits established for 2009 based on (±3σ) was 84.1-104.7%. There was one certified reference material recovery above and four below the 3σ control limit. The value at 121.0% was within the actual control limit of 75-125% used in the laboratory and no additional action was taken.

Frontier received new shipments of NIST 1641d in September of 2009, and it was noticed that NIST had recertified the value of the CRM from 1.590 mg/kg to 1.557 mg/kg with a density of 1.007 g/mL. The first dataset with the new NIST 1641d was MDN-143, which was analyzed on September 4, 2009.

In 2009, the mean of 88 blank spikes and blank spike duplicated for methyl mercury was 103.0% with a standard deviation of 15.0%. There was no blank spike with recovery outside the control limit of 57.9% -148.0% based on ±3σ for 2009. There were two blank spikes above and one value below the actual laboratory control limit of 70-130%.

The average RPD value for the BS/BSD was 11.7% (n =44), with a standard deviation of 9.7%. Five values were above the actual control limit used in the laboratory of 25%, four were above the upper control lit based on 3σ at 29%.

Total Mercury CRM Recovery
n = 454 average = 94.4%, Stdev = 3.4%
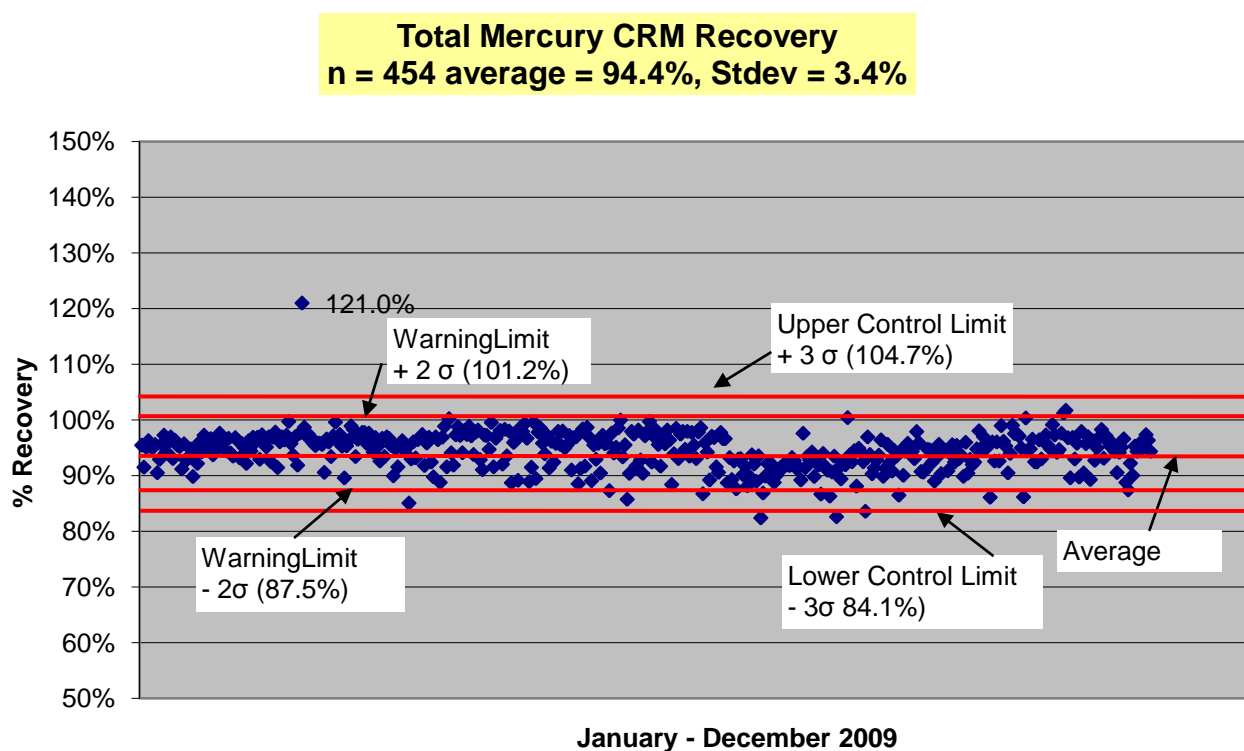
Figure 15 - Control Chart for Total Mercury Percent Recovery in Certified Reference Material Samples During 2009
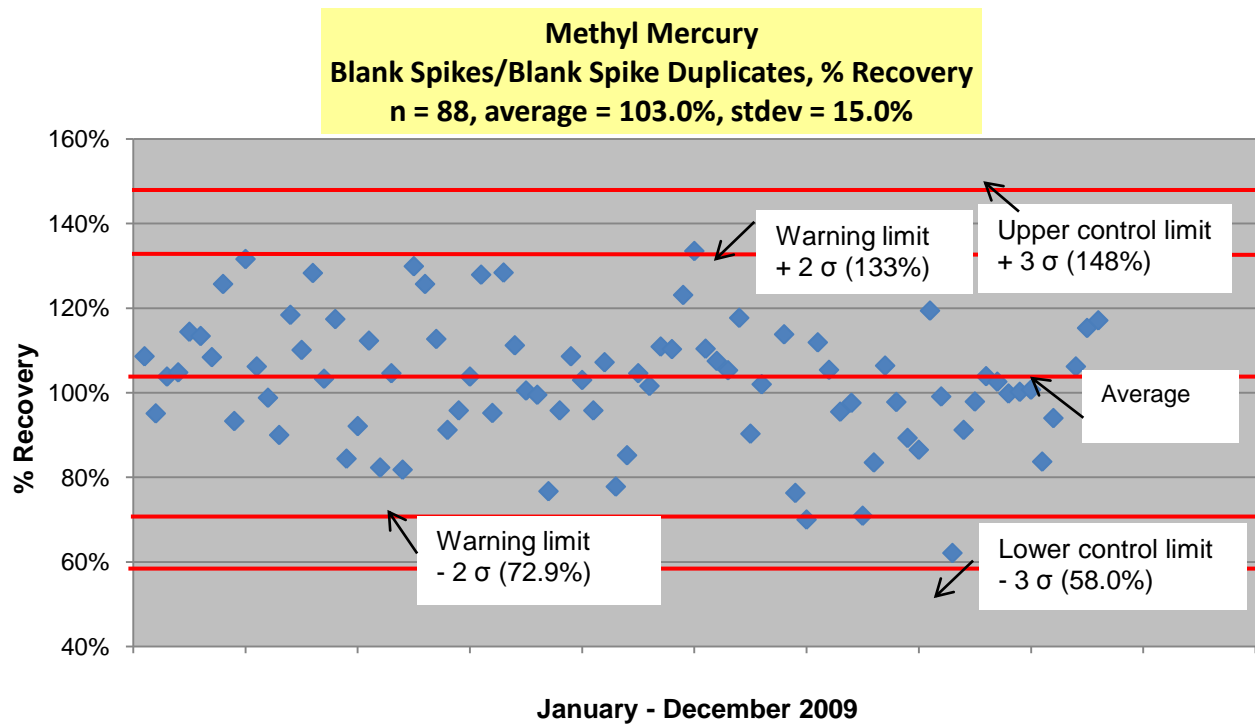
Figure 16 - Control Chart for Methyl Mercury Percent Recovery in Blank Spikes/Blank Spikes Duplicates Samples During 2009
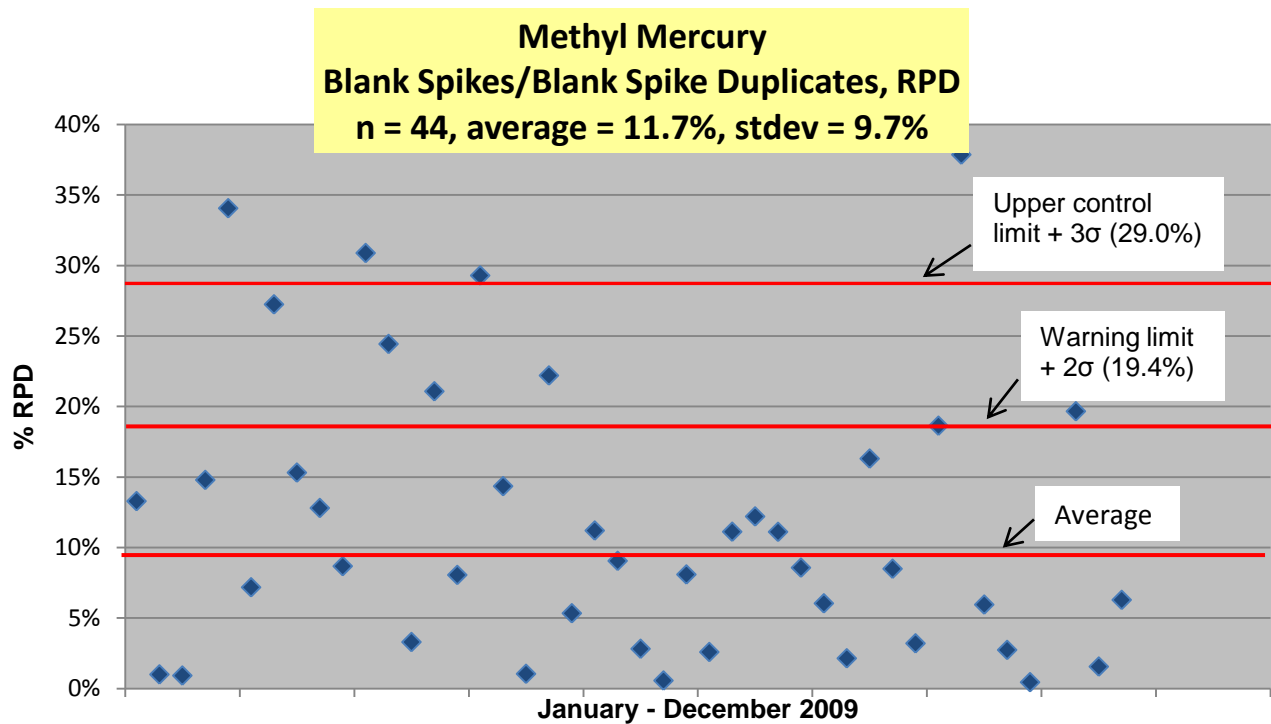
Figure 17 - Control Chart for Methyl Mercury Percent Relative Difference (%RPD) in Blank Spikes/Blank Spikes Duplicates Samples During 2009

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 (in) * 25.4 (mm/in)

If this is selected then Subppt is

=BottleCatch (in) * 25.4 (mm/in)*0.003108

Note: 0.003108 comes from 1 inch of capture in sample bottle according to glass funnel area = 322 mL) (0.003108 = 1/322)

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 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 (CCVs), 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   Trap Set:
D=Duplicate Analysis   S=Sample Spike @ 1.00ng

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

Key
- Reference materials
- Preparation blanks
- Matrix duplicates
- Matrix spikes
- CCVs
- CCBs

Figure 18 - Example of Sample Analysis Worksheet

5. Proficiency Tests and Laboratory Intercomparison Studies

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.

5.1 Proficiency Tests

The following proficiency tests were completed by Frontier during 2009. Results for these tests are available upon request.

Table 8 - 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	03/05/2009
Soil-66	ERA- Environmental Resource Associates	06/04/2009
WP-172 (water pollution)	ERA- Environmental Resource Associates	06/25/2009
Non-Potable Water/Solid & Hazardous Waste/Air Emissions Proficiency Study 325	New York Department of Health	08/27/2009
DMRQA-29 (water pollution)	ERA- Environmental Resource Associates	8/31/2009
WP-177 (water pollution)	ERA-Environmental Resource Associates	11/23/2009
Soil 68	ERA-Environmental Resource Associates	12/03/2009

5.2 Laboratory Intercomparison Studies

In the past, Frontier has participated in the Mercury Round Robin Study, organized by the Florida Department of Environmental Protection, Bureau of Laboratories. This study was cancelled during 2009. Frontier views the opportunity to participate in intercomparison studies as a valuable tool for internal quality control.

The following laboratory intercomparison study was completed by FGS during 2009. Results for these tests are available upon request.

Table 9 - Intercomparison Studies during 2009

Laboratory Intercomparison Name	Organization
EA 452 inter-laboratory comparison Exercise "Trace Elements and Methyl mercury in Scallop"	International Atomic Energy Agency (IAEA)

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 any collector openings. All field bottle blanks that maintain enough of the initial 20mL 1% hydrochloric acid charged, so at least 15mL can be measured out as aliquot size, are analyzed for total mercury. 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, therefore no dilution is needed.

6.1.2 Purpose

Outside of the controlled laboratory environment, ambient mercury levels increase and additional sample handling occurs. Because such contamination sources are inevitable, 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 it is then at risk for dust contamination.

6.1.3 Discussion

In 2009, the mean of 164 Field Bottle Blanks was 0.083ng/bottle with a standard deviation of 0.182ng/bottle. Included in Figure19, three samples show elevated mercury values in the field blanks, these samples are NV02200901113 (0.659ng/bottle), AZ0220091006 (1.911ng/bottle), and AZ0220091110 (0.926ng/bottle). All three sites are located in a desert region.

NV02 had 6 other field blanks from 2009 with an average of 0.053 ng/ and were all less than the average of the Field Bottle Blanks of 0.083ng/bottle.

AZ02 had 4 other field blanks from 2009 with an average of 0.858 ng/ and were above the average of the Field Bottle Blanks of 0.083ng/bottle.

If the three data points are excluded, the average calculation for the year is 0.063 ng/bottle, with a standard deviation of 0.077ng/bottle. This suggests that the MDN collector protects the sample train and bottle well and the field exposure is minimal.

**Total Mercury
Field Bottle Blanks
n = 164, average = 0.083ng/bottle, Stdev = 0.182**
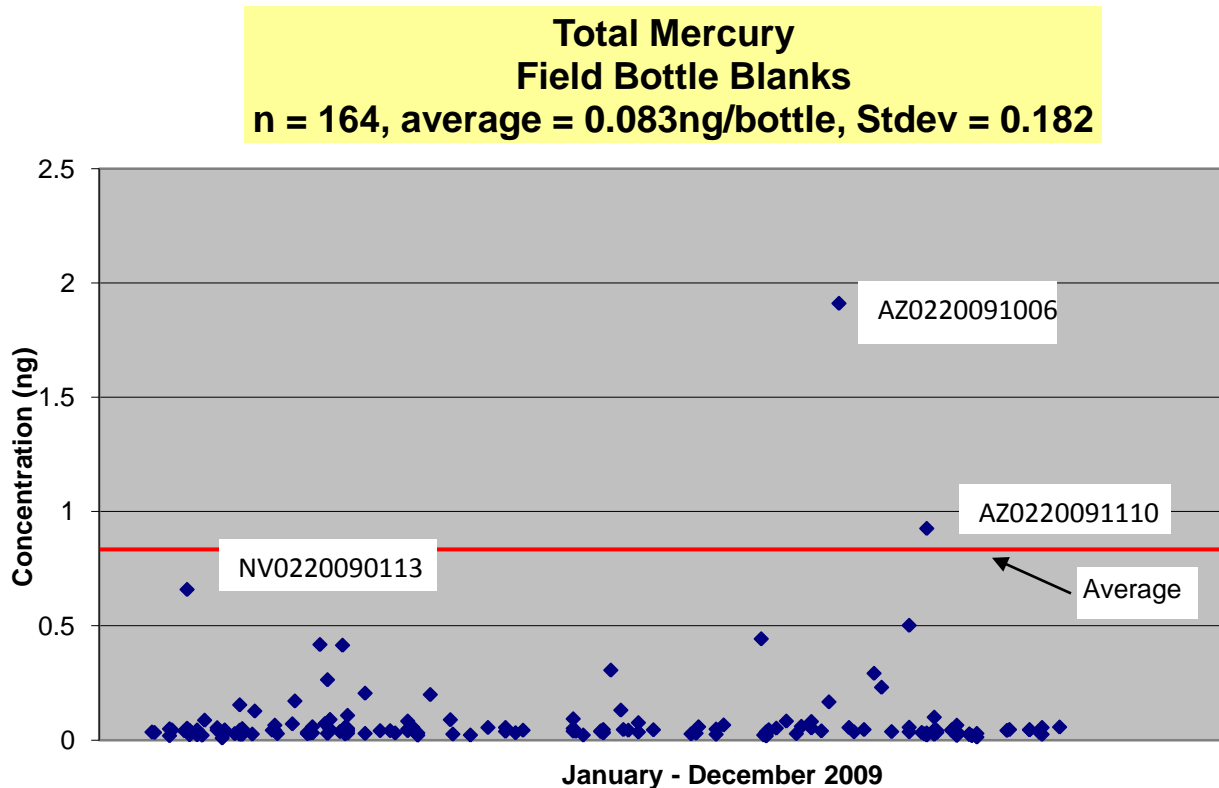
Figure 19 - Time Series Plot of Total Mercury Concentrations in Field Bottle Blanks During 2009

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. 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 2009, the mean of 38 system blanks was 0.043ng/aliquot with a standard deviation of 0.025ng/aliquot. This suggests that the MDN sample train is well protected.

2009 MDN Total Mercury System Blanks n = 38
Control Average = 0.012 ng/aliquot, Stdev = 0.010
System Blank Average = 0.043 ng/aliquot, Stdev = 0.025
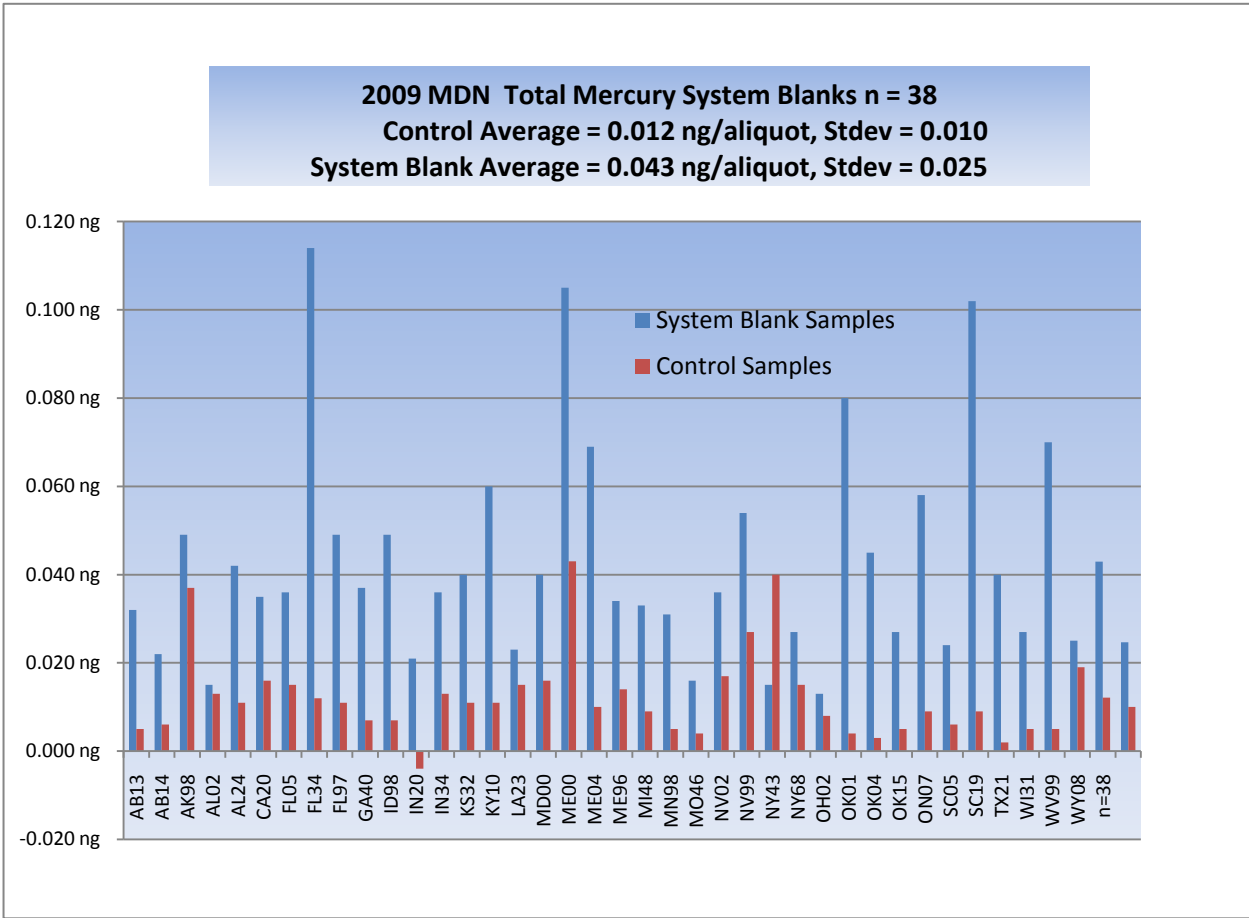
Figure 20 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2009

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 is modeled on the NADP AIRMoN QR. 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 6748 samples in 2009. 3154 samples received a QR code of A, 3122 received a B QR code, and 472 received a C QR code. HAL continued to maintain and demonstrate acceptable quality control in 2009. This comparison is based on HAL assessing the QR codes. These codes can later be changed by the Program Office.

Of the 472 "C" coded samples for 2009, 2 are due to laboratory error. 1) During receipt at the lab, the sample bottle was knocked over and the cap broke. This resulted in 32.3 mL of the sample being lost. This invalidated sample IL1120090303. 2) Instrument peak was lost during analysis, due to equipment malfunction. No result recorded and no sample volume remaining for re-analysis. This invalidated sample MN1620090113.

2009 Distribution of MDN Quality Rating Codes

7.0% C coded samples

46.7% A coded samples

46.3% B coded samples
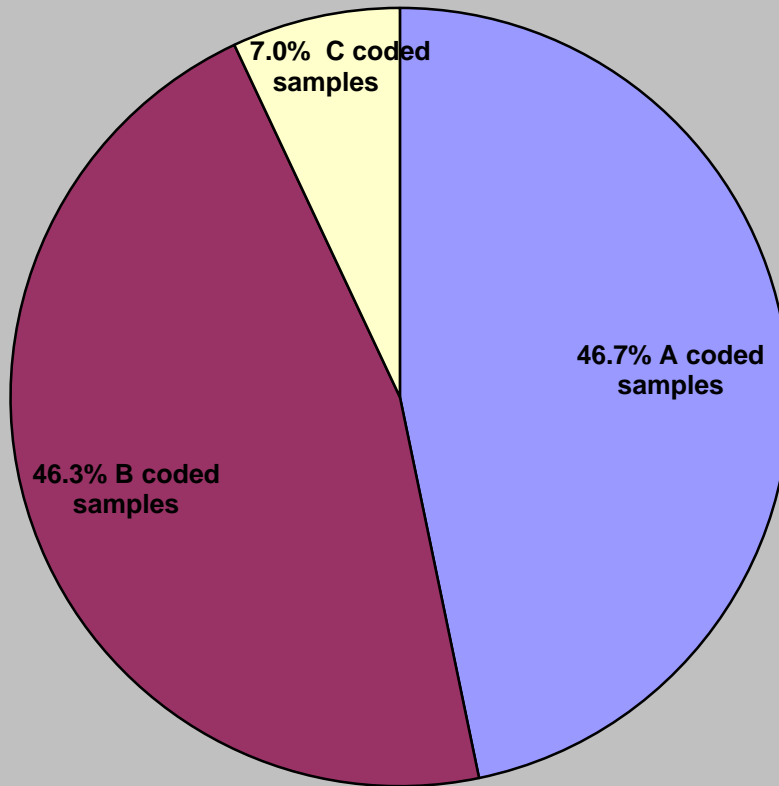
Figure 21 - Distribution of Quality Rating Codes for Samples Received in 2009
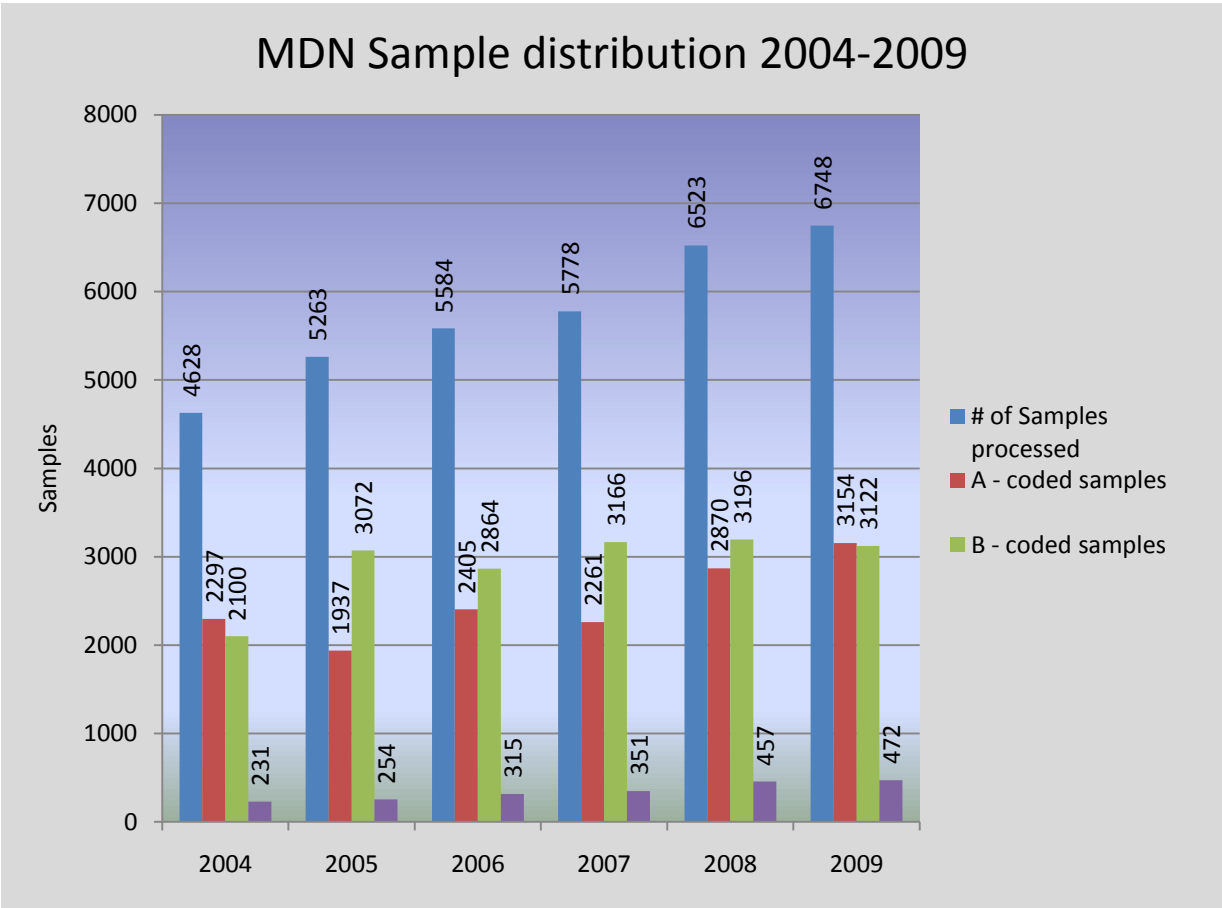
Figure 22 - Distribution of Quality Rating Codes for Samples Received from 2004 to 2009

8. Summary and Conclusions

The HAL continued to maintain and demonstrate acceptable quality control in 2009. The five DQOs, precision, accuracy, representativeness, comparability, and completeness, were all met. Figure 9, the control chart for methyl mercury in continuing calibration blanks for methyl mercury during 2009, showed elevated CCBs during the first part of the year. The root cause to the problem was never determined, but the following corrections solved the problem:

-The split bottle used for the acetate buffer was changed.

-Thorough maintenance was performed on both instruments.

Frontier received new shipments of NIST 1641d in September of 2009, and it was noticed that NIST had recertified the value of the CRM from 1.590 mg/kg to 1.557 mg/kg with a density of 1.007 g/mL. The first dataset with the new NIST 1641d was MDN-143, which was analyzed on September 4, 2009. All the reported data was recalculated to reflect the new NIST 1641d value, but this may account for the slight decline in recovery in the third quarter of 2009.

The HAL will continue to look for ways to improve the program to ensure the highest quality.

Table 10 - QC Criteria for EPA 1631E and 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	The laboratory must obtain a 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 OPR (77-123%).	The laboratory must obtain a 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 OPR (77-123%).
ICV	Ongoing Precision and Recovery (OPR) Standard at 5.0ng/L required at the beginning and end of each run, 77-123% recovery	Ongoing Precision and 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 $\leq$ 24 Frequency of 1 MS/MSD per 10samples. 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 10samples. 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 < 0.50ng/L.	Minimum of 3.Mean <0.045 ng/L Variability <0.015 ng/L

9. Appendix A. Matrix Specific MDL Studies

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

Prepared by Adela Blaga, Jason Karlstrom, and Kristina Spadafora
THg09-090416-1
Date: 5/02/2009

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 **0.052 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 $SnCl_2$, 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# 0900011) was pipette into a 1000 mL volumetric flask and brought up to volume with reagent water. 10 mL of BrCl was then added to the solution, resulting in a sample with a concentration of 0.50 ng/L of THg oxidized to 1% (v/v) BrCl. This was done on 090401. LIMS #0900011 expired on 090407. The results of these measurements are found in the table on the page 2, and in the raw data sheets (ID # THg09-090416-1).

All results are reported **corrected** for the method blanks and 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, σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.
MDL = t*σ = (2.821) * (0.018) = **0.052 ng/L**.

Dataset THg09-090416-1 was used for the MDL study. All ten replicates showed a percent recovery between 70-130% (100.0% ± 3.7%), 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 MDN MDL Study: Total Mercury in Water CV-AFS #9

	[THg], ng/L
BrCl-1	0.024
BrCl-2	0.014
BrCl-3	0.020
Mean	**0.019**
SD	**0.005**

	Result [THg], ng/L	Spike Level, [TV], ng/L	[%Rec]
MDL-Rep1	0.53	0.50	106.0%
MDL-Rep2	0.47	0.50	94.0%
MDL-Rep3	0.49	0.50	98.0%
MDL-Rep4	0.49	0.50	98.0%
MDL-Rep5	0.49	0.50	98.0%
MDL-Rep6	0.50	0.50	100.0%
MDL-Rep7	0.49	0.50	98.0%
MDL-Rep8	0.50	0.50	100.0%
MDL-Rep9	0.52	0.50	104.0%
MDL-Rep10	0.52	0.50	104.0%
Mean	**0.50**	**0.50**	**100.0%**
SD	**0.018**	**0.00**	**3.7%**

	[THg], ng/L	Certified Value	[%Rec]
NIST 1641d	7619	8005	**95.2%**

MDL	0.052
PQL/MDL	9.71

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

Analyzed by Adela Blaga
THg10-090416-1
Prepared by: Kristina Spadafora
Date: 5/5/2009

Objective

On an annual basis to determine the Method Detection Limit (MDL) for instrument CV-AFS#10 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 0.048 ng/L THg for CV-AFS#10.

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 $SnCl_2$, 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# 0900011) was pipette into a 1000 mL volumetric flask. 10 mL of BrCl was then added and the solution was brought up to a final volume of 1000 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 2, as well in the raw data sheets ID # THg10-090416-1.

All results are reported <u>corrected</u> for the method blanks and 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, σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

MDL = t*σ = (2.821) * (0.017) = <u>0.048 ng/L</u>.

Dataset THg10-090416-1 was used for the MDL study. All ten replicates showed a percent recovery between 70-130% (117.2% ± 3.4%), making this dataset eligible for determining an MDL and to verify the PQL value. The PQL value for this study is <u>0.50 ng/L</u> which is the same as the spiking level.

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

Sample	[THg], ng/L
BrCl-1	0.023
BrCl-2	0.024
BrCl-3	0.023
Mean	**0.023**
SD	**0.001**

	Result [THg], ng/L	Spike Level, [TV], ng/L	[%Rec]
MDL-Rep1	0.57	0.50	114.0%
MDL-Rep2	0.58	0.50	116.0%
MDL-Rep3	0.56	0.50	112.0%
MDL-Rep4	0.58	0.50	116.0%
MDL-Rep5	0.59	0.50	118.0%
MDL-Rep6	0.59	0.50	118.0%
MDL-Rep7	0.57	0.50	114.0%
MDL-Rep8	0.60	0.50	120.0%
MDL-Rep9	0.61	0.50	122.0%
MDL-Rep10	0.61	0.50	122.0%
Mean	**0.59**	**0.50**	**117.2%**
SD	**0.017**	**0.00**	**3.4%**

	[THg], ng/L	Certified Value	[%Rec]
NIST 1641d	7644	8005	**95.5%**

MDL	0.048
PQL/MDL	10.35

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

July 27, 2009

By Adela Blaga, Ryan Nelson, and Kristina Spadafora

MHg07-090717-1 Sequence# 9G17004

Batch# F907066

WO# 0907084

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 **0.0231 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 0.854 was used.

The MDL study consisted of the distillation and analysis of ten water replicates prepared to 0.050 ng/L of MHg (45 µL @ 0.05 ng/mL spiked into 45 mL distillation vials – LIMS # 0900555). The results of these measurements are found in the table on the next page, as well in the raw data sheets (ID # MHg07-090717-1,9G17004). 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 σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

MDL = t*σ

The MDL calculated from these data is (2.821)*(0.0082), or **0.0231 ng/L**.

MDL and PQL Validation.

The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, RSD CF, etc.) passed. All 10 replicates showed a percent recovery between 70-130% (107.0 ± 14.9%), making this dataset eligible for determining both an MDL and a PQL value. Using the mean of the true values (TVs), gives a PQL of 0.050 ng/L. For this dataset, the PQL is 2.17 times the MDL.

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

Sample	[MHg], ng/L		
F907066-BLK1	0.021		
F907066-BLK2	0.016		
F907066-BLK3	0.008		
Mean	**0.015**		
SD	**0.006**		

% Recovery Limits

70-130%

	[MHg], ng/L	Spike Level, [TV], ng/L	[%Rec]
0907084-01	0.060	0.050	119.4%
0907084-02	0.048	0.050	96.9%
0907084-03	0.057	0.050	113.8%
0907084-04	0.048	0.050	96.9%
0907084-05	0.064	0.050	127.9%
0907084-06	0.051	0.050	102.5%
0907084-07	0.041	0.050	82.7%
0907084-08	0.043	0.050	127.9%
0907084-09	0.064	0.050	96.9%
0907084-10	0.048	0.050	105.0%
Mean	**0.053**	**0.050**	**107.0%**
SD	**0.0082**	**0.000**	**14.9%**

		Certified Value	[%Rec]	[%RPD]
F907066-BS1	1.91	**2.00**	**95.7%**	
F907066-BSD1	1.97	**2.00**	**98.5%**	**2.91%**

MDL	0.0231
PQL/MDL Ratio	2.17

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

July 27, 2009

By Adela Blaga, Ryan Nelson, and Kristina Spadafora

MHg15-090717-1 Sequence# 9G17005

Batch# F907067

WO# 0907084

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 **0.0162 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 0.854 was used.

The MDL study consisted of the distillation and analysis of ten water replicates prepared to 0.050 ng/L of MHg (45 µL @ 0.05 ng/mL spiked into 45 mL distillation vials – LIMS # 0900555). The results of these measurements are found in the table on the next page, as well in the raw data sheets (ID # MHg15-090717-1,9G17005). 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 σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

MDL = t*σ

The MDL calculated from these data is (2.821)*(0.0057), or **0.0162 ng/L**.

MDL and PQL Validation.

The dataset was peer reviewed and all qualifying parameters (ICV, CCV, CCB, LCS, RSD CF, etc.) passed. All 10 replicates showed a percent recovery between 70-130% (102.4 ± 10.2%), making this dataset eligible for determining both an MDL and a PQL value. Using the mean of the TVs, gives a PQL of 0.050 ng/L. For this dataset, the PQL is 3.09 times the MDL.

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

Sample	[MHg], ng/L		
F907067-BLK1	-0.002	**% Recovery Limits 70-130%**	
F907067-BLK2	-0.001		
F907067-BLK3	0.003		
Mean	**0.000**		
SD	**0.002**		
		Spike Level, [TV], ng/L	**[%Rec]**
0907084-01RE1	0.047	0.050	94.3%
0907084-02RE1	0.059	0.050	118.9%
0907084-03RE1	0.046	0.050	91.3%
0907084-04RE1	0.047	0.050	94.3%
0907084-05RE1	0.046	0.050	91.3%
0907084-06RE1	0.049	0.050	97.4%
0907084-07RE1	0.053	0.050	106.6%
0907084-08RE1	0.059	0.050	115.9%
0907084-09RE1	0.058	0.050	109.7%
0907084-10RE1	0.055	0.050	103.9%
Mean	**0.052**	**0.050**	**102.4%**
SD	**0.0057**	**0.000**	**10.2%**
		Certified Value	**[%Rec]**	**[%RPD]**
F907067-BS1	1.79	**2.00**	**89.6%**	
F907067-BSD1	2.10	**2.00**	**104.9%**	**15.81%**

MDL	0.0162
PQL/MDL Ratio	3.09