National Atmospheric Deposition Program

Mercury Analytical Laboratory

2012 Annual Quality Assurance Report

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Introduction

Eurofins Frontier Global Sciences Inc. (EFGS) has served as the Mercury Analytical Laboratory (HAL) and Site Liaison Center for the Mercury Deposition Network (MDN) since January 1996. MDN which is coordinated through the National Atmospheric Deposition Program (NADP) was designed with the primary objective of quantifying the wet deposition of mercury in North America to determine long-term geographic and temporal distributions. The MDN consisted of 110 active sites in the United States and Canada at the end of 2012. In 2012 4 sites were shut down, two new sites were added and two sites were re-started

The HAL analyzes weekly precipitation samples for total mercury from all active MDN sites and for methyl mercury from 23 sites. The analytical technique, a modified EPA Method 1631, was developed by Nicolas S. Bloom, one of FGS' founders. FGS also served as the referee lab for the EPA Method 1631 "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" final validation study.

EFGS continued to maintain and demonstrate acceptable quality control in 2012. EFGS 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 in 2012.

- On September 1, 2012 Frontier Global Sciences was acquired by Eurofins and became Eurofins Frontier Global Sciences.
- On September 29, 2012 Kristina Spadafora departed Eurofins Frontier Global Sciences to explore some other opportunities.
- On October 12, 2012 David Wunderlich was hired as the new QA Manager.

1. Quality Assurance

1.1 Philosophy and Objectives

Eurofins Frontier Global Sciences Inc. (EFGS) 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 EFGS' Data Quality Objectives (DQO). Our DQOs consist of five components: ***Precision, Accuracy, Representativeness, Comparability, and Completeness.***

- **Precision** is a measure of data reproducibility. HAL assesses analytical precision using matrix duplicates. The acceptance criterion for 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 (σ) is taken from the resulting data and the MDL is determined as t * σ of the replicates. For ten replicates, the MDL is calculated as follows: MDL=2.821 * σ. This value should not be interpreted as the method reporting limit.

The Practical Quantitation Limit (PQL) is the reporting limit for the method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3 and TNI Standard EL V1M4-2009 section 1.7.1.1.h.iii). The PQL is determined by running ten replicate samples with a concentration that must have the same recovery criteria as for the lowest calibration point.

The ratio between the 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 2012. All MDL and PQL studies are on file with the Quality Assurance department and are available upon request.

The MDL studies for total mercury for instrument #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.

Table 1 - MDL Studies for 2012 Summary Table

Instrument	Dataset	MDL (ng/L)	PQL (ng/L)	PQL/MDL
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
CV-AFS#9	MDN IDL THg09-111219-1	0.074	0.50	6.81

1.3 Accreditations

Eurofins Frontier Global Sciences currently holds certifications through departments in eight 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 State of New Jersey Department of Environmental Protection, 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 Eurofins 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 2012, no laboratory bottle blank was higher than the MDL for total mercury performed for 2012 of 0.074 ng/L.

In 2012, there were two laboratory bottle blanks near but still below the MDL for methyl mercury. 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

2012 Laboratory Bottle Blanks	n	Average (ng/bottle)	Standard Deviation	MDL (ng/L)	PQL (ng/L)
Total Mercury	119	0.015	0.008	0.074	0.50
Methyl Mercury	11	0.004	0.010	0.019	0.050

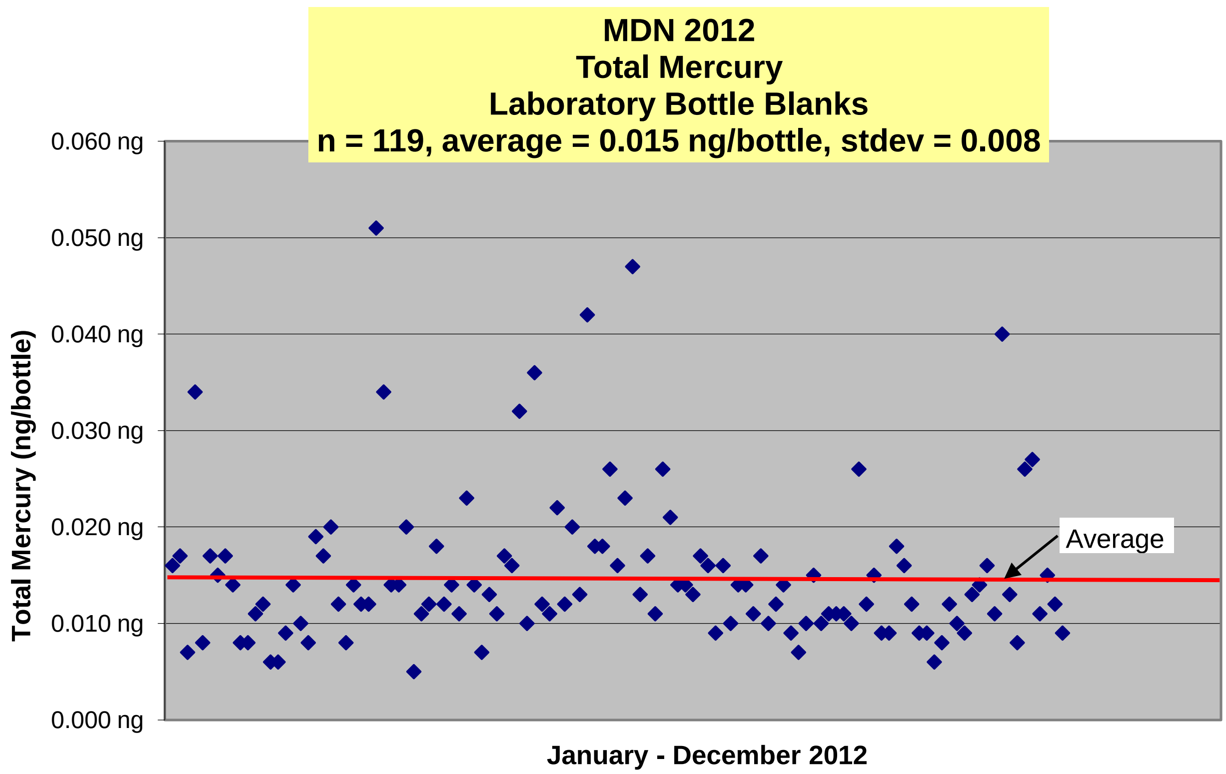

Figure 1 - 2012 Plot of Total Mercury Mass in Laboratory Bottle Blanks for 119 Samples

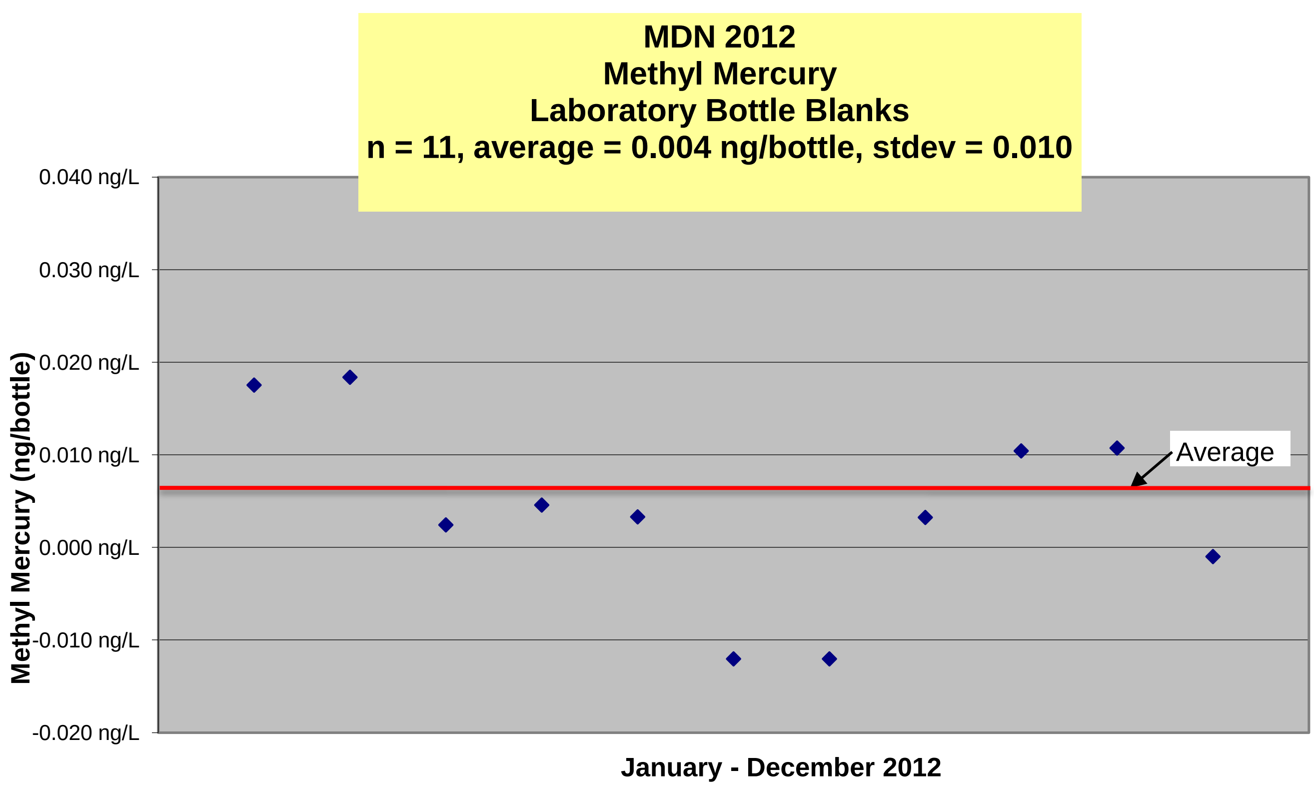

Figure 2 - 2012 Plot of Methyl Mercury Mass in Laboratory Bottle Blanks for 11 Samples

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. 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 2012, 15 preparation blanks for total mercury were above the calculated $\bar{x}+3\sigma$ limit of 0.131 ng/L. All the preparation blanks analyzed during 2012 were less than the control limit of <0.25 ng/L used at the laboratory and less than the EPA criteria of 0.50 ng/L (table 3 and figure 3).

In 2012, 3 preparation blanks for methyl mercury were above the calculated $\bar{x}+3\sigma$ limit of 0.0346 ng/L. None of the preparation blanks was higher than the EFGS control limit of 0.045 ng/L (figure 4). The standard deviation for 2012 of 0.010 ng/L is less than the EPA requirement of <0.015 ng/L.

Table 3 - Preparation Blanks Summary Table

2012 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	651	0.035	0.032	0.101	0.132	0.25	< 0.50
Methyl Mercury	99	0.0046	0.010	0.019	0.0346	0.045	Mean <0.045 σ<0.015

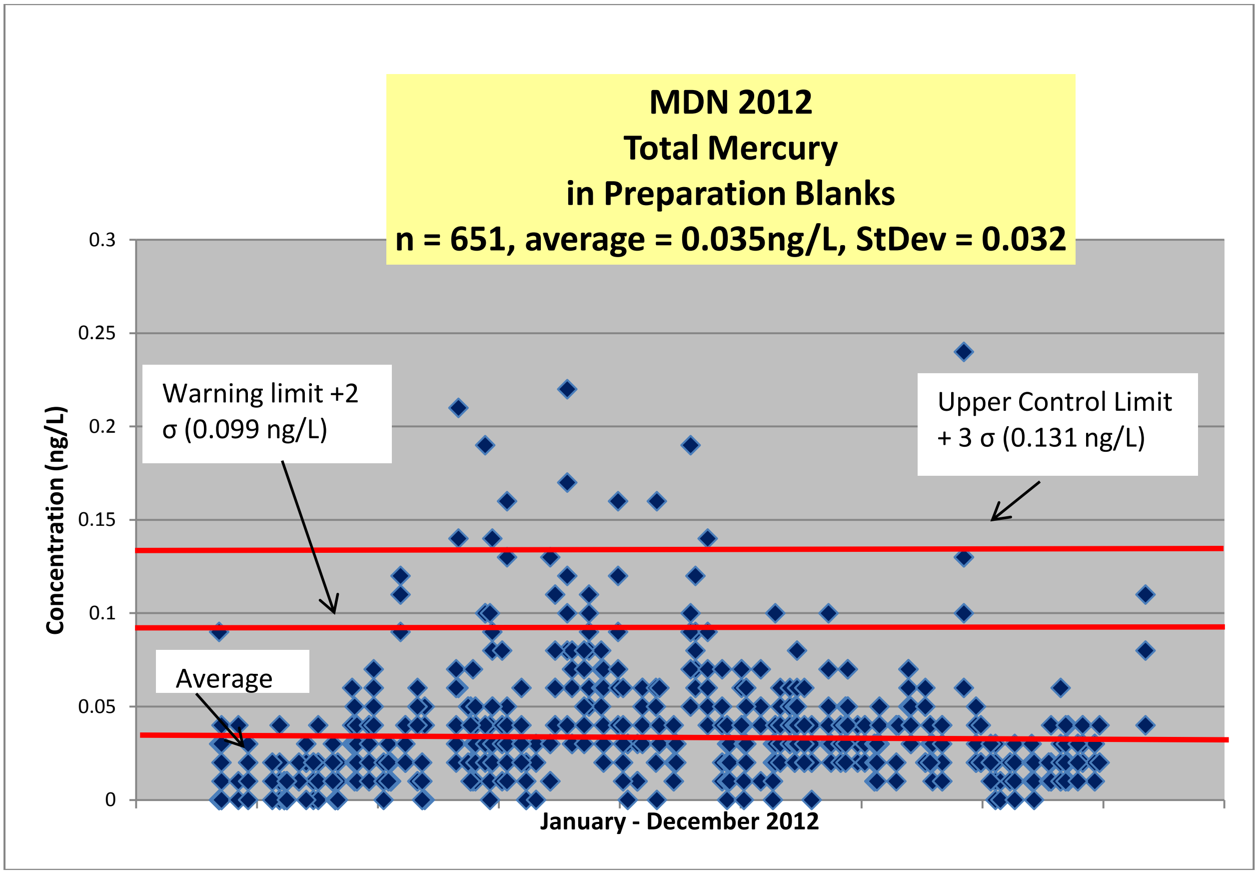

Figure 3 - 2012 Control Chart for Total Mercury Concentration in Reagent Preparation Blanks

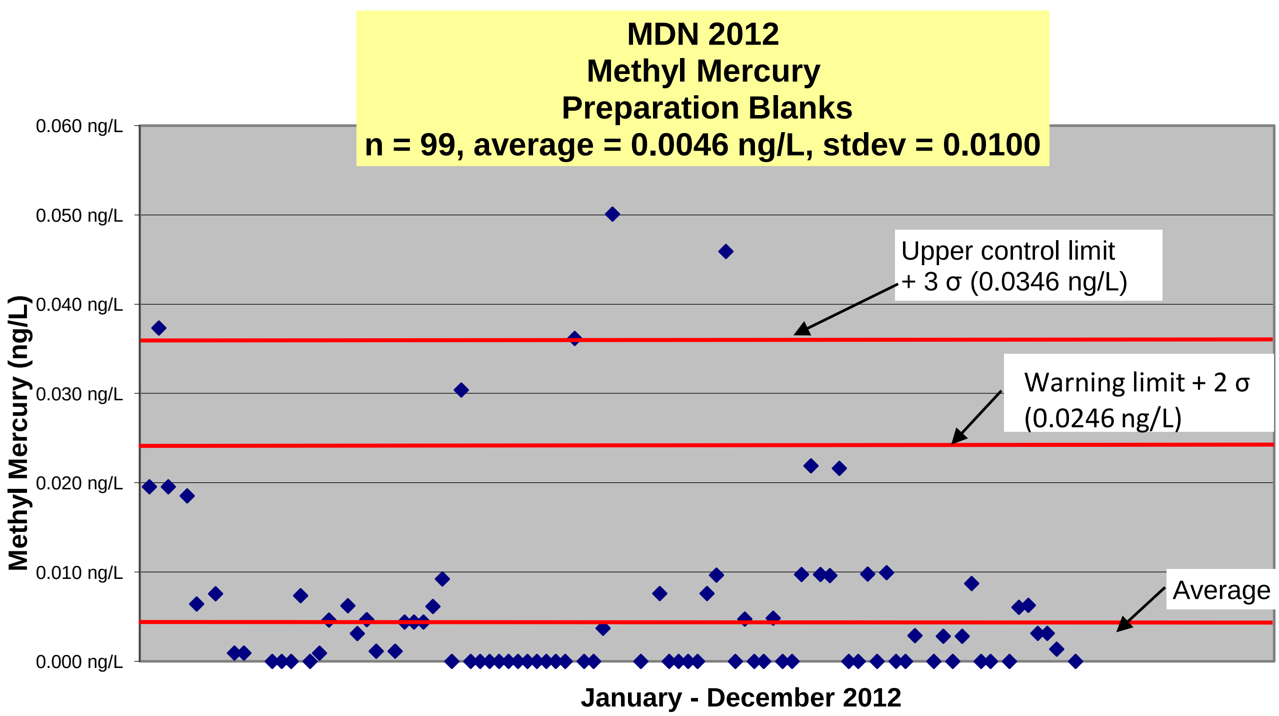

Figure 4 - 2012 Control Chart for Methyl Mercury Concentration in Reagent Preparation Blanks

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 2012, the range was between 92.1-107.5% for total mercury CCV. No samples were above the calculated control limit of 107.6% ($\bar{x}+3\sigma$), and six samples were below the $\bar{x}-3\sigma$ of 92.0%. These values were all within the control limit of 80-120% used at HAL (figure 5).

No reportable CCV recoveries were outside the $\bar{x}\pm3\sigma$ control limit of 66.7-115.5% for methyl mercury (figure 6).

Table 4 - Continuing Calibration Standard Summary Table

2012 Continuing Calibration Standard	n	Average recovery (%)	Stdev of recovery (%)	±3σ Control Limit (%)	EPA 1631E/1630 Control Limits (%)
Total Mercury	742	99.8	2.6	92.0-107.6	77-123
Methyl Mercury	136	91.1	8.1	66.8-115.4	67-133

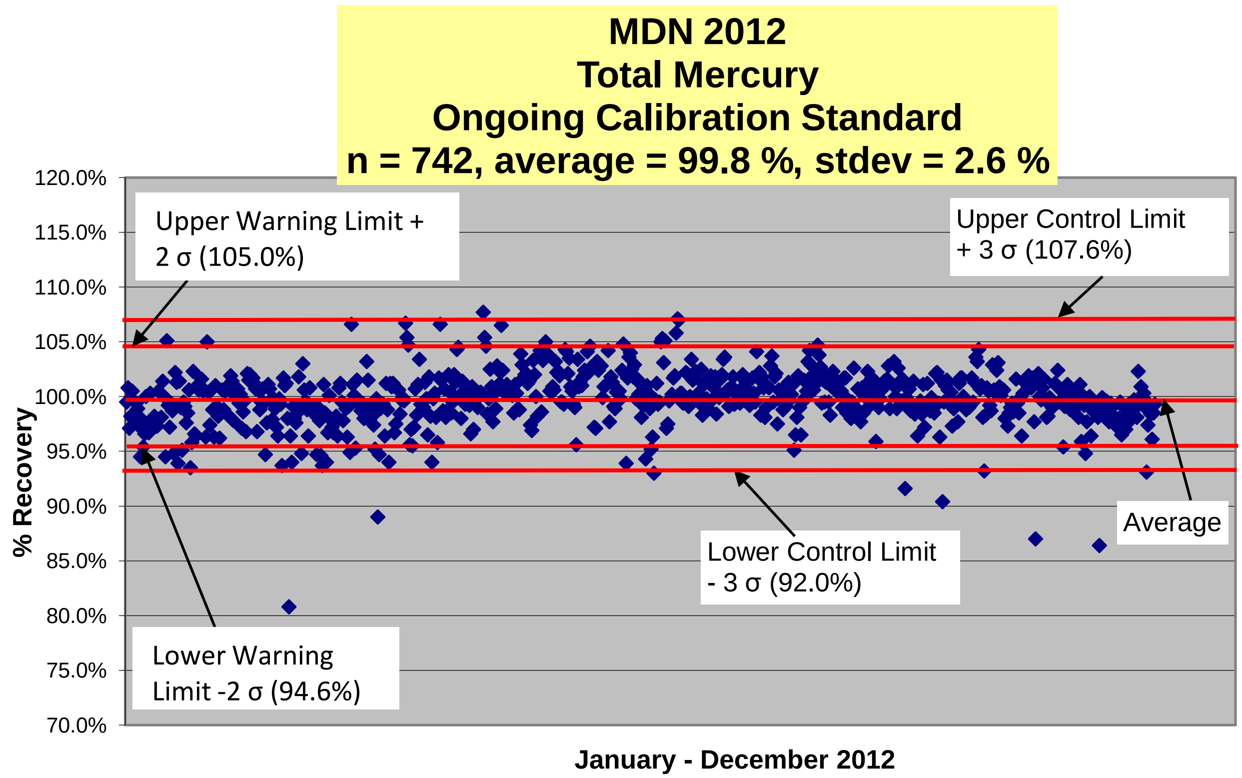

Figure 5 - 2012 Control Chart for Total Mercury Continuing Calibration Standard Percent Recovery

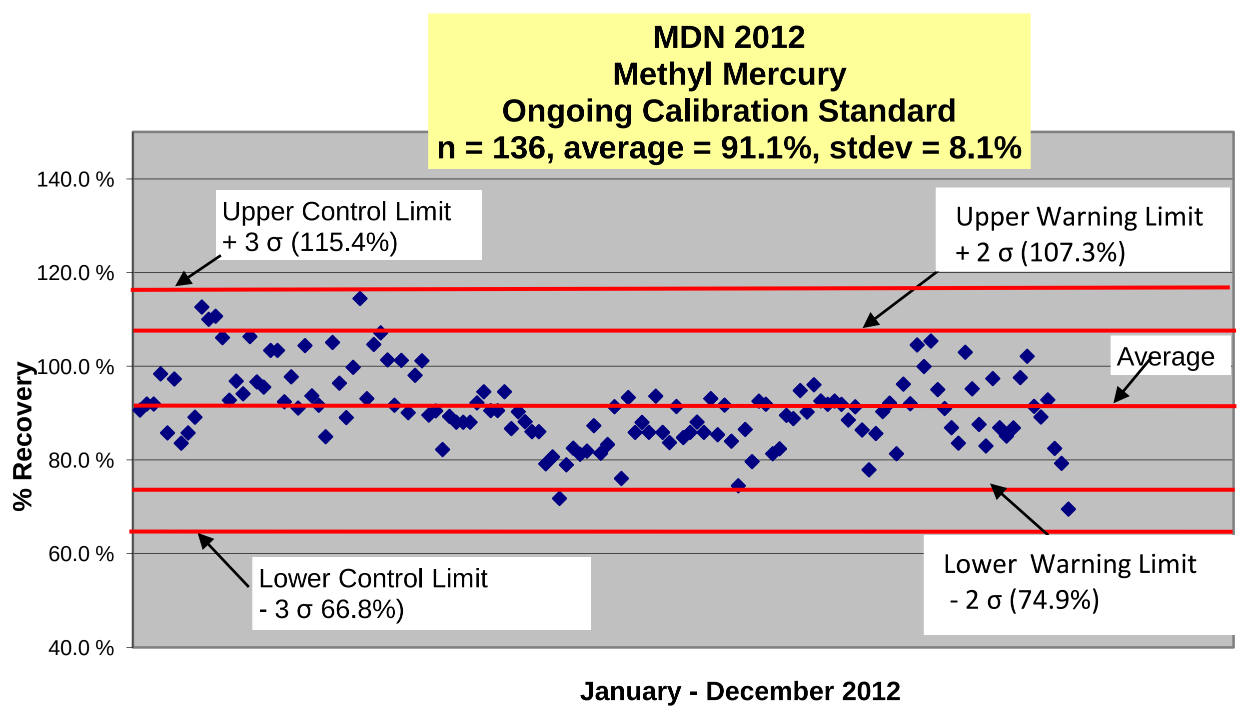

Figure 6 - 2012 Control Chart for Methyl Mercury Ongoing Calibration Standard Percent Recovery

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 2012 for total mercury that were outside the calculated control limit of 0.080 ng/L ($\bar{x}$+3σ). No CCBs exceeded 0.25 ng/L, which is the control limit that is used for MDN analysis at HAL (table 5 and figure 7).

For 2012, no ongoing CCBs for methyl mercury were above the upper control limit of 0.010 ng/L($\bar{x}$+3σ) (table 5 and figure 8).

Table 5 - Ongoing Calibration Blanks Summary Table

2012 Ongoing Calibration Blanks	n	Average (ng/L)	Stdev (ng/L)	MDL (ng/L)	Upper control Limit +3σ (ng/L)	EPA 1631E/1630 Control Limits
Total Mercury	1611	0.0004	0.027	0.074	0.080	Individually <0.50 ng/L, mean <0.25 ng/L with a standard deviation <0.10 ng/L
Methyl Mercury	141	0.001	0.003	0.019	0.010	NA

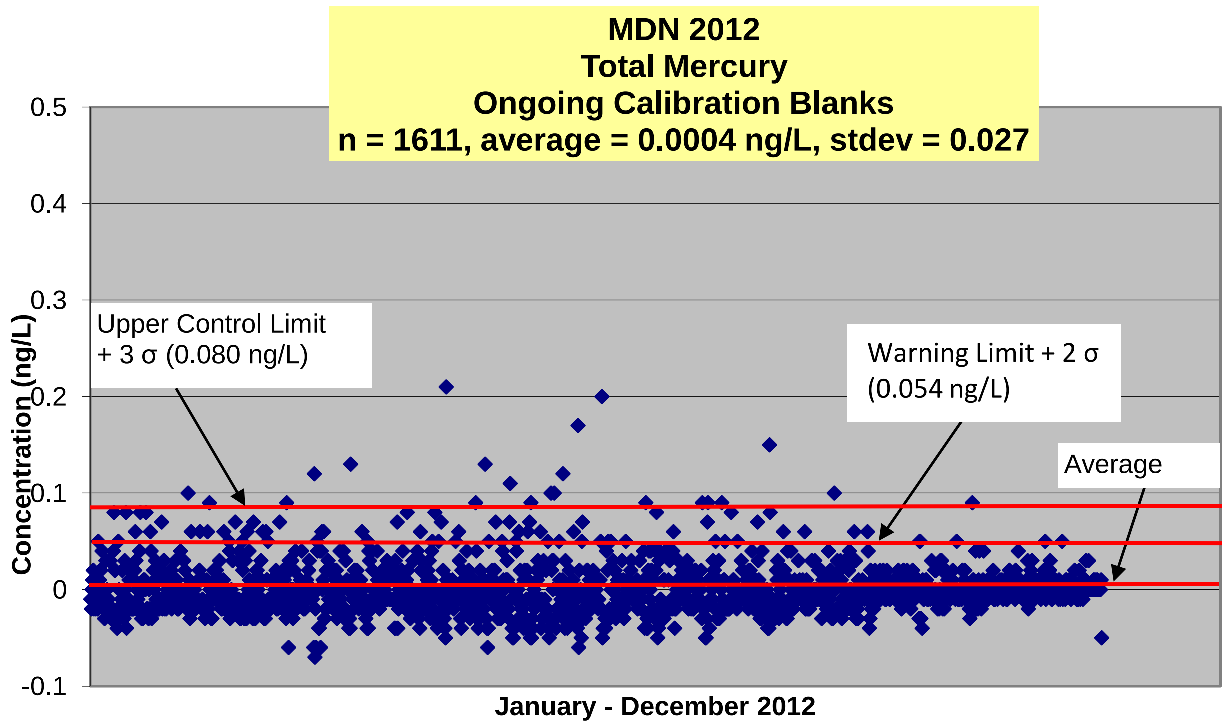

Figure 7 - 2012 Control Chart for Total Mercury Continuing Calibration Blanks

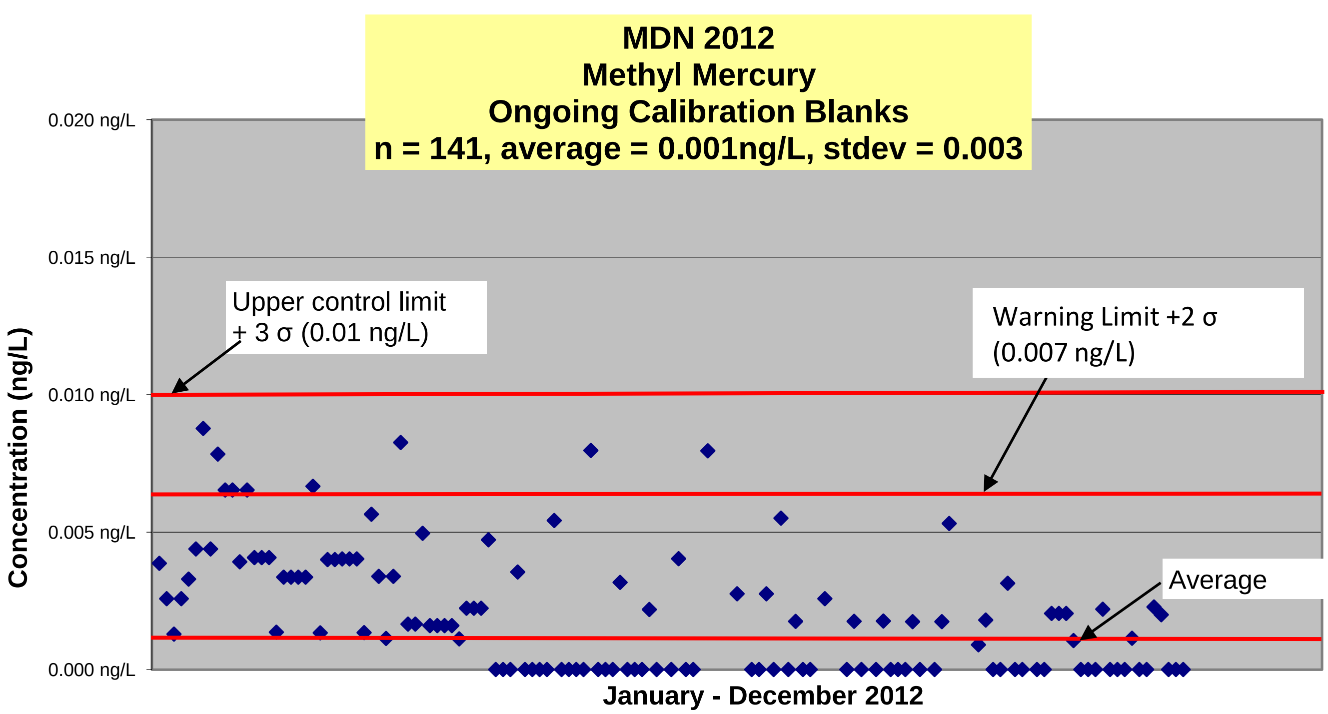

Figure 8 - 2012 Control Chart for Methyl Mercury Continuing Calibration Blanks

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 2012, the calculated control limit for total mercury based on $\bar{x}+3\sigma$ was 12.9% RPD (table 6). No duplicate samples were above the upper control limit of 25% RPD used at HAL (figure 9).

For methyl mercury, the calculated control limit of $\bar{x}+3\sigma$ was 49.6% RPD and no duplicate pairs for methyl mercury were above the control limit (table 6 and figure 10). 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.) 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 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 2012

2012 Matrix Duplicates	n	Average RPD (%)	Stdev (%)	Upper control Limit +3σ (%)	EPA 1631E/1630 Control Limits
Total Mercury	645	3.14	3.2	12.7	NA
Methyl Mercury	26	14.8	11.6	49.6	NA

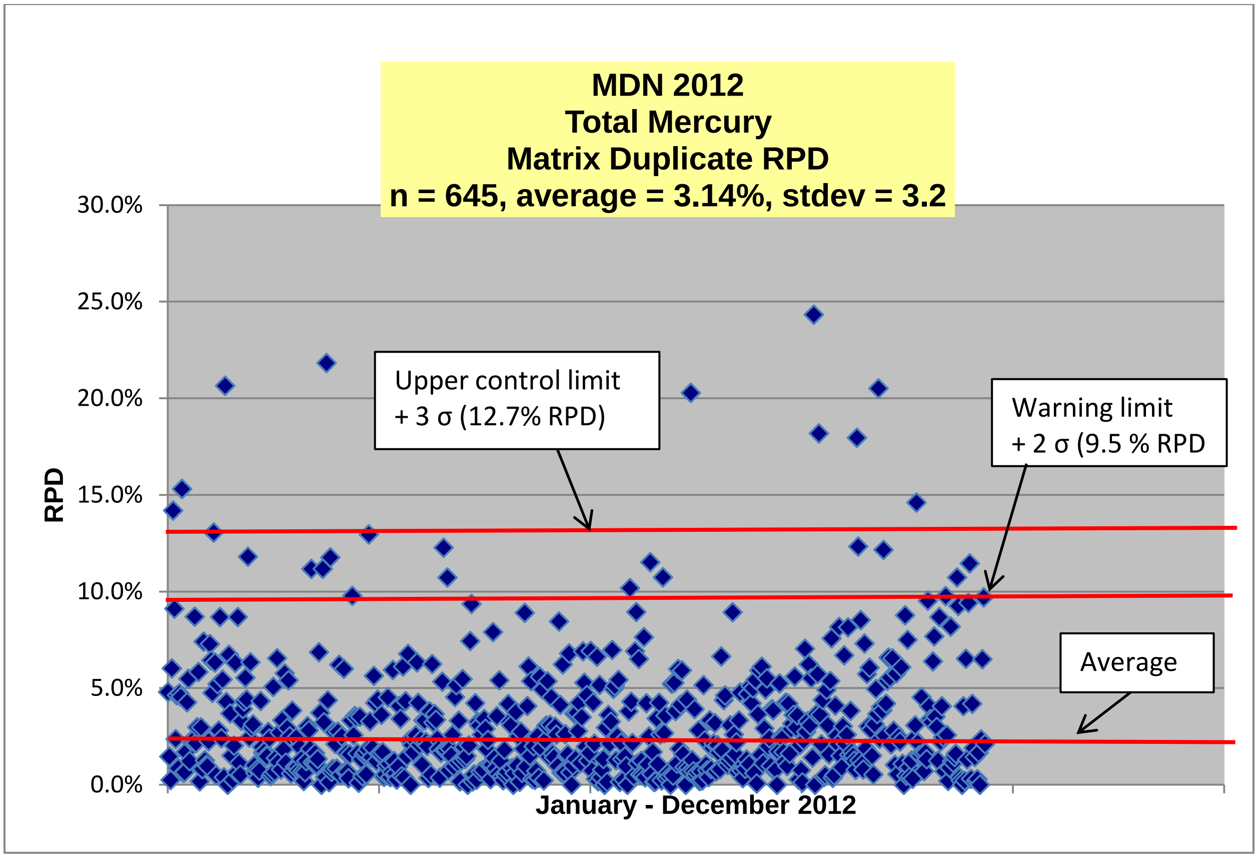

Figure 9 - 2012 Control Chart of the Relative Percent Differences for Total Mercury Concentrations in Matrix Duplicates

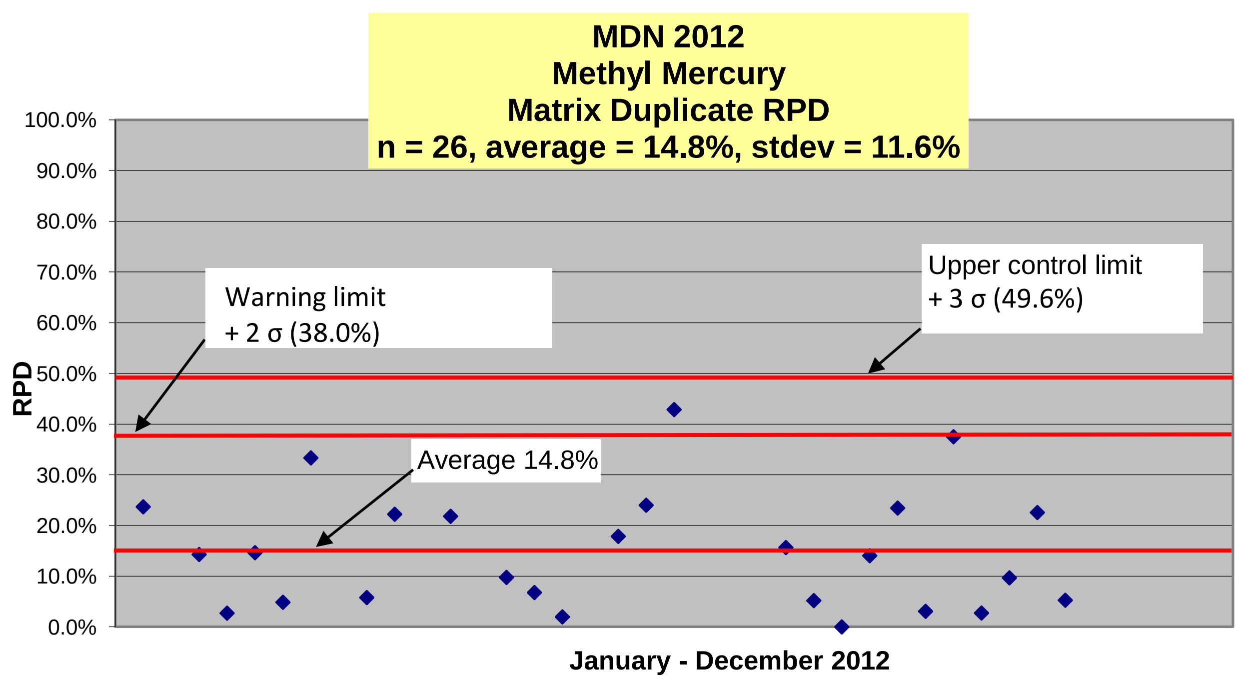

Figure 10 - 2012 Control Chart of the Relative Percent Differences for Methyl Mercury Concentrations in Matrix Duplicates

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 desired for the source sample, the matrix duplicate and the matrix spike, and for potential reanalysis of these QC samples. No RPD data for MS/MSD is available for total mercury since only a MS is analyzed. A MS/MSD is performed for methyl mercury and the control limit for the RPD is $\pm$25%.

2.5.2 Purpose

The purpose of analyzing a MS and MSD is to demonstrate the performance of the analytical method in a particular sample matrix, and to account for matrix interference. To prepare a MS/MSD, predetermined quantities of the analyte are added to a sample matrix before (when possible) extraction or digestion of samples, in this case preservation with BrCl for total mercury and preservation with HCl and distillation for methyl mercury analysis. If the sample is spiked with the analyte of interest after extraction or digestion, this is considered an analytical spike and an analytical spike duplicate (AS/ASD). If low recovery of a matrix spike 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 $\bar{x} \pm 3\sigma$ is 88.6%-108.2% (table 7). For 2012, six values were greater than 108.2%. There were several values less than 88.6%. All values are within the 75-125% control limit used at HAL(figure 11).

For methyl mercury, a control limit 78.4%-124.6% was calculated based on $\bar{x} \pm 3\sigma$ for the recovery of the matrix spike and the matrix spike duplicate (table 7). During 2012, no MS % recovery was greater than the calculated control level124.8%. No values were below the calculated laboratory control level of 78.2% recovery (figure 12).

The relative percent difference (RPD) of the methyl mercury matrix spike/matrix spike duplicates had a calculated control limit of 21.7% ($\bar{x} + 3\sigma$) for 2012. No RPD exceeded 25% (figure 13).

Table 7 - Matrix Spike Recoveries for 2012 Samples

2012 Matrix Spikes	n	Average Recovery (%)	Stdev of Recovery (%)	Control Limits ±3σ (%)	HAL Control Limits	EPA 1631E/1630 Control Limits (%)
Total Mercury	645	98.4	4.32	88.6–108.2	75-125	71-125
Methyl Mercury	90	101.5	7.7	78.4-124.6	65-135	65-135

Table 8 - Matrix Spike/Matrix Spike RPD for 2012 Samples

2012 Matrix Spikes	n	Average RPD (%)	Stdev (%)	+3σ (%)	EPA 1630 Control limits RPD (%)
Methyl Mercury	45	5.8	5.3	21.7	<35%

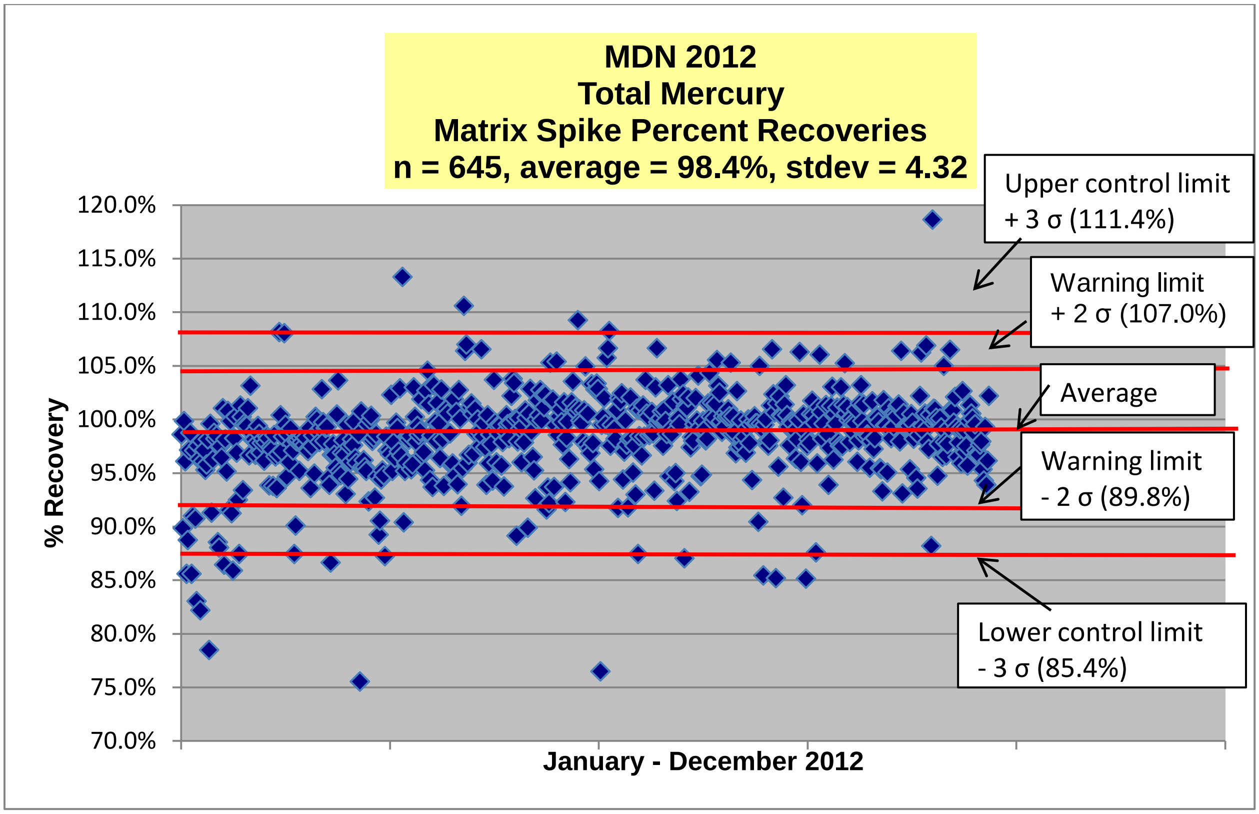

Figure 11 - Control Chart for Total Mercury Percent Recovery in Matrix Spikes During 2012

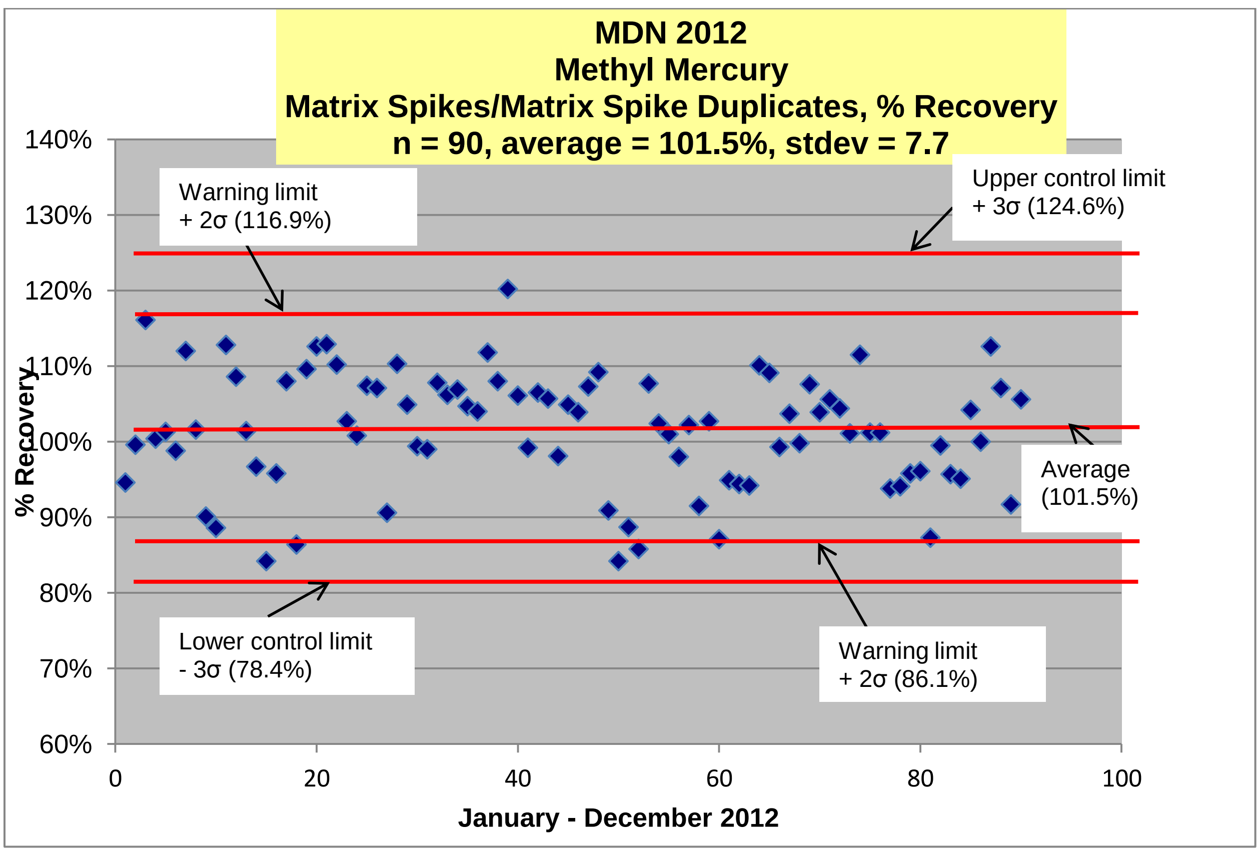

Figure 12 - Control Chart for Methyl Mercury Percent Recovery in Matrix Spikes During 2012

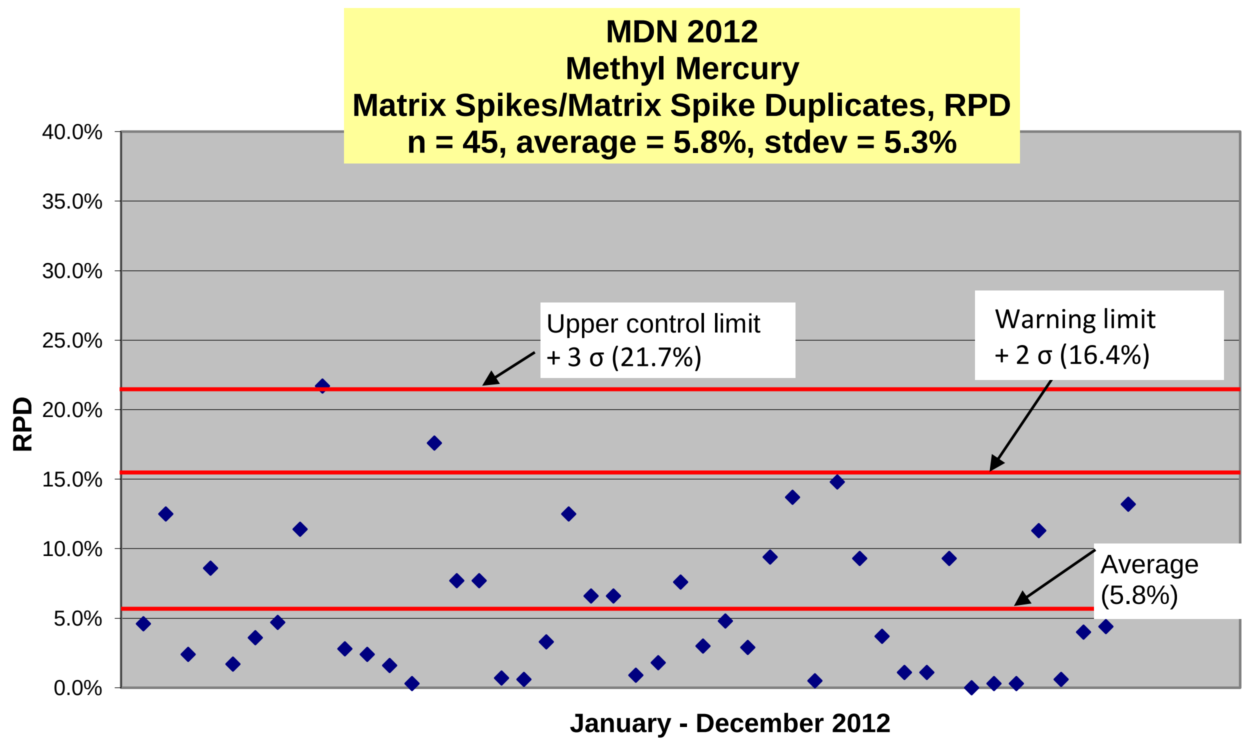

Figure 13 - Control Chart of the Relative Percent Differences for Methyl Mercury Matrix Spike/Matrix Spike Duplicate Pairs during 2012.

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 2012, the mean of 433 certified reference material recoveries for total mercury was 95.4% with a standard deviation of 2.5% (figure 14). There were two certified reference material recovery above the upper control limit of 102.9% ($\bar{x}$+3σ) and two below the lower control limit of 87.9% ($\bar{x}$-3σ). All CRM values were within the actual control limit of 75-125% used in the laboratory. The average RPD value for the CRM/CRM duplicate was 2.9% (n=217), with a standard deviation of 2.4%. One RPD values was above the upper control limit calculated by $\bar{x}$ ±3σ of 10.1%. All the RPD values were below the 25% used in the laboratory and shows high precision between the samples (figure 15).

In 2012, the mean recovery of 68 blank spikes and blank spike duplicates (BS/BSD) for methyl mercury was 102.4% with a standard deviation of 8.7% (figure 16). There was one blank spike with recovery above the upper control limit of 128.4% based on $\bar{x}$±3σ and one blank spike was below the lower control limit of 76.3% ($\bar{x}$-3σ). The average RPD value for the BS/BSD was 8.5% (n=34) with a standard deviation of 6.0%. All the RPD values were below the 25% used in the laboratory and shows high precision between the samples (figure 17).

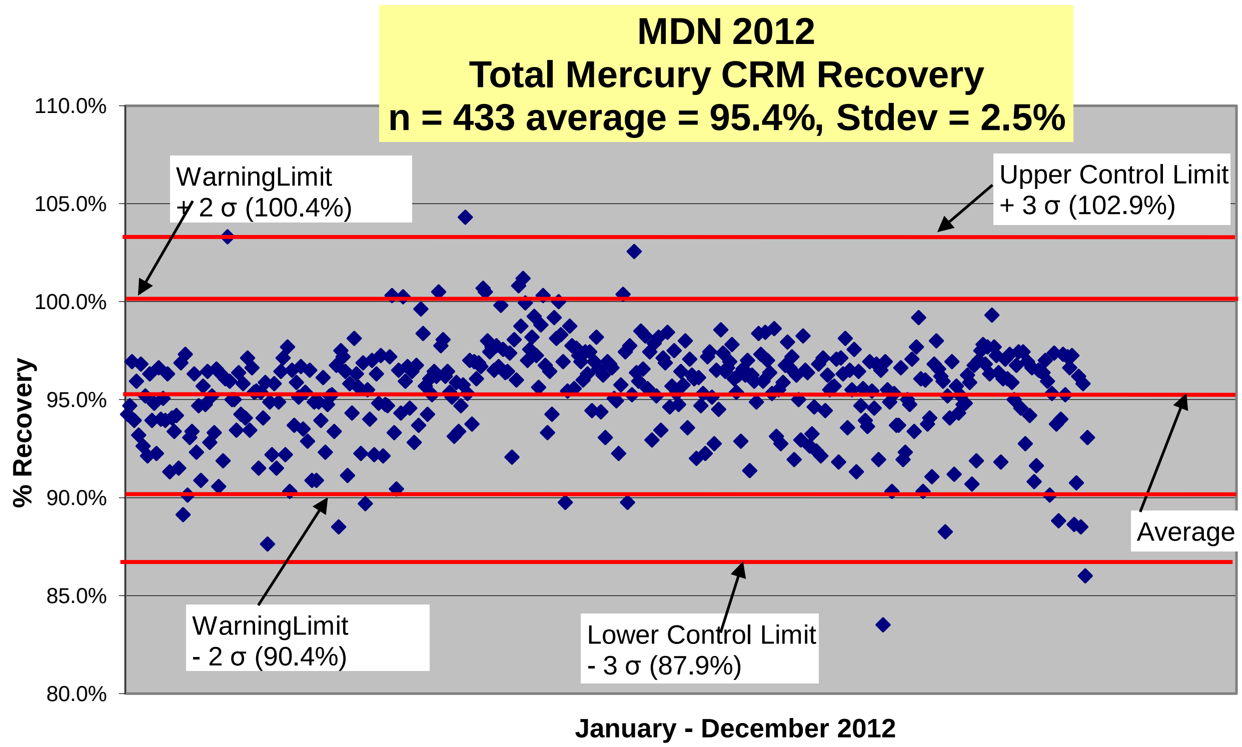

Figure 14 - Control Chart for Total Mercury Percent Recovery in Certified Reference Material Samples During 2012

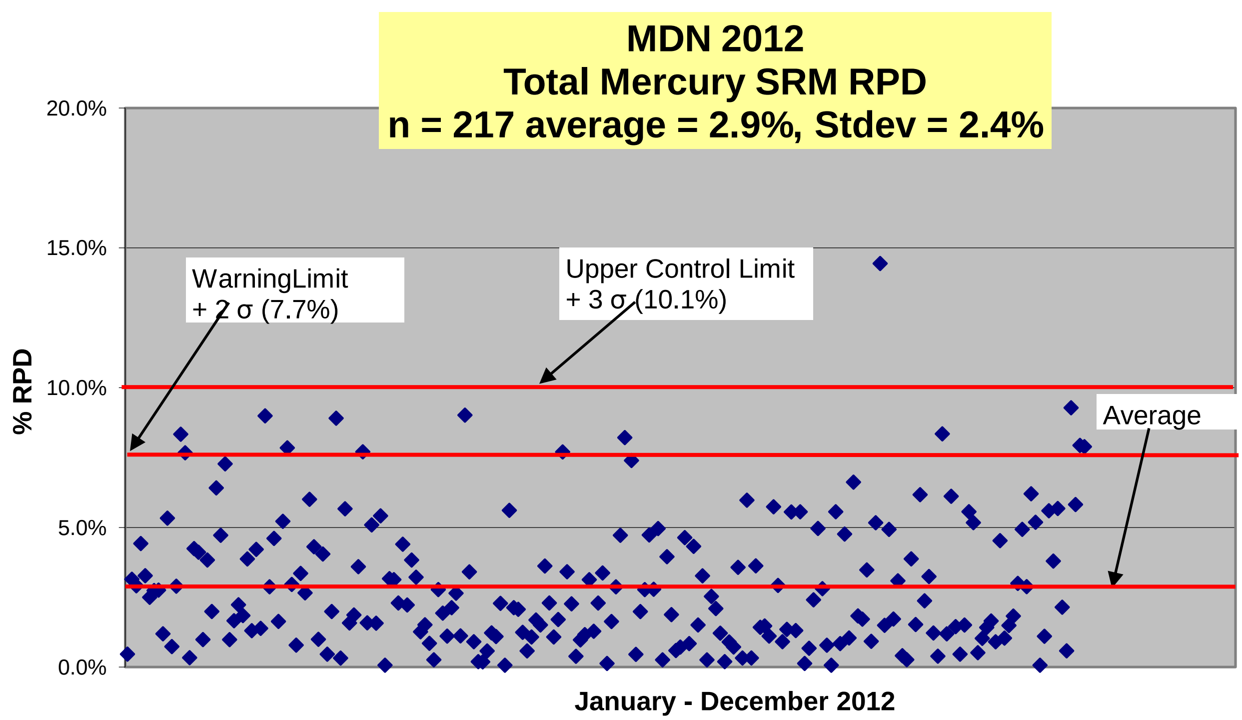

Figure 15 - Control Chart for Total Mercury Relative Percent Difference (%RPD) in CRM /CRM Duplicates Samples During 2012

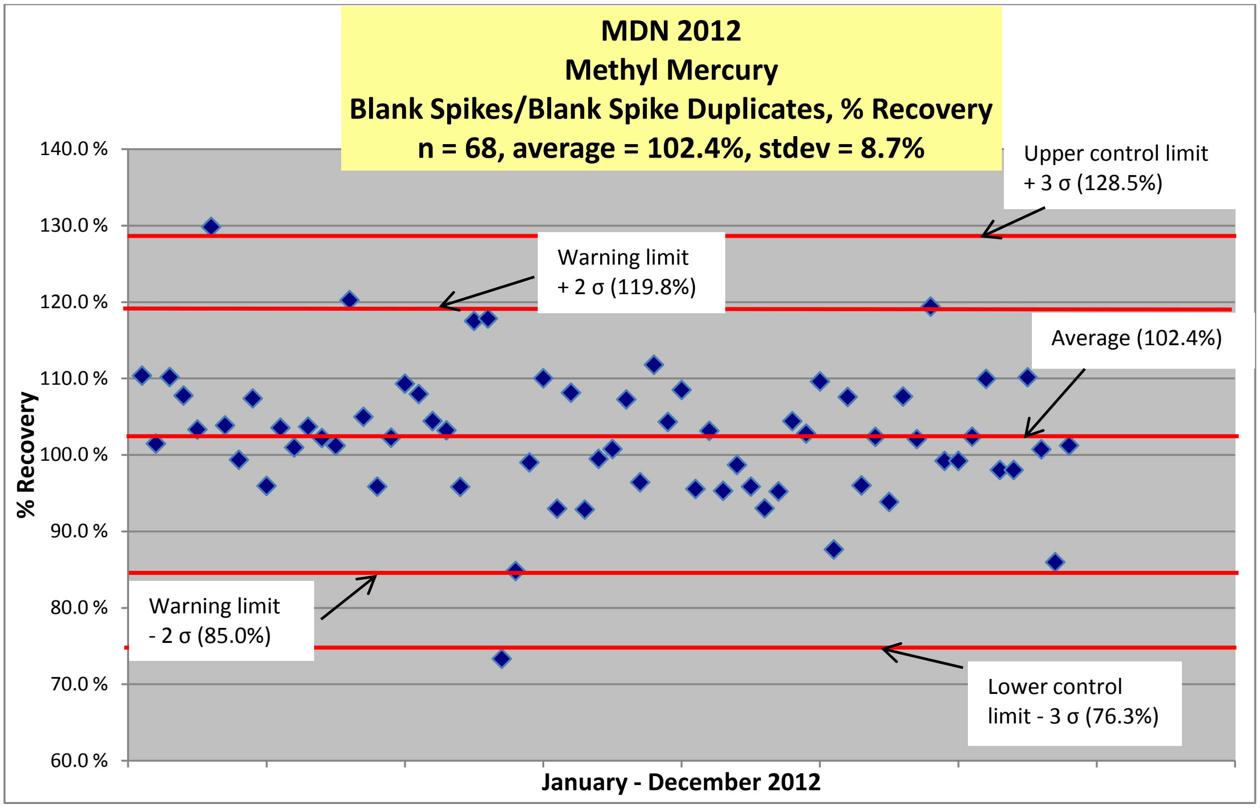

Figure16 - Control Chart for Methyl Mercury Percent Recovery in Blank Spikes/Blank Spikes Duplicates Samples During 2012

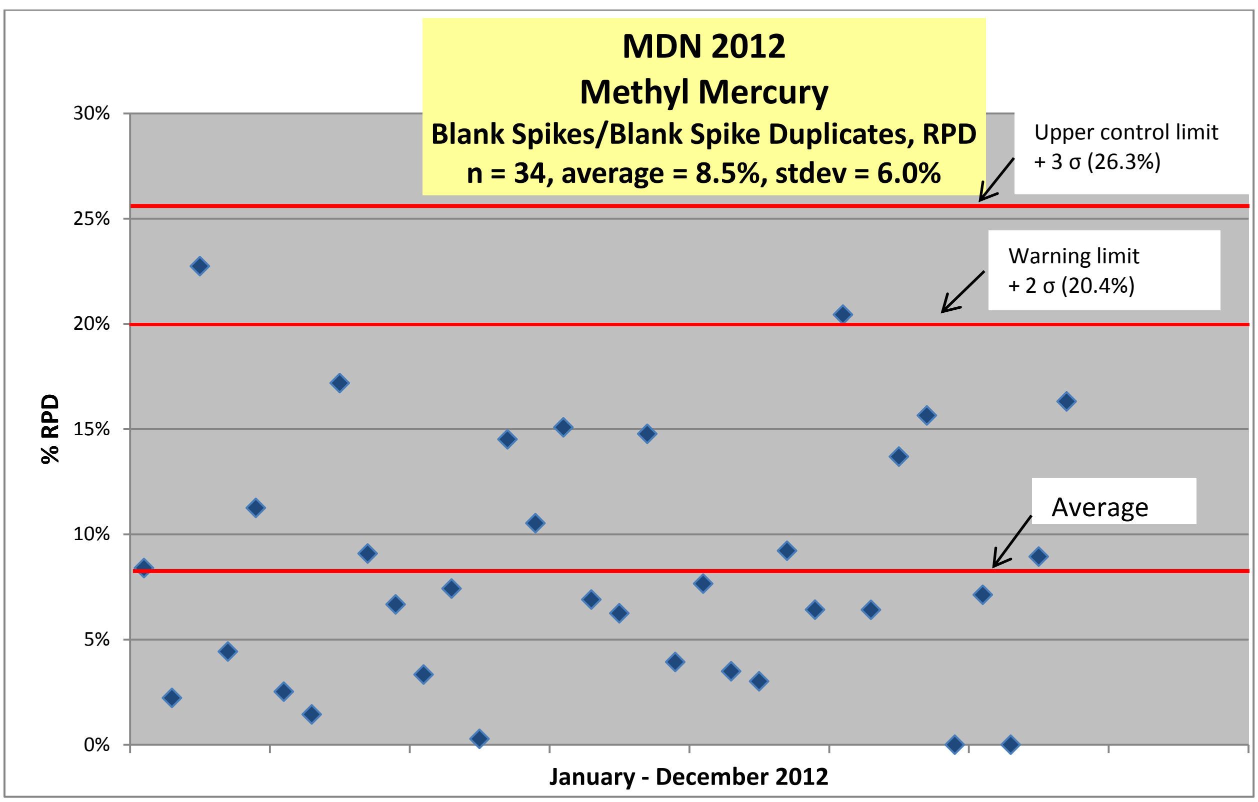

Figure 17 - Control Chart for Methyl Mercury Relative Percent Difference (%RPD) in Blank Spikes/Blank Spikes Duplicates Samples During 2012

3. 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:
Analysis Date: MDN LAB DATA SET CODE:
Analyzer: REVIEWER: DATE:
Analyst:

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

Eurofins 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 in table 9 were completed by EFGS during 2012, in addition to the monthly USGS samples that are not included in the table. Results for any tests are available upon request. Control charts for the USGS samples may be viewed at http://bqs.usgs.gov.

Table 9 - Proficiency Tests

Proficiency Test	Organization	Open-close date
RR-10683	Phenova	10/31/2012 - 12/4/2012
Soil-79	Environmental Resource Associates	7/23/2012 - 9/6/2012
WP-210	Environmental Resource Associates	7/16/2012 - 8/30/2012
052112M (SOIL)	Environmental Resource Associates	5/21/2012 - 7/5/2012
SOIL-78	Environmental Resource Associates	4/23/2012 - 6/7/2012
032012B (WS)	Environmental Resource Associates	3/20/2012 - 5/4/2012
DMR-QA 32	Environmental Resource Associates	3/19/2012 - 7/6/2012)
SOIL-77	Environmental Resource Associates	1/23/2012 - 3/8/2012)
WP-204	Environmental Resource Associates	1/16/2012 - 3/1/2012)
RR-10683	Phenova	10/31/2012 - 12/4/2012

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 55 samples in 2012 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 shown in figure 19.

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 2012, the mean of 135 Field Bottle Blanks was 0.035 ng/bottle with a standard deviation of 0.024 ng/bottle. Figure 19 shows sample MN1820120918 with an elevated mercury value in the field blank of 0.253 ng. No sites showed consistent high field blanks.

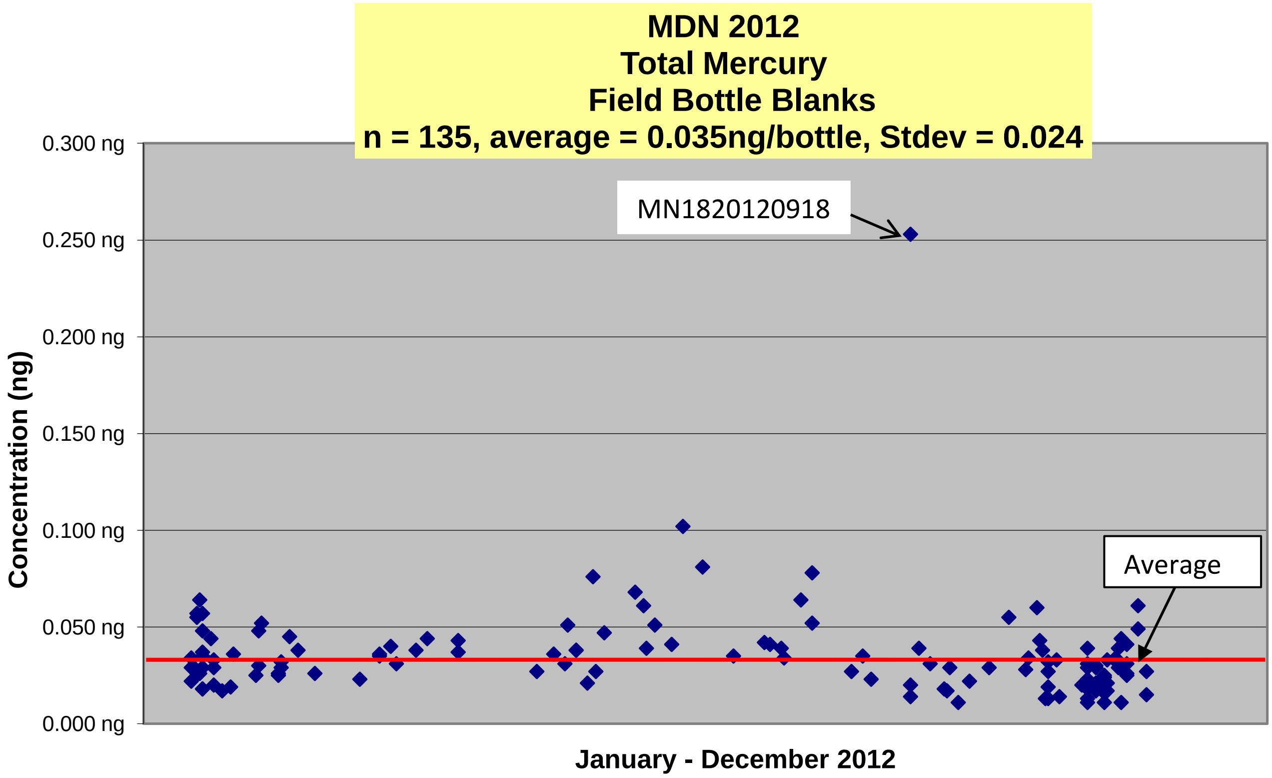

Figure 19 - Time Series Plot of Total Mercury Concentrations in Field Bottle Blanks During 2012

6.2 Field System Blanks

6.2.1 Description

A field system blank is essentially a field bottle blank in which a solution (DI-water) is poured through the wet side collection sample train that was installed in the field for an entire week with no precipitation. The system blank total mercury concentration is compared to the total mercury concentration of an aliquot of the same solution that was not poured through the sample train (i.e. control sample).

6.2.2 Purpose

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

6.2.3 Discussion

In 2012, the mean of 51 system blanks was 0.073 ng/aliquot with a standard deviation of 0.135 ng/aliquot compared to the control sample with a mean of 0.008 ng/aliquot and a standard deviation of 0.004 ng/aliquot. 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 2012, no locations had higher levels of mercury in their control sample compared to the system blank. A system blank processed at VT99 (sample VT9920121120) had a mercury concentration of 0.819 ng/aliquot.

The lab noted dirt particles in the sample. One other field blank, sample ON0720120828 had a mercury concentration of 0.512 ng/aliquot. Figure 20 illustrates the system blank results for 2012.

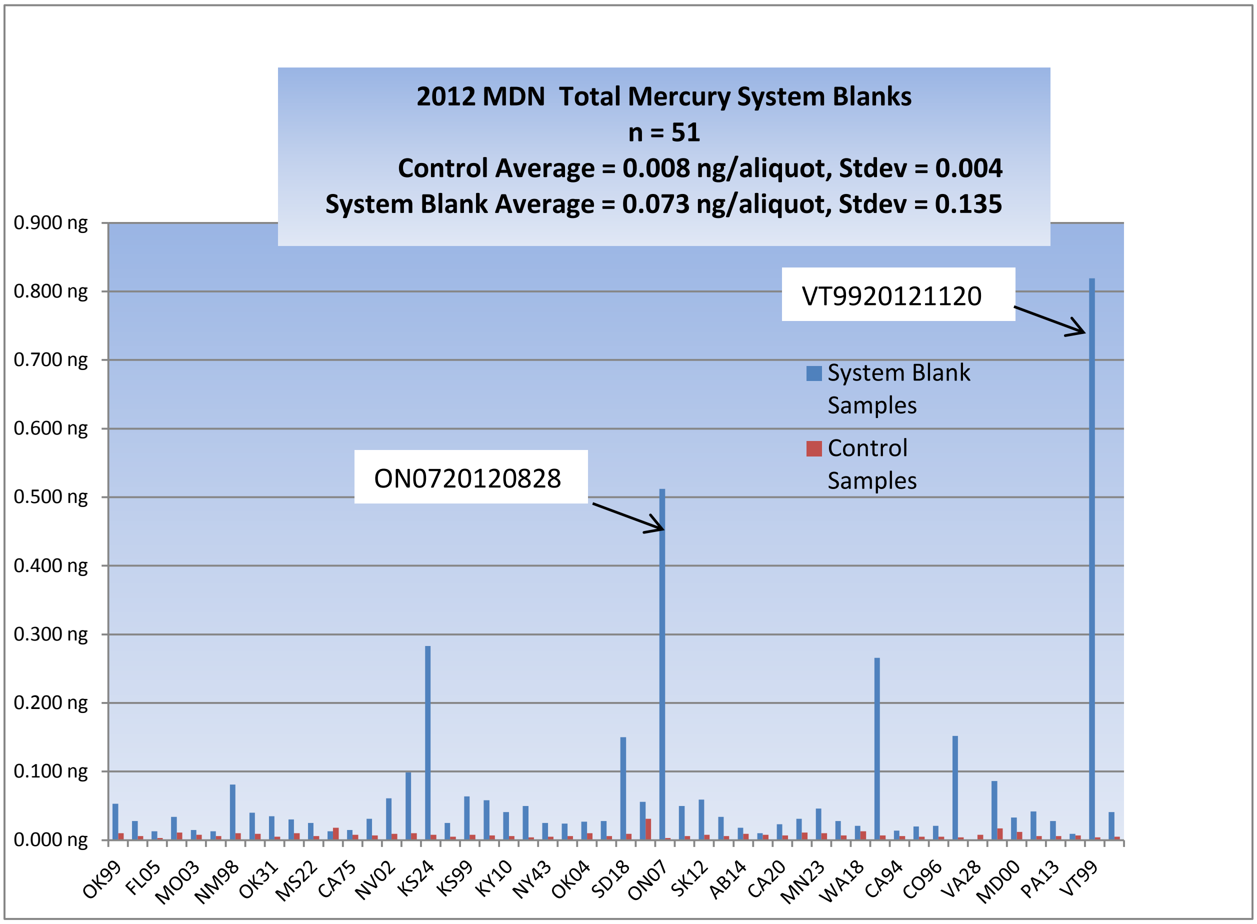

Figure 20 - Total Mercury Concentration Data for USGS System Blanks and Control Samples During 2012

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 6234 samples in 2012, which is comparable to the 6259 samples that were processed during 2011. There were 1,025 samples that received a QR code of "A" while 4,798 samples received a "B" QR code, and 409 samples received a "C" QR code. This distribution is illustrated in figure 21. HAL continued to maintain and demonstrate acceptable quality control in 2012. This comparison is based on HAL assessing the QR codes. These codes can later be changed by the NADP Program Office (PO).

Of the 409 "C" coded samples for 2012, 1 incident occurred at the laboratory.

1. Samples NY0620120925 was under preserved, due to misreading the empty weight.

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% and to 6.6% in 2012. This is illustrated in Figure 22. A comparison of "C"-coded sample error types is shown in Table 10.

The number of "B"-coded samples increased during 2012 to 77.0% compared to 61.7% during 2011. The number of "A"-coded samples decreased to 16.4 %, compared to 30.8% for 2011.

The trend of the increasing "B"-coded samples continued during 2012, the note codes for the "B"-coded samples were reviewed and is illustrated in figure 22. The total number of "d" note-coded samples (d=debris in sample) increased from 2,419 during 2011 to 3,769 during 2012. During 2011, samples with debris were noted by the laboratory 1,050 times compared to 1,664 times during 2012. The total number of "h" note-coded samples (h=sample handling problems) increased from 584 in 2011 to 1,626 in 2012, whereof samples that leaked increased from 438 to 938. The total number of "m" note-coded samples (m=missing information) decreased from 970 to 941. These results indicate that the increase of "B"-coded samples, is mainly due to increased number of samples with "debris" in them.

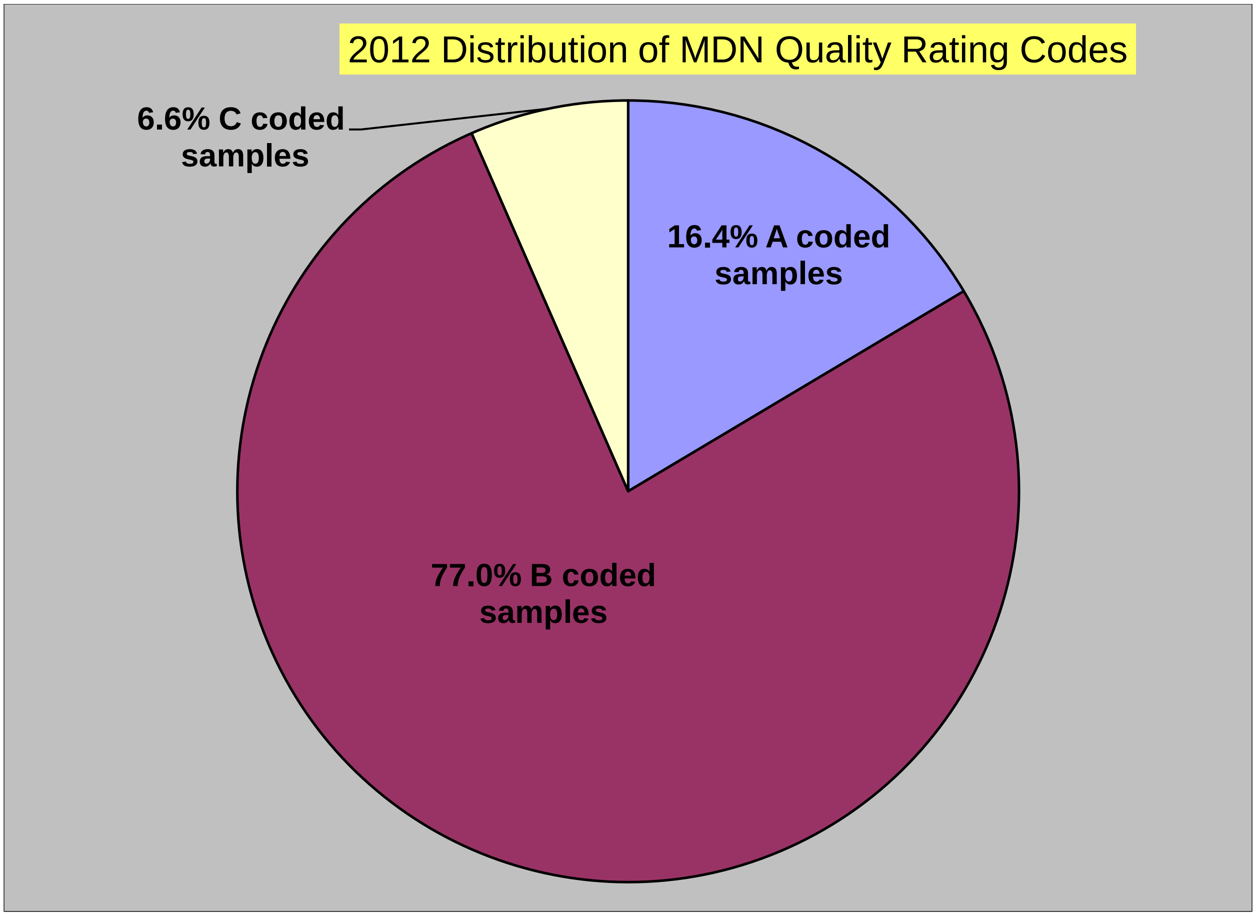

Figure 21 - Distribution of Quality Rating Codes for Samples Received in 2012

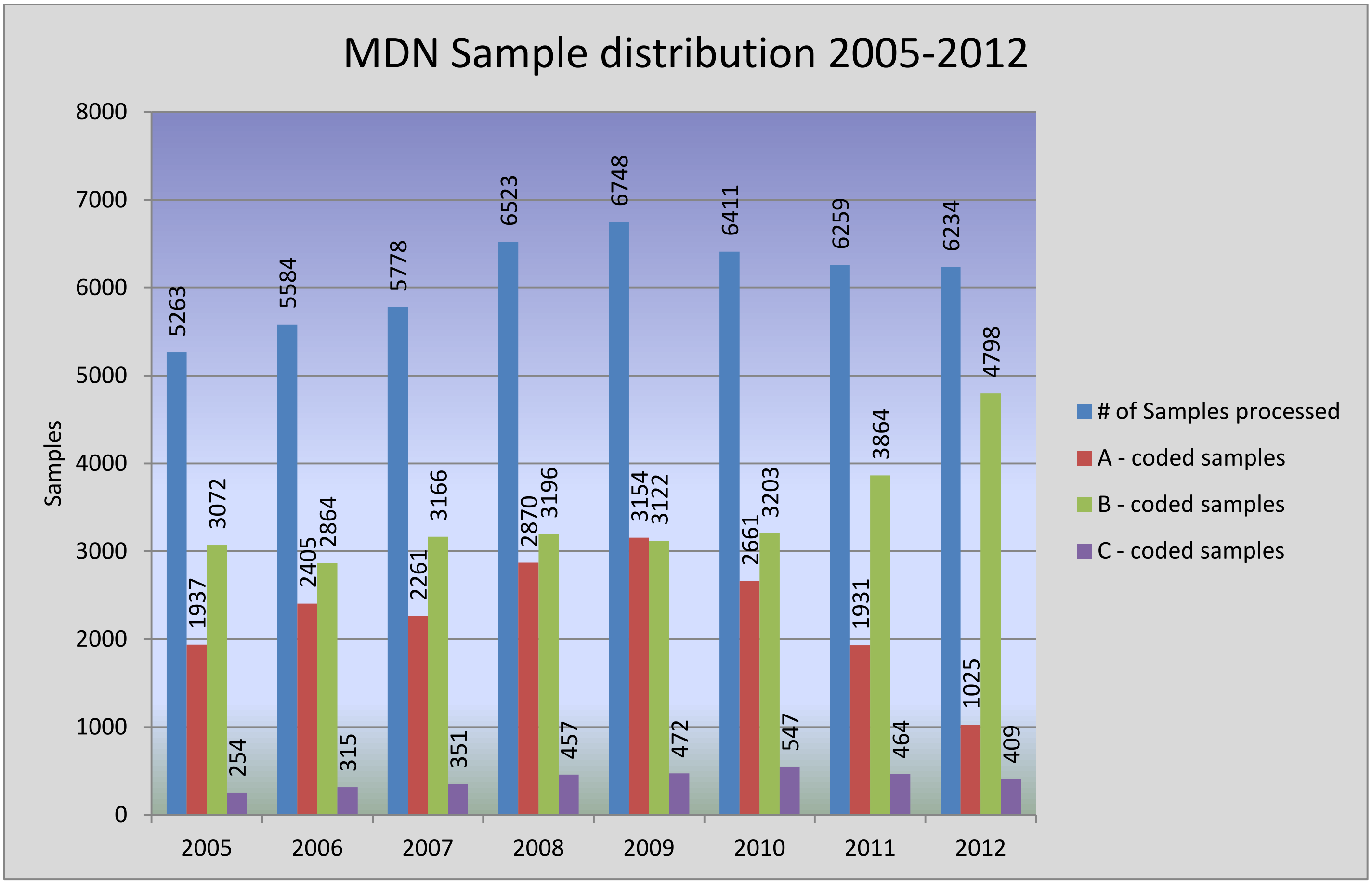

Figure 22 - Distribution of Quality Rating Codes for Samples Received from 2005 to 2012

Error Type	2009	2010	2011	2012
Bulk Sample	42	46	49	45
Undefined Sample	56	108	71	77
Site Environment	4	0	1	0
Sample Condition	111	128	119	68
Field Protocol	13	13	10	10
Lab Protocol	2	8	7	1
Contaminated	1	2	0	0
Volume Discrepancy	193	244	238	221
Total	422	549	464	409

Table 10 - C-Coded Samples by Error Type, 2009-2012

8. Summary and Conclusions

The HAL continued to maintain and demonstrate acceptable quality control in 2012. 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 0.015 ng Hg/bottle and 0.004 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 $\pm$25%. External proficiency testing by ERA, Absolute Standards, and USGS yielded acceptable results.

Field bottle blanks (n=135) and system blanks (n=51) indicated that field contamination levels continue to be low with two samples that had unusually high total Hg contamination, the maximum of which was 0.815 ng/sample.

The percentage of C-coded samples decreased from 7.4% (2011) to 6.6% during 2012 compared to a steady increase from 2005 to 2010. During 2012 the percentage of A coded samples decreased from 30.9% (2011) to 16.4% during 2012. The number of B coded samples has increased from 61.7% (2011) to 77.0% for 2012.

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 ≤ 24% Frequency of 1 MS/MSD per 10 samples. MS/MSD spiking level shall be 1-5 times the sample concentration.	65-135% recovery with RPD ≤ 35% Frequency of 1 MS/MSD per 10 samples. MS/MSD spiking level shall be 1-5 times the sample concentration.
Bubbler blanks	Individually <0.5ng/L, mean <0.25ng/L with a standard deviation <0.10ng/L. All bubbler blanks are analyzed before the calibration curve.	A single, or more, Ethylation Blanks are analyzed with each analytical run. The value is used to blank correct the standard curve.
ICB and CCB	No ICB, CCBs required.	No ICB, CCBs required.
Preparation Blanks	Minimum of 3, individually <0.50 ng/L.	Minimum of 3. Mean <0.045 ng/L Variability <0.015 ng/L

Table 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
EFGS	Eurofins Frontier Global Sciences
HAL	Mercury (Hg) Analytical Laboratory
IAEA	International Atomic Energy Agency
ICB	Initial Calibration Blank
ICV	Initial Calibration Verification
IDL	Instrument Detection Limit
ISO/IEC	International Organization for Standardization (ISO) / International Electrotechnical Commission (IEC)
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MD	Matrix Duplicate
MDL	Method Detection Limit
MDN	Mercury Deposition Network
MMHg	Methyl Mercury
MRL	Method Reporting Limit
MS/MSD	Matrix Spike/ Matrix Spike Duplicate
NADP	National Atmospheric Deposition Program
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System

NRCC	National Research Council Canada
PO	Program Office
PQL	Practical Quantitation Limit
PT	Proficiency Test
QA	Quality Assurance
QC	Quality Control
QR	Quality Rating
QCS	Quality Control Sample
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
TNI	The NELAC Institute
THg	Total Mercury (Hg)
TV	True Value
USGS	United States Geological Survey