National Atmospheric Deposition Program

Mercury Deposition Network

Mercury Analytical Laboratory 2004 Annual Quality Assurance Report

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Frontier GeoSciences Inc.

414 Pontius Ave. N. Seattle WA 98109 206.622.6960 www.frontiergeosciences.com In 2005, scientists, students, educators, and others interested in the National Atmospheric Deposition Program (NADP) logged more than 310,000 sessions and viewed nearly 93,000 maps on the NADP Web site. Users downloaded 18,564 data files from this site, which now annually receives more than 1.2 million hits. These data are used to address important questions about the impact of the wet deposition of nutrients on eutrophication in coastal estuarine environments; the relationship between wet deposition, the health of unmanaged forests, and the depletion of base cations from forest soils; the impact of pollutant emissions changes on precipitation chemistry; and the rate at which precipitation delivers mercury to remote lakes and streams.

The NADP was organized in 1977 under State Agricultural Experiment Station (SAES) leadership to address the problem of atmospheric deposition and its effects on agricultural crops, forests, rangelands, surface waters, and other natural and cultural resources. In 1978, sites in the NADP precipitation chemistry network first began collecting one-week, wet-only deposition samples analyzed by the Central Analytical Laboratory (CAL) at the Illinois State Water Survey. The network was established to provide data on amounts, temporal trends, and geographic distributions of the atmospheric deposition of acids, nutrients, and base cations by precipitation. The NADP initially was organized as SAES North Central Regional Project NC-141, which all four SAES regions endorsed as Interregional Project IR-7 in 1982. A decade later, IR-7 was reclassified as National Research Support Project NRSP-3, which it remains.

In October 1981, the federally supported National Acid Precipitation Assessment Program (NAPAP) was established to increase understanding of the causes and effects of acidic precipitation. This program sought to establish a long-term precipitation chemistry network of sampling sites distant from point source influences. Because of its experience in organizing and operating a national-scale network, the NADP agreed to coordinate operation of NAPAP's National Trends Network (NTN). To benefit from identical siting criteria and operating procedures and a shared analytical laboratory, NADP and NTN merged with the designation NADP/NTN. Many NADP/NTN sites were supported by the U.S. Geological Survey, NAPAP's lead federal agency for deposition monitoring. Under Title IX of the federal Clean Air Act Amendments of 1990, NAPAP continues. Today there are more than 250 sites in the network, and the network designation has been shortened to NTN.

In October 1992, the Atmospheric Integrated Research Monitoring Network (AIRMoN), currently with seven sites, joined the NADP. AIRMoN sites collect samples daily when precipitation occurs. Samples are refrigerated until analysis at the CAL for the same constituents measured in NTN samples. The AIRMoN seeks to investigate pollutant source/receptor relationships and the effect of emissions changes on precipitation chemistry, combining measurements with atmospheric models. The AIRMoN also evaluates sample collection and preservation methods.

In January 1996, the Mercury Deposition Network (MDN), currently with more than 90 sites, joined the NADP. MDN sites collect wet-only deposition samples that are sent to the MDN analytical laboratory at Frontier Geosciences, Inc. The MDN was formed to provide data on the wet deposition of mercury to surface waters, forested watersheds, and other receptors. Forty-five states and eight Canadian provinces have advisories against consuming fish from lakes with high mercury concentrations in fish tissues. MDN data enable researchers to investigate the link between mercury in precipitation and this problem.

The NADP receives support from the U.S. Geological Survey; Environmental Protection Agency; National Park Service; National Oceanic and Atmospheric Administration; U.S. Department of Agriculture - Forest Service; U.S. Fish & Wildlife Service; Tennessee Valley Authority; Bureau of Land Management; and U.S. Department of Agriculture - Cooperative State Research, Education, and Extension Service under agreement 2002-39138-11964. Additional support is provided by other federal, state, local, and tribal agencies, State Agricultural Experiment Stations, universities, and nongovernmental organizations. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the U.S. Department of Agriculture or any other sponsor.

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Definitions of Acronyms and Abbreviations

etinitio	ns of Acronyms and Appreviation
CAL	Central Analytical Lab
CCB	•
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
MD	Matrix Duplicate
MDL	Method Detection Limit
MDN	
MOF	
MS	
MSD	
NADP	
NED	and the second s
PB	
PE	
PT	Proficiency Test
QA/QC	
QAP	
QR	
RL	
RPD	Relative Percent Difference

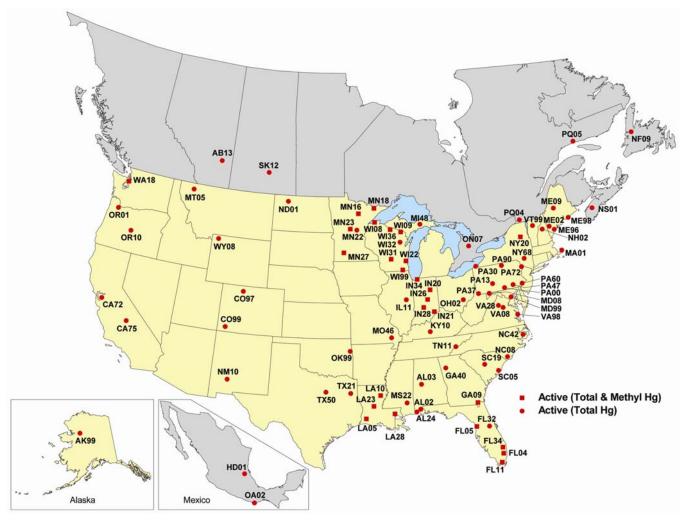
SOP Standard Operating Procedure SRM Standard Reference Material

1. Introduction

Since January 1996, Frontier GeoSciences 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 over 87 sites in the United States, Canada, and Mexico. In 2005, MDN is expected to incorporate 10-15 additional new sites.

As HAL, FGS receives weekly precipitation samples to be analyzed for total mercury. HAL also analyzes samples for methylmercury from selected sites participating in the methylmercury program. The analytical technique — 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.

Robert Brunette, Principle Investigator and HAL Director, oversees FGS's involvement in MDN. He serves as the HAL contact for the multiple agencies currently sponsoring MDN. His multiple roles require him to provide guidance and direction to all HAL staff and to maintain his proficiency in all aspects of HAL activities, including MDN site selection and equipment installation, MDN equipment troubleshooting, field and laboratory training, analysis and report writing, as well as research on new MDN initiatives including Trace Metals (in addition to mercury) in Wet Deposition.



Mr. Brunette is assisted by Gerard Van der Jagt - the MDN Group Leader, and an analytical laboratory staff skilled in processing incoming samples, analyzing sample sets, cleaning glassware, shipping weekly field equipment, and entering data. Senior Research Scientist, Eric M. Prestbo, serves as a Science Advisor for HAL, and helps support MDN related research initiatives. The Project Investigator also works closely with FGS' Laboratory Manager, Eric Wyse and FGS' Quality Assurance Program Director, Carl Hensman Ph.D., to ensure that all Quality Control (QC) parameters are consistently maintained, and that FGS' standards of professional and scientific quality are met.

FGS continued to maintain and demonstrate acceptable quality control in 2004. Due to the addition of new MDN sites, the number of quality control points increased from 1,214 in 2003, to more than 1,500 quality control measurements in 2004. FGS demonstrated consistency and reproducibility in bottle blanks, preparation blanks, certified reference materials, matrix duplicates, and matrix spikes. All of these parameters are plotted control charts in this report.

Outlook

The MDN continues to gain attention as the largest and longest-running national mercury wet deposition network in North America. Feedback from sponsors and other interested organizations indicates that MDN will experience significant growth in 2005-2006. With this growth, HAL will continue to look for ways to improve the program to ensure the highest quality. The following are goals HAL has set to maintain and improve quality throughout 2005-2006:

- HAL will continue to improve our database in 2005.
- HAL and the NADP Program Office incorporated dual data entry verification to all database operations.
- HAL will continue trace metals in wet deposition research in 2005. There is a strong indication that
 there are many sponsors that will want to participate in a combined mercury and trace metals
 program. In 2004, five MDN sites were collecting samples for trace metals following HAL's retrofit and
 trace metal standard operating procedures.
- HAL research in dry deposition of mercury and trace metals in sites in the southern U.S. will continue, likely through 2005. HAL expects this research to lay the groundwork for a potential non-NADP product for interested MDN sponsors.

2. Quality Assurance

2.1. Philosophy and Objectives

Frontier GeoSciences Inc. (FGS) is committed to a rigorous quality assurance program and philosophy. Quality control begins at the bench level. Process improvements are solicited from laboratory technicians and analysts. Management implements the improvements. The Quality Assurance program is a system for ensuring that all information, data, and interpretation 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 experimental 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 a measure of how variable one set of data is 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. HAL DQO for MDN project is at least 95% completeness.

2.2. Method Detection Limits

Method detection limit (MDL) studies are maintained for most matrix/analyte combinations available at FGS. Studies are performed using the protocols in 40 CFR, Section 136, Appendix A. Specifically; seven or more low-level, matrix-specific spikes are processed according to preparation and analytical method protocols. MDL is determined as t*SD of the replicates (where t is the Student's T-value for the number of replicates and SD is the standard deviation). The HAL updates MDL studies periodically for the MDN project. See Appendix A for the latest MDL study results.

2.3. Accreditations

FGS currently holds certifications through departments in eight states: the California Department of Health, the Florida Department of Health, the Louisiana Department of Environmental Quality, the Minnesota Department of Health, the New Jersey Department of Environmental Protection, the New York Department of Health, the Washington Department of Ecology, and the Wisconsin Department of Natural Resources. The Florida Department of Health acts as FGS' primary accreditor under the National Environmental Laboratory Accreditation Program (NELAP).

3. Quality Control

Quality Control (QC) samples each have an expected target value that can be used to objectively assess preparation and analytical method performance. If performance on these known samples is acceptable, client sample results and other *unknowns* are assumed to be acceptable, as well. Conversely, 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: laboratory bottle blanks, preparation blanks, ongoing calibration standards, ongoing calibration blanks, matrix duplicates, matrix spikes, certified reference materials, field blanks, and system blanks.

3.1. Laboratory Bottle Blanks

3.1.1. Description

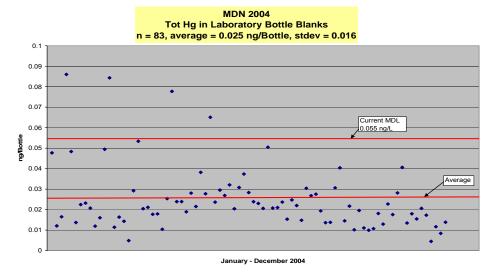
Following cleaning, HAL bottles are charged with 20mL of 1% hydrochloric acid. A random selection of these bottles is then analyzed for total mercury.

3.1.2. 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.

3.1.3. Discussion

In 2004, the mean of 83 laboratory bottle blanks was 0.025ng/bottle with a standard deviation of 0.016ng/bottle. In 2004, four laboratory bottle blanks were higher than MDL. Laboratory bottle 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.



3.2. Preparation Blanks

3.2.1. Description

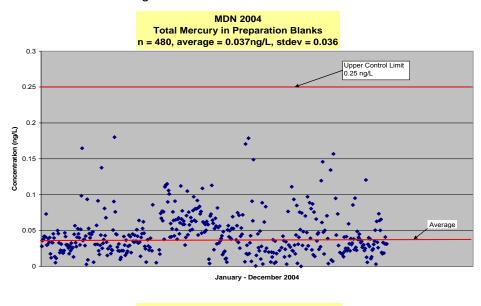
Preparation blanks for total mercury consist of 1% (v/v) 0.2N bromine monochloride, 0.2mL 20% hydroxylamine hydrochloride, and 0.3mL 20% stannous chloride in 100mL of reagent water. Preparation blanks for methylmercury consist of hydrochloric acid, APDC solution, ethylating agent, acetate buffer, and reagent water.

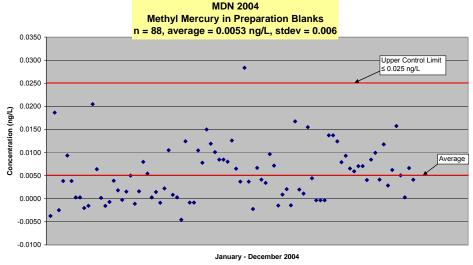
3.2.2. Purpose:

Mercury content is inherent even in FGS' preparatory and analytical reagents. 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.

3.2.3. Discussion

In 2004, the mean for total mercury of 480 preparation blanks was 0.037ng/L with a standard deviation of 0.036ng/L. In 2004, no preparation blanks for total mercury were above the control limit of 0.25ng/L. In 2004, the mean for methylmercury of 87 preparation blanks was 0.0053ng/L with a standard deviation of 0.006ng/L. In 2004, one preparation blank for methylmercury was above the control limit of 0.025ng/L.





3.3. Ongoing Calibration Standards

3.3.1. Description

Ongoing calibration standards are continuously analyzed during the course of sample analysis, typically after a suite of ten samples and at the end of each analytical day. A 1.0ng standard for

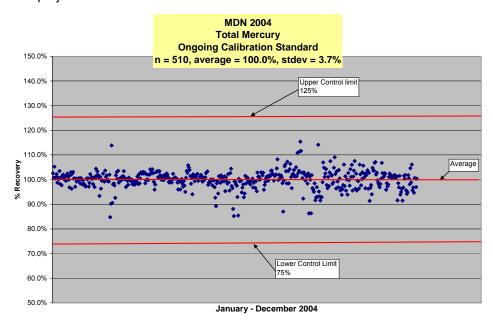
total mercury and a 0.1ng standard for methylmercury are typically analyzed as an ongoing calibration standard.

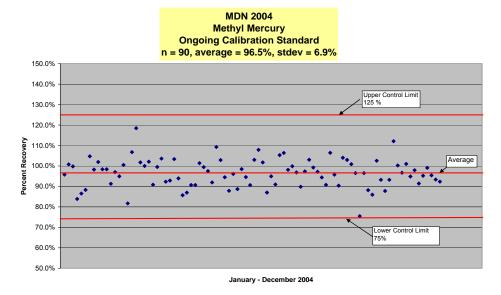
3.3.2. Purpose

Ongoing calibration standards verify that the analytical system is in control. All total mercury standard solutions are traceable to certified standards or manufacturer lot number. Currently there is no commercial available methylmercury standard. All raw data references a unique laboratory ID number for associated standards. This ID may then be traced through the standards logbooks to the original shipment, container, and certification.

3.3.3. Discussion

In 2004, the mean of 510 ongoing calibration standard recoveries for total mercury was 100.0% with a standard deviation of 3.7%. In 2004, no ongoing calibration standards were out statistical control. In 2004, the mean of 90 ongoing calibration standard recoveries for methylmercury was 96.5% with a standard deviation of 6.9 %. There were no ongoing calibration standard recoveries for the MDN project in 2004 that were out of statistical control.





3.4. Ongoing Calibration Blanks

3.4.1. Description

Ongoing calibration blanks are continuously analyzed during the course of sample analysis, typically after a suite of ten samples and at the end of each analytical day.

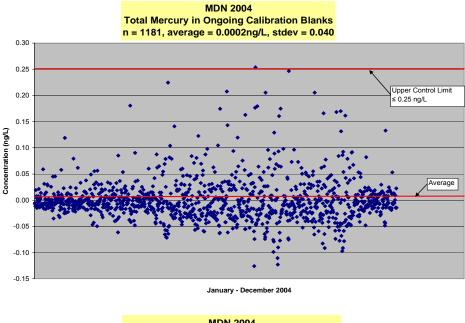
3.4.2. Purpose

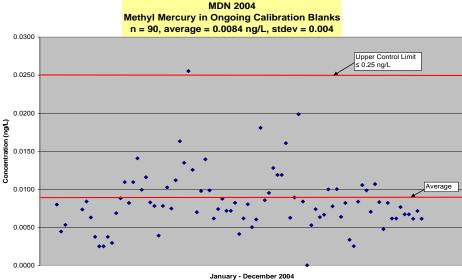
Instrument blanks are used to demonstrate freedom from system contamination, carryover, and to monitor baseline drift.

3.4.3. Discussion

In 2004, the mean concentration of 1181 ongoing calibration blanks for total mercury was 0.0002ng/L with a standard deviation of 0.040. There was one ongoing calibration blank for the MDN project in 2004 that was above the upper control limit (0.25ng/L). In 2004, the mean concentration of 90 ongoing calibration blanks for methylmercury was 0.0084ng/L with a standard deviation of 0.004. There was one ongoing calibration blank for methylmercury that was above the upper control limit (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.





3.5. Matrix Duplicates

3.5.1. Description

Matrix duplicates are created when an existing sample is split into two portions that can then be compared analytically.

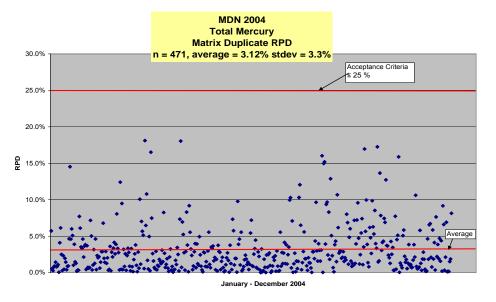
3.5.2. Purpose

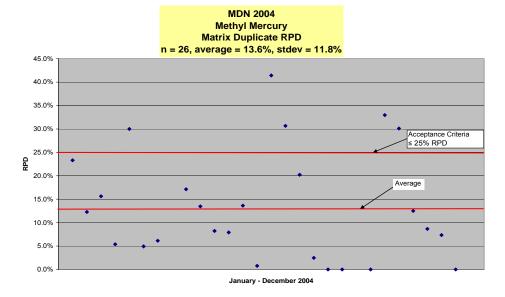
As there is no theoretical difference between a pair of matrix duplicates, their relative percent difference (RPD) is expected to be less than 25%. Out of control results are indicative of a heterogeneous sample matrix and/or poor analytical precision.

3.5.3. Discussion

In 2004, the mean RPD of 471 matrix duplicate pairs for total mercury was 3.12% with a standard deviation of 3.3%. This low mean reflects the homogeneous nature of the MDN sample matrix, as well as the analytical precision of HAL. In 2004, the mean RPD of 26 matrix duplicate pairs for

methylmercury was 13.6 % with a standard deviation of 11.8%. Several RPDs were above the 25% RPD acceptance level. However, all of these matrix duplicates concentrations were less than or equal to five times MDL. At such low concentrations, variability is expected to increase. Therefore, the larger RPD values at low concentrations are not of concern. No corrective action was taken.





3.6. Matrix Spikes

3.6.1. Description

A matrix spike is created when an MDN sample with known mercury content is supplemented with an additional 1.00ng of mercury standard.

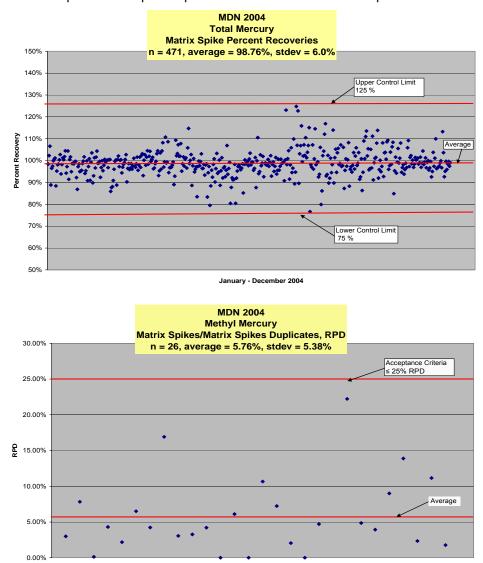
3.6.2. Purpose

As the combined mercury content of the matrix spike sample is known in theory, matrix spike recoveries are expected to be within 75% and 125% of this theoretical value. Matrix spike recoveries determine if, and how, the sample matrix interferes with target analyte recovery. They

also ensure that HAL's preparation and analytical procedures do not result in significant analyte losses.

3.6.3. Discussion

In 2004, the mean of 471 matrix spike recoveries for total mercury was 98.76% with a standard deviation of 6.0%. There were no unacceptable matrix spike recoveries for the MDN project in 2004. This is indicative of a chemically passive sample matrix, as well as good analytical accuracy. Had any Matrix Spikes fallen outside the 75%-125% control limits, involved samples would have been rerun to investigate possible matrix interference. In 2004, the mean RPD of 26 matrix spike/matrix spike duplicates for methyl mercury was 5.76% with a standard deviation of 5.38%. No matrix spike/matrix spike duplicate RPD was above the acceptance criteria.



3.7. Certified Reference Materials

3.7.1. Description

Certified reference materials are commercially available samples containing known quantities of analyte in a specific matrix. Currently, there is no available Reference Material matching the MDN rainwater matrix. Instead, HAL uses National Institute of Standards and Technology

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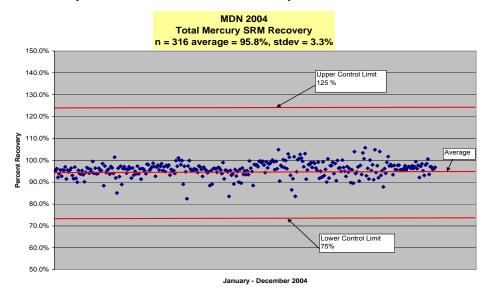
Reference Material 1641d – Total Mercury in Water. For methylmercury, HAL uses National Research Council Canada Reference Material DORM-2.

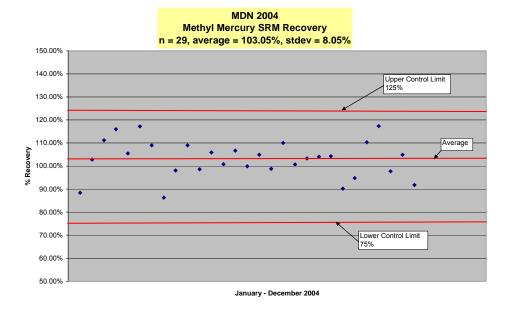
3.7.2. Purpose

Certified reference materials are used to demonstrate HAL's ability to recover a target analyte from a specific matrix. They are also a secondary source for verifying the validity of the analytical curve.

3.7.3. Discussion

In 2004, the mean of 316 certified reference material recoveries for total mercury was 95.8% with a standard deviation of 3.5%. For methylmercury, the mean of 29 certified reference material recoveries was 103.05% with a standard deviation of 8.05%. In 2004, there were no recoveries outside the control limits for total and methylmercury. Failing recoveries are immediately rerun to ensure that the analytical failure is isolated rather than systemic.





4. Calculations

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

4.1. Calculation: Gross MDN Sample Concentration

```
{(Sample PA - Ave BB) / Slope} - {(Aliquot * BrCl RB) / 100} = ng Hg/aliquot (mL)
```

Sample PA = sample peak area (PA units)
Ave BB = average bubbler blank (PA units)
Slope = slope (PA units/ng)
Aliquot = volume of sample analyzed (mL)
BrCl RB = BrCl reagent blank value (ng/mL of preservative)
1/100 = correction for 1% preservation concentration

4.2. 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

4.3. Calculation: MDN Deposition

```
(net ng Hg/L) * (precip vol (mL) / 120.0 \text{cm}^2) * (1/1000 \text{mL}) * (10000 \text{cm}^2/\text{m}^2) = (1/1000 \text{mL})
```

Alternatively, because there are 10000 cm² in 1m²:

```
(net ng Hg/L) * (precip vol (mL)_/ 120.0cm^2)*10 = (ng/m^2)
```

```
120.0cm<sup>2</sup> = Area of MDN Funnel
Precip volume (mL) = Precipitation Volume — see below
```

The standard rain gauge (Belfort) is used for the precipitation volume when the rain gauge data has passed Quality Assurance.

Precip volume (Rain Gauge (mL)) = Inches of Rain (rain gauge) * (825mL / Inch Belfort)

When the standard rain gauge (Belfort) has not passed Quality Assurance, we use the Bottle Catch to calculate deposition (as long as the Event Recorder shows that the collector worked properly).

Precip volume (Bottle Catch (mL)) = Total mL of sample captured in MDN Sample Bottle minus 20mL preservative

5. Analytical Run Sequence

HAL routinely includes the aforementioned 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 superceded with a matrix duplicate, a matrix spike, ongoing calibration standard, and an ongoing calibration blank. 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:										
	And	ılyzer:		REVIEWER:					DATE:	
Analytical Run D=Duplicate Analysis S=Sample Spike @ 1,00ng										
Run	Тр	Bub	HAL Code	Sample ID	PA	% BrCl	Aliquot Volume	THg per Aliquot	THg Conc (Net)	Remarks
1	1	1		4.00 ng						
3	2	2		2.00 ng 1.00 ng						
4	4	4		0.50 ng						
. 5	5	1		0.05 ng						
6	6	2		BB-1						
7	7	3 4		BB-2						
8 9	8	1		BB-3 NIST1641d		2				
10	10	2		BrCl-1						
11	10	3		BrCl-2		1		T,		
12	2	4		BrCl-3		1		-K	ey	
13	3	1		BB-4		1				
14	4	2		Sample #1				R	eference	materials
15	5	3		Sample #1 D						
16	6	4		Sample #1 S				D	roporatio	n blanks
17	7	1		Sample #2				F	ерагано	H DIAHKS
18	8	2		Sample #3						
19 20	9 10	3		Sample #4				I N	latrix du	plicates
21	10	1		Sample #5 Sample #6						
22	2	2		Sample #7				N	latrix spi	kec
23	3	3		Sample #8				14	iauin spi	AC3
24	4	4		Sample #9						
25 26	5	2		Sample #10 1,00		-		C	ngoing c	alibration
27	7	3		BB-5						
28	8	4		Sample #11					ngoing (alibration
29	9	3		Sample #12				O	ingoing C	unorunon
30 31	10 1	4		Sample #13 Sample #14						
32	2	2		Sample #14 Sample #15						
33	3	3		Sample #16						
34	4	4		Sample #17						
35	5	1		Sample #18						
<u>36</u> 37	6 7	3		Sample #19 Sample #20		1				
38	8	4		Sample #11 D						
39	9	3		Sample #11 S						
40	10	4		1.00		1				
41 42	2	2		BB-6 NIST1641d						
43	3	3		Sample #21						
44	4	4		Sample #22						
45	5	1		Sample #23						
46 47	6	2		etc		1				
48	8	4		1						
49	9	1								
50	10	2								
51	1	3								
52	2	4		Sample #21 N		1			 	
53 54	4	2		Sample #21 D Sample #21 S		+				
55	5	3		1,00						
56	6	4		BB-7						

6. Proficiency Tests and Laboratory Intercomparisons

Proficiency tests (PT) and laboratory intercomparisons are an important part of the Quality Assurance Program. Each year, FGS completes at least four PTs representing a suite of trace metals in wastewater and solid waste matrices. While these studies are a requirement of accreditation, they are also a valuable tool for internal quality control.

6.1. Proficiency Tests

The following proficiency tests were completed by HAL during 2004. Results for these tests are available upon request.

Table 1

Non-Potable Water / Solid and Hazardous	New York Department of Health	01/2004
Waste Proficiency Study		
Water Pollution January 2004	Analytical Products Group	01/2004
Water Pollution June 2004	Analytical Products Group	06/2004
Water Pollution August 2004/DMR-QA 24	Analytical Products Group	08/2004
Non-Potable Water / Solid and Hazardous	New York Department of Health	07/2004
Waste Proficiency Study		

6.2. Laboratory Intercomparisons

HAL participates in a U.S. Geological Survey PE sample laboratory intercomparison program. This program is coordinated by the USGS.

FGS is also an invited participant in several domestic and international laboratory intercomparisons each year. Many intercomparison participants are fellow world leaders in mercury and trace metals analysis. While functionally similar to PTs, these studies often involve more complex matrices or additional analytes and while project-specific intercomparison studies are helpful for assessing interlaboratory comparability, they do not necessarily address individual laboratory accuracy, and are not designed to function as third party validation. For these reasons although FGS does provide proficiency test study results, clients are not provided with intercomparison study results.

The following laboratory intercomparison studies were completed by HAL during 2004.

Table 2

Trace Elements in Surface Waters and Total	National Water Research	01/2004
Mercury Study 83 Winter 2003	Institute	
17th Intercomparison for Metals in Marine	National Research Council —	06/2004
Sediments & Biological Tissues	Canada	
Standard Reference Sample Spring 2004	United States Geological Survey	02/2004
Trace Elements in Surface Waters: Study	National Water Research	06/2004
FP84	Institute — Canada	
Mercury Round Robin HgRR5	Florida Department of	08/2004
	Environmental Protection	
Standard Reference Sample Fall 2004	United States Geological Survey	10/2004
Trace Elements in Surface Waters and Total	National Water Research	12/2004
Mercury Study 85 Winter 2004	Institute	

7. Field Quality Control

7.1. Field Bottle Blanks

7.1.1. Description

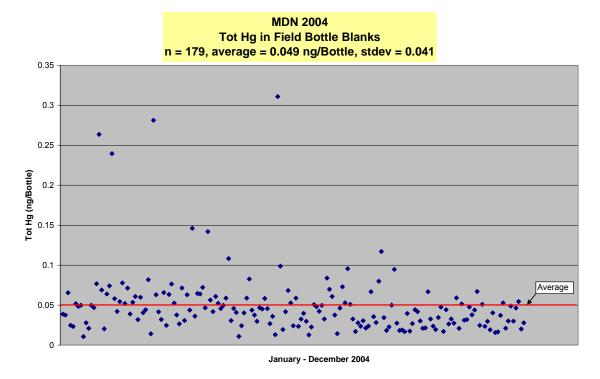
A field bottle blank has the same contents as a laboratory bottle blank. However, this blank is left exposed at the sampling site for the entire collection period without any collector openings. All field bottle blanks that maintain at least 15mL of the initial 20mL1% hydrochloric acid charge are then analyzed for total mercury.

7.1.2. 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 objectively subtracted from final sample results.

7.1.3. Discussion

In 2004, the mean of 179 Field Bottle Blanks was 0.049ng/bottle with a standard deviation of 0.041ng/bottle. This suggests that the MDN aerochem collector protects the sample train and bottle well and the field exposure is minimal.



7.2. Field System Blanks

7.2.1. Description

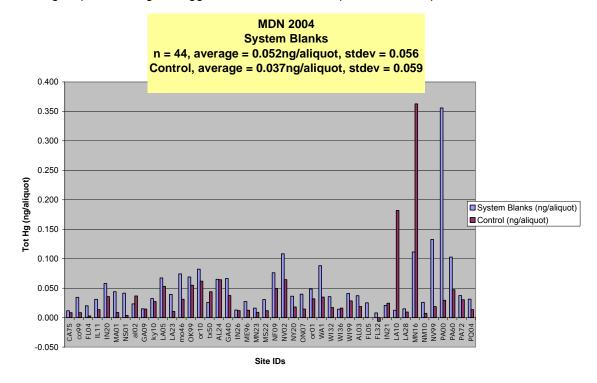
A field system blank is essentially a field bottle blank in which a solution is poured through the wet side collection sample train that was installed in the field for an entire week with no precipitation.

7.2.2. 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.

7.2.3. Discussion

In 2004, the mean of 44 system blanks was 0.052ng/aliquot with a standard deviation of 0.056ng/aliquot. This again suggests that the MDN sample train is well protected.

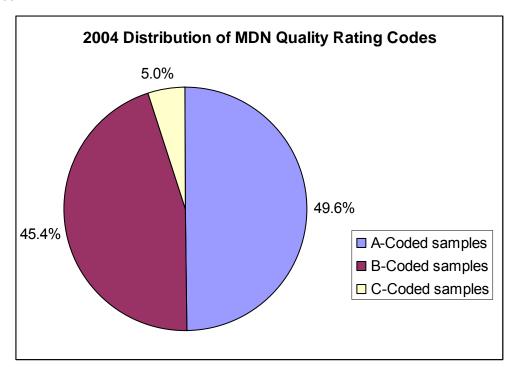


8. Quality Rating Codes

The quality rating code (QR) is designed as a user-friendly method to indicate the overall quality of each individual MDN data value. The MDN QR is modeled directly from 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 water; 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 data. These data are used along with A 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 4628 samples in 2004. 2297 samples received a QR code of A, 2100 received a B QR code, and 231 received a C QR code. FGS continued to maintain and demonstrate acceptable quality control in 2004.



Appendix A

Matrix Specific MDL Studies

Matrix Specific MDL Study 1

Objective

Determine the method detection limit (MDL) for total mercury in water using preservation method FGS 012 and analysis method FGS 069, and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for total mercury in water was determined to be 0.096ng/L.

Analytical Method A calibration was performed according to FGS 069. Briefly, this method incorporates oxidation with the addition of BrCl, reduction of mercury in the sample aliquot with SnCl₂, analysis by purge and trap and dual amalgamation CVAFS. The MDL study consisted of the analysis of nine replicates of a waters sample spiked with 0.5ng/L mercury oxidized with 1% BrCI. The results of these measurements are found in the table below, as well in the raw data sheets (ID # THg9-050331-1). All results are reported uncorrected for 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 s is the standard deviation of the results obtained on samples spiked at a level near the MDL.

MDL = t*s

The MDL calculated from these data is (2.821)*(0.034), or 0.096ng/L.

Total Mercury in Water (THg) MDL Study (CVAFS #9) March 31, 2005

Sample	THg (ng/L)	%Rec
method blank #1	0.039	-
method blank #2	0.018	-
method blank #3	0.030	-
Mean	0.029	-
SD	0.011	-
IPR-1(5.0 ng/L)	5.044	100.9
IPR-2(5.0 ng/L)	4.995	99.9
IPR-3(5.0 ng/L)	5.173	103.5
IPR-4(5.0 ng/L)	5.144	102.9
Mean	5.089	101.8
SD	0.084	1.7
MDL-1 (0.5 ng/L)	0.510	102.0
MDL-2 (0.5 ng/L)	0.601	120.2
MDL-3 (0.5 ng/L)	0.480	96.0
MDL-4 (0.5 ng/L)	0.511	102.2
MDL-5 (0.5 ng/L)	0.521	104.2
MDL-6 (0.5 ng/L)	0.524	104.8
MDL-7 (0.5 ng/L)	0.492	98.4
MDL-8 (0.5 ng/L)	0.479	95.8
MDL-9 (0.5 ng/L)	0.478	95.6
MDL-10 (0.5 ng/L)	0.511	102.2
Mean	0.511	102.1
SD	0.034	6.9
NIST 1641d	16.167	101.0
certified value NIST 1641 d	16.010	-

Matrix Specific MDL Study 2

Objective

Determine the method detection limit (MDL) for total mercury in water using preservation method FGS 012 and analysis method FGS 069, and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for total mercury in water was determined to be 0.055ng/L.

Analytical Method A calibration was performed according to FGS 069. Briefly, this method incorporates oxidation with the addition of BrCl, reduction of mercury in the sample aliquot with SnCl₂, analysis by purge and trap and dual amalgamation CVAFS. The MDL study consisted of the analysis of nine replicates of a waters sample spiked with 0.5ng/L mercury oxidized with 1% BrCI. The results of these measurements are found in the table below, as well in the raw data sheets (ID # THg9-050331-1). All results are reported uncorrected for 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 2.896 was used in the following equation, where s is the standard deviation of the results obtained on samples spiked at a level near the MDL.

MDL = t*s

The MDL calculated from these data is (2.896)*(0.019), or 0.055ng/L.

Total Mercury in Water (THg) MDL Study (CVAFS #10) March 31, 2005

Sample		THg (ng/L)	%Rec
method blank #1		0.040	-
method blank #2		0.062	-
method blank #3		0.035	-
	Mean	0.046	-
	SD	0.014	-
IPR-1(5.0 ng/L)		5.020	100.4
IPR-2(5.0 ng/L)		5.186	103.7
IPR-3(5.0 ng/L)		5.129	102.6
IPR-4(5.0 ng/L)		5.122	102.4
(0 /	Mean	5.114	102.3
	SD	0.069	1.4
MDL-1 (0.5 ng/L)		0.542	108.4
MDL-2 (0.5 ng/L)		0.480	96.0
MDL-3 (0.5 ng/L)		0.533	106.6
MDL-4 (0.5 ng/L)		0.510	102.0
MDL-5 (0.5 ng/L)		0.517	103.4
MDL-6 (0.5 ng/L)		0.514	102.8
MDL-7 (0.5 ng/L)		0.547	109.4
MDL-8 (0.5 ng/L)		0.524	104.8
MDL-9 (0.5 ng/L)		0.515	103.0
` ' '	Mean	0.520	104.0
	SD	0.019	3.8
NIST 1641d		15.853	99.0
certified value NIST	1641 d	16.010	-

Matrix Specific MDL Study 3

Objective

Determine the method detection limit (MDL) for methyl mercury in water, using distillation method FGS 013, and following the protocols outlined in 40 CFR 136. As detailed below, the MDL for methylmercury in water was determined to be 0.015ng/L.

Analytical Method A calibration was performed according to FGS 070. Briefly, this method incorporates distillation followed by analysis utilizing aqueous phase ethylation, CV purge and trap, thermal desorption, GC separation, pyrolytic decomposition, and detection using CVAFS. The MDL study consisted of the distillation and analysis of nine waters spiked with 0.111ng/L of MHg. The results of these measurements are found in the table below, as well in the raw data sheets (ID # MHg1-050616-1). All results are reported uncorrected for the method blanks.

MDL Calculation

Using 40 CFR 136, the MDL was calculated using the standard deviation of the spiked samples, with n=9 replicates (8 degrees of freedom). In this case, the t value of 2.896 was used in the following equation, where s is the standard deviation of the results obtained on samples spiked at a level near the MDL.

MDL = t*s

The MDL calculated from these data is (2.896)*(0.005), or 0.015ng/L.

Methyl Mercury in Water (MHg) MDL Study (CV-GC-AFS #1) June 16, 2005

Sample method blank #1 method blank #2 method blank #3		MeHg (ng/L) 0.019 0.017 0.014	%Rec - - -
	Mean	0.017	-
	SD	0.003	-
MDL #1+ 0.111 ng/L MDL #2+ 0.111 ng/L MDL #3+ 0.111 ng/L MDL #4+ 0.111 ng/L MDL #5+ 0.111 ng/L MDL #6+ 0.111 ng/L		0.116 0.110 0.113 0.119 0.100 0.114	104.6 99.3 102.0 107.3 90.4 102.8
MDL #7+ 0.111 ng/L		0.110	99.3
MDL #8+ 0.111 ng/L		0.111	100.2
MDL #9+ 0.111 ng/L		0.110	99.3
	Mean	0.112	100.6
	SD	0.005	0.0
DORM-2 (4470ug/L)		4415	98.8

Appendix B

QC Summary Tables

2004 Annual Quality Assurance Report

Mercury Analytical Laboratory

MDN Quarterly Analysis QC Summary, Quarter 1 of 2004

<u>Analysis</u>	<u>C</u>	alibration R	BrCl Blk Conc	SRM (Nist 1 TV=8.005 ng/m		<u>Duplica</u> Bottle ID	ates RPD	Spik Bottle ID	<u>es</u> Rec.	Bottle Bottle ID	Blanks Conc
2004-001	CVAFS-10 1/20/2004 CVAFS-9	0.99988	0.034 ng/L	7.62 ng/mL 7.70 ng/mL	95.2% 96.2%	MDN2113 MDN2203 MDN2439	5.7% 0.5% 0.3%	MDN2113 MDN2203 MDN2439	102.3% 98.4%		.014 ng/Bottle
2004-002	1/20/2004 (CVAFS-10	0.99989	0.042 ng/L	7.38 ng/mL 7.51 ng/mL	92.1% 93.8%	MDN0774 MDN0952 MDN2418	0.8% 0.9% 1.4%	MDN0774 MDN0952 MDN2418	97.4%		.020 ng/Bottle .100 ng/Bottle
2004-003	1/22/2004 (CVAFS-9	0.99987	0.044 ng/L	7.65 ng/mL 7.42 ng/mL	95.6% 92.7%	MDN0183 MDN2321 MDN2443	0.8% 0.9% 1.1%	MDN0183 MDN2321 MDN2443	99.9%		
2004-004	1/22/2004 (CVAFS-10	0.99996	0.038 ng/L	7.65 ng/mL 7.64 ng/mL	95.6% 95.4%	MDN2014 MDN2069 MDN2145	0.1% 4.1% 6.1%	MDN2014 MDN2069 MDN2145	98.1%		
2004-005	1/26/2004 (CVAFS-9	0.99996	0.021 ng/L	7.76 ng/mL 7.32 ng/mL	97.0% 91.4%	MDN0597 MDN0819 MDN2048 MDN2275	65.1% 2.5% 0.3% 2.3%	MDN0597 MDN0819 MDN2048 MDN2275	102.7% 98.4%		.016 ng/Bottle .059 ng/Bottle
2004-006	1/26/2004 (CVAFS-10	0.99999	0.039 ng/L	7.65 ng/mL 7.58 ng/mL	95.6% 94.7%	MDN0680 MDN2316 MDN2497	0.5% 2.0% 1.4%	MDN0680 MDN2316 MDN2497	93.9%	MDN0943 0	.027 ng/Bottle
2004-007	2/3/2004 CVAFS-9	0.99985	0.010 ng/L	7.65 ng/mL 7.72 ng/mL	95.6% 96.4%	MDN0145 MDN2127 MDN2402	0.4% 0.9% 0.9%	MDN0145 MDN2127 MDN2402	104.4%		
2004-008	2/2/2004 (CVAFS-10	0.99998	0.026 ng/L	7.45 ng/mL 7.33 ng/mL	93.0% 91.6%	MDN0156 MDN2361 MDN2375	4.6% 14.5% 4.6%	MDN0156 MDN2361 MDN2375	97.2%		.027 ng/Bottle .023 ng/Bottle
2004-009	2/3/2004 CVAFS-10	0.99950	0.025 ng/L	7.75 ng/mL 7.34 ng/mL	96.9% 91.7%	MDN1739 MDN2383 MDN2401	6.0% 5.1% 1.0%	MDN1739 MDN2383 MDN2401	101.7%		
2004-010	2/4/2004 CVAFS-9	0.99898	0.024 ng/L	7.20 ng/mL 7.64 ng/mL	90.0% 95.4%	MDN2122 MDN2352 MDN3009	3.9% 1.5% 1.3%	MDN2122 MDN2352 MDN3009	98.7%		
2004-011	2/10/2004 (CVAFS-9	0.99999	0.029 ng/L	7.52 ng/mL 7.50 ng/mL	93.9% 93.7%	MDN1969 MDN2028 MDN2534	0.2% 0.3% 0.3%	MDN1969 MDN2028 MDN2534			.014 ng/Bottle .021 ng/Bottle
2004-012	2/10/2004 (CVAFS-10	0.99998	0.034 ng/L	7.63 ng/mL	95.3%	MDN0163	7.7%	MDN0163	92.2%		
2004-013	2/16/2004 (CVAFS-10	0.99968	0.025 ng/L	7.48 ng/mL 7.22 ng/mL	93.4% 90.2%	MDN0915 MDN2049 MDN2523	6.1% 3.5% 3.3%	MDN0915 MDN2049 MDN2523			
2004-014	2/18/2004	0.99997	0.028 ng/L	7.56 ng/mL	94.5%	MDN2246	4.6%	MDN2246	95.5%	MDN2395 0	.020 ng/Bottle

	CVAFS-9			7.74 ng/mL	96.6%	MDN2313 MDN2397	2.1% 3.6%	MDN2313 MDN2397		
2004-015	2/18/2004 CVAFS-10	0.99997	0.022 ng/L	7.71 ng/mL 7.54 ng/mL	96.3% 94.2%	MDN0910 MDN2358 MDN2430	3.8% 0.4% 3.7%	MDN0910 MDN2358 MDN2430	98.6%	
2004-016	2/20/2004 CVAFS-9	0.99999	0.045 ng/L	7.68 ng/mL 7.58 ng/mL	95.9% 94.7%	MDN0177 MDN1913 MDN1996	0.7% 0.6% 0.7%	MDN0177 MDN1913 MDN1996	95.3%	MDN2391 0.057 ng/Bottle MDN0425 0.095 ng/Bottle
2004-017	2/20/2004 CVAFS-10	0.99989	0.040 ng/L	7.96 ng/mL 7.53 ng/mL	99.5% 94.0%	MDN0683 MDN2085 MDN2370	7.2% 5.0% 0.4%	MDN0683 MDN2085 MDN2370	100.8%	MDN2028 0.013 ng/Bottle
2004-018	2/25/2004 CVAFS-9	0.99998	0.038 ng/L	7.72 ng/mL 7.52 ng/mL	96.4% 93.9%	MDN0487 MDN0976 MDN2107 MDN2470	1.0% 3.2% 1.3% 4.6%	MDN0487 MDN0976 MDN2107	103.5%	
2004-019	2/27/2004 CVAFS-9	0.99912	0.105 ng/L	7.51 ng/mL 7.72 ng/mL	93.9% 96.4%	MDN2105 MDN2324 MDN2421	0.4% 2.3% 2.0%	MDN2105 MDN2324 MDN2421		
2004-020	2/27/2004 CVAFS-10	0.99958	0.037 ng/L	7.64 ng/mL 7.63 ng/mL	95.5% 95.3%	MDN2158 MDN2263 MDN2400	2.2% 0.6% 1.4%	MDN2158 MDN2263 MDN2400	104.3%	MDN0735 0.020 ng/Bottle
2004-021	3/2/2004 CVAFS-9	0.99972	0.025 ng/L	7.88 ng/mL 7.07 ng/mL	98.5% 88.4%	MDN0266 MDN2195 MDN2514	2.9% 2.9% 6.8%	MDN0266 MDN2195 MDN2514		
2004-022	3/2/2004 CVAFS-10	0.99982	0.052 ng/L	7.80 ng/mL 7.56 ng/mL	97.4% 94.4%	MDN2153 MDN2457 MDN3003	2.0% 1.4% 2.9%	MDN2153 MDN2457 MDN3003	92.4%	MDN1910 0.016 ng/Bottle
2004-023	3/10/2004 CVAFS-10	0.99899	0.021 ng/L	7.64 ng/mL 7.68 ng/mL	95.4% 96.0%	MDN0832 MDN0909 MDN2438	1.3% 2.0% 0.3%	MDN0832 MDN0909 MDN2438	97.9%	
2004-024	3/16/2004 CVAFS-9	0.99911	0.047 ng/L	7.50 ng/mL 7.78 ng/mL	93.7% 97.2%	MDN2142 MDN2321 MDN2399	0.4% 3.6% 0.3%	MDN2142 MDN2321 MDN2399	99.9%	
2004-025	3/18/2004 CVAFS-10	0.99949	0.012 ng/L	7.72 ng/mL 7.53 ng/mL	96.5% 94.0%	MDN2192 MDN2277 MDN2295	2.8% 2.2% 3.3%	MDN2192 MDN2277 MDN2295	100.4%	MDN0925 0.035 ng/Bottle MDN2292 0.006 ng/Bottle
2004-026	3/17/2004 CVAFS-10	0.99956	0.029 ng/L	8.12 ng/mL	101.4%	MDN2280	4.1%	MDN2280	85.9%	
2004-027	3/21/2004 CVAFS-9	0.99940	0.043 ng/L	7.36 ng/mL 6.81 ng/mL	91.9% 85.1%	MDN0437 MDN2331 MDN2553	2.6% 3.9% 8.1%	MDN0437 MDN2331 MDN2553		
2004-028	3/21/2004 CVAFS-10	0.99937	0.070 ng/L	7.71 ng/mL 7.41 ng/mL	96.4% 92.5%	MDN2110 MDN2353 MDN2451	3.3% 2.7% 0.4%	MDN2110 MDN2353 MDN2451	100.3%	MDN2520 0.064 ng/Bottle
2004-029	3/29/2004	0.99990	0.032 ng/L	7.79 ng/mL	97.3%	MDN0739	12.4%	MDN0739	100.5%	

	CVAFS-9			7.12 ng/mL	88.9%	MDN2275 MDN2522	0.5% 9.5%	MDN2275 MDN2522		
2004-030	3/29/2004 CVAFS-10		0.064 ng/L	7.70 ng/mL 7.77 ng/mL	96.2% 97.1%	MDN0862 MDN2086 MDN2201	0.4% 3.2% 0.8%	MDN0862 MDN2086 MDN2201	100.1%	MDN0146 0.025 ng/Bottle
2004-031	3/31/2004 CVAFS-10		0.025 ng/L	7.69 ng/mL 7.54 ng/mL	96.1% 94.1%	MDN1756 MDN2409 MDN2439	2.6% 0.3% 2.3%		98.3%	
2004-032	3/30/2004 CVAFS-10		-0.050 ng/L	7.66 ng/mL 7.77 ng/mL	95.7% 97.0%	MDN0783 MDN2261 MDN2308	3.3% 2.8% 0.9%	MDN0783 MDN2261 MDN2308	99.1%	
2004-033	3/31/2004 CVAFS-9	0.99998	0.021 ng/L	7.71 ng/mL 7.35 ng/mL	96.3% 91.9%	MDN0405 MDN1987 MDN2103	0.3% 3.3% 0.8%	MDN0405 MDN1987 MDN2103	96.4% 90.3% 98.6%	
2004-158	1/3/2004 CVAFS-9	0.99998	0.034 ng/L	7.77 ng/mL 7.76 ng/mL	97.1% 97.0%	MDN0677 MDN2103 MDN2170	2.1% 6.9% 0.1%	MDN0677 MDN2103 MDN2170	92.6% 95.1% 99.7%	MDN2697 0.010 ng/Bottle
3004-012	2/16/2004 CVAFS-9	0.99998	0.028 ng/L	7.67 ng/mL 7.69 ng/mL	95.8% 96.1%	MDN0132 MDN2437 MDN2545	0.2% 0.2% 1.5%	MDN0132 MDN2437 MDN2545	98.4% 95.9% 99.6%	
3004-026	3/19/2004 CVAFS-10	0.99990	0.034 ng/L	7.75 ng/mL	96.8%	MDN0419 MDN0731	1.9% 8.1%	MDN0419 MDN0731	99.0% 97.4%	
	ly Mean: Std Dev:	0.99974 ±0.00029	0.032 ng/L ±0.021		95.0% ±2.6%		3.4% ±6.2%		99.5% ±14.9%	0.036 ng/Bottle ±0.031

MDN Quarterly Analysis QC Summary, Quarter 2 of 2004

<u>Analysis</u>	<u>C</u>	alibration R	BrCl Blk Conc	SRM (Nist 1) V=8.005 ng/m		<u>Duplica</u> Bottle ID	ates RPD	Spik Bottle ID	<u>es</u> Rec.	Bottle Bottle ID	<u>e Blanks</u> Conc
2004-034	4/4/2004 CVAFS-9	0.99984	0.107 ng/L	7.73 ng/mL 7.46 ng/mL	96.5% 93.2%	MDN0716 MDN0750 MDN2099	0.1% 1.8% 2.6%	MDN0716 MDN0750 MDN2099			
2004-035	4/4/2004 CVAFS-10	0.99952	0.055 ng/L	7.60 ng/mL 7.51 ng/mL	95.0% 93.9%	MDN0683 MDN1928 MDN2269	3.8% 1.0% 0.1%	MDN0683 MDN1928 MDN2269 MDN2319	97.5% 101.0%		0.024 ng/Bottle 0.021 ng/Bottle
2004-036	4/8/2004 CVAFS-9	0.99995	0.027 ng/L	7.79 ng/mL 7.51 ng/mL	97.3% 93.8%	MDN0847 MDN1981 MDN2317	2.8% 0.6% 10.1%	MDN0847 MDN1981 MDN2317	98.5%	MDN0427	0.021 ng/Bottle
2004-037	4/8/2004 CVAFS-10	0.99975	0.015 ng/L	7.69 ng/mL 7.31 ng/mL	96.1% 91.4%	MDN2344 MDN2358 MDN2481	1.2% 7.0% 5.7%	MDN2344 MDN2358 MDN2481	98.0%	MDN2206	0.012 ng/Bottle
2004-038	4/20/2004 CVAFS-9	0.99997	0.011 ng/L	7.70 ng/mL 7.69 ng/mL	96.2% 96.0%	MDN0896 MDN1759 MDN2129	5.1% 0.5% 18.1%	MDN0896 MDN1759 MDN2129	96.8%		
2004-039	4/19/2004 CVAFS-10	0.99976	0.029 ng/L	7.62 ng/mL 7.51 ng/mL	95.2% 93.8%	MDN0795 MDN0899 MDN2181	6.5% 10.8% 1.7%	MDN0795 MDN0899 MDN2181	102.7%	MDN0898	0.032 ng/Bottle
2004-040	4/20/2004 CVAFS-10	0.99939	0.025 ng/L	7.86 ng/mL 7.84 ng/mL	98.2% 98.0%	MDN0267 MDN2051 MDN2131	0.5% 4.9% 0.3%	MDN0267 MDN2051 MDN2131	101.6%		
2004-041	4/22/2004 CVAFS-9	0.99987	0.034 ng/L	7.64 ng/mL 7.70 ng/mL	95.4% 96.1%	MDN1929 MDN2463 MDN2555	16.5% 7.5% 2.6%	MDN1929 MDN2463 MDN2555	102.0%	MDN1742	0.093 ng/Bottle
2004-042	4/22/2004 CVAFS-10	0.99969	0.012 ng/L	7.76 ng/mL 7.90 ng/mL	97.0% 98.7%	MDN0640 MDN0844 MDN2524	1.6% 0.7% 0.5%	MDN0640 MDN0844 MDN2524	100.6%		
2004-043	4/29/2004 CVAFS-9	0.99993	0.036 ng/L	7.77 ng/mL 7.42 ng/mL	97.1% 92.7%	MDN1953 MDN2379 MDN2443	2.9% 0.4% 1.0%	MDN1953 MDN2379 MDN2443	98.5%		
2004-044	4/23/2004 CVAFS-9	0.99993	0.038 ng/L	7.75 ng/mL 7.83 ng/mL	96.8% 97.8%	MDN0492 MDN0802 MDN1921	0.9% 1.8% 1.5%	MDN0492 MDN0802 MDN1921	99.7%	MDN2143	0.028 ng/Bottle
2004-045	4/23/2004 CVAFS-10	0.99998	0.042 ng/L	7.65 ng/mL 7.79 ng/mL	95.5% 97.3%	MDN0225 MDN2043 MDN2490	1.2% 3.1% 1.5%	MDN0225 MDN2043 MDN2490	93.1%		
2004-046	4/29/2004 CVAFS-10	0.99955	0.037 ng/L	7.88 ng/mL 7.63 ng/mL	98.5% 95.3%	MDN0255 MDN2445 MDN2509	8.2% 2.7% 0.7%	MDN0255 MDN2445 MDN2509	108.2%		

2004-047	5/3/2004 CVAFS-9	0.99999	0.046 ng/L	7.77 ng/mL 7.59 ng/mL	97.0% 94.8%	MDN0656 MDN0740 MDN2049	1.1% 1.9% 0.6%	MDN0656 MDN0740 MDN2049	97.0%	MDN1974 0.028 ng/Bottle
2004-048	5/3/2004 CVAFS-10	0.99960	0.046 ng/L	7.82 ng/mL 7.77 ng/mL	97.7% 97.1%	MDN0633 MDN2310 MDN3007	0.2% 2.1% 3.2%	MDN0633 MDN2310 MDN3007	108.6%	MDN2263 0.022 ng/Bottle
2004-049	5/6/2004 CVAFS-9	0.99998	0.010 ng/L	7.83 ng/mL 7.46 ng/mL	97.8% 93.2%	MDN0120 MDN2295 MDN2529	0.4% 0.8% 0.1%	MDN0120 MDN2295 MDN2529	96.7%	
2004-050	5/13/2004 CVAFS-9	0.99996	0.030 ng/L	7.67 ng/mL 7.60 ng/mL	95.9% 94.9%	MDN0085 MDN2127 MDN2195	0.4% 0.4% 1.7%	MDN0085 MDN2127 MDN2195	99.4%	
2004-051	5/13/2004 CVAFS-10	0.99998	0.015 ng/L	7.63 ng/mL 7.52 ng/mL	95.3% 94.0%	MDN0448 MDN2275 MDN2527	1.1% 3.4% 2.5%	MDN0448 MDN2275 MDN2527	92.9%	MDN2234 0.034 ng/Bottle
2004-052	5/20/2004 CVAFS-9	0.99992	0.035 ng/L	7.99 ng/mL 7.79 ng/mL	99.8% 97.3%	MDN1931 MDN2137 MDN2334	0.2% 7.3% 18.0%	MDN1931 MDN2137 MDN2334	103.2%	
2004-053	5/20/2004 CVAFS-10	0.99958	-0.009 ng/L	8.09 ng/mL 8.01 ng/mL	101.1% 100.1%	MDN1996 MDN2121 MDN2302	0.7% 7.0% 5.2%	MDN1996 MDN2121 MDN2302	102.0%	
2004-054	5/21/2004 CVAFS-9	0.99989	-0.008 ng/L	7.85 ng/mL 8.00 ng/mL	98.0% 99.9%	MDN0735 MDN0847 MDN2454	2.7% 0.3% 2.9%	MDN0735 MDN0847 MDN2454	101.6%	
2004-055	5/21/2004 CVAFS-10	0.99974	0.011 ng/L	7.13 ng/mL 7.79 ng/mL	89.0% 97.3%	MDN0256 MDN2202 MDN2227	8.3% 3.8% 0.1%	MDN0256 MDN2202 MDN2227	97.5%	MDN2473 0.027 ng/Bottle
2004-056	5/25/2004 CVAFS-9	0.99980	0.073 ng/L	7.58 ng/mL 6.60 ng/mL 7.79 ng/mL	94.7% 82.4% 97.4%	MDN2031 MDN2319 MDN2358	9.2% 5.5% 3.2%	MDN2031 MDN2319 MDN2358	114.7%	
2004-057	5/25/2004 CVAFS-10	0.99995	0.059 ng/L	7.99 ng/mL 7.68 ng/mL	99.9% 96.0%	MDN0020 MDN0493 MDN2364	2.4% 0.4% 0.9%	MDN0020 MDN0493 MDN2364	100.1%	MDN2441 0.077 ng/Bottle
2004-058	5/27/2004 CVAFS-10	0.99998	0.113 ng/L	7.62 ng/mL 7.63 ng/mL	95.2% 95.3%	MDN2129 MDN2342 MDN2482	2.9% 4.0% 0.7%	MDN2129 MDN2342 MDN2482	97.6%	MDN1972 0.045 ng/Bottle MDN2277 0.033 ng/Bottle MDN0448 0.027 ng/Bottle
2004-059	6/2/2004 CVAFS-9	0.99991	0.104 ng/L	7.69 ng/mL 7.66 ng/mL	96.1% 95.7%	MDN0289 MDN0421 MDN1989	3.9% 1.2% 1.0%	MDN0289 MDN0421 MDN1989	94.8%	
2004-060	6/2/2004 CVAFS-10	0.99997	0.067 ng/L	7.67 ng/mL 7.56 ng/mL	95.8% 94.5%	MDN2160 MDN2530 MDN2546	4.9% 2.4% 0.9%	MDN2160 MDN2530 MDN2546	99.8%	
2004-061	6/3/2004 CVAFS-9	0.99986	0.057 ng/L	7.79 ng/mL 7.77 ng/mL	97.4% 97.0%	MDN0716 MDN2184 MDN2523	0.4% 0.1% 2.8%	MDN0716 MDN2184 MDN2523	103.1%	

	/2004 0.9 AFS-9	99994 (•		92.7%	MDN0861 MDN0954 MDN2539	0.8%	MDN0861 MDN0954 MDN2539	98.3% 96.4% 96.4%		
	/2004 0.9 AFS-10	99994 (- C	0	95.9%	MDN0494 MDN0689 MDN0822	3.0%	MDN0689	93.3% 98.0% 98.5%		
	4/2004 0.9 AFS-10	99996 (•		94.3%	MDN0187 MDN0292 MDN1927	0.7%	MDN0292	97.3% 94.4% 83.3%		.036 ng/Bottle .035 ng/Bottle
	5/2004 0.9 AFS-9	99981 (•	0	88.4%	MDN0945 MDN2157 MDN2158	3.7%	MDN2157	79.5% 95.6% 88.4%		.024 ng/Bottle .037 ng/Bottle
	5/2004 0.9 AFS-10	99998 (•		89.1%	MDN0661 MDN1760 MDN2163	0.4%	MDN0661 MDN1760 MDN2163	98.3%	MDN2640 0	.050 ng/Bottle
	6/2004 0.9 AFS-10	99997 (96.3%	MDN0816 MDN1913 MDN2408	3.7%	MDN1913	96.3% 103.3% 90.2%		
	8/2004 0.9 AFS-10	99996 (•		94.6%	MDN0199 MDN0288 MDN2490	0.4%		94.1% 94.7% 100.2%		
	2/2004 0.9 AFS-10	99996 (•		96.5%	MDN0663 MDN0741 MDN0774	0.7%	MDN0663 MDN0741 MDN0774	101.3% 88.6% 95.3%	MDN1989 0	.036 ng/Bottle
	3/2004 0.9 AFS-10	99995 (•		93.9%	MDN0676 MDN2301 MDN2422	1.1%	MDN0676 MDN2301 MDN2422	96.6% 97.2% 92.1%	MDN2382 0	.046 ng/Bottle
Quarterly Me Std I		99986 (00015).045 ng/L ±0.029		95.7% ±2.8%		2.8% ±3.4%		99.3% ±10.5%	0.0	036 ng/Bottle ±0.018

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MDN Quarterly Analysis QC Summary, Quarter 3 of 2004

<u>Analysis</u>	<u>c</u>	Calibration R	BrCl Blk Conc	SRM (Nist 1 V=8.005 ng/m		<u>Duplica</u> Bottle ID	ates RPD	Spik Bottle ID	es Rec.	Bottle I Bottle ID	Blanks Conc
2004-071	7/1/2004 CVAFS-9	0.99948	0.080 ng/L	7.92 ng/mL 7.33 ng/mL	99.0% 91.5%	MDN0638 MDN0640 MDN0655	2.7% 1.7% 0.1%	MDN0638 MDN0640 MDN0655			
2004-072	7/1/2004 CVAFS-10	0.99992	0.075 ng/L	7.64 ng/mL 7.63 ng/mL	95.5% 95.3%	MDN1950 MDN2329 MDN2379	3.8% 1.2% 0.4%	MDN1950 MDN2329 MDN2379	96.4%		
2004-073	7/2/2004 CVAFS-9	0.99997	0.073 ng/L	7.58 ng/mL 6.68 ng/mL	94.7% 83.5%	MDN1924 MDN2055 MDN2148	7.3% 5.8% 1.0%	MDN1924 MDN2055 MDN2148	92.1%	MDN2523 0.0	033 ng/Bottle
2004-074	7/2/2004 CVAFS-10	0.99993	0.078 ng/L	7.63 ng/mL 7.46 ng/mL	95.3% 93.2%	MDN0122 MDN1962 MDN2117	1.9% 1.9% 0.1%	MDN0122 MDN1962 MDN2117	91.2%	MDN2069 0.0	037 ng/Bottle
2004-075	7/8/2004 CVAFS-9	0.99994	0.072 ng/L	7.50 ng/mL 7.14 ng/mL	93.7% 89.1%	MDN2001 MDN2388 MDN2549	9.8% 3.9% 4.6%	MDN2001 MDN2388 MDN2549	95.2%	MDN3011 0.0	029 ng/Bottle
2004-076	7/7/2004 CVAFS-10	0.99995	0.056 ng/L	7.67 ng/mL 7.43 ng/mL	95.8% 92.8%	MDN0085 MDN2584 MDN2643	1.0% 5.5% 0.3%	MDN0085 MDN2584 MDN2643	195.4%	MDN0698 0.0 MDN2540 0.0	
2004-077	7/8/2004 CVAFS-10	0.99999	0.057 ng/L	7.59 ng/mL 7.21 ng/mL	94.9% 90.0%	MDN0983 MDN1976 MDN2438	0.5% 0.8% 1.8%	MDN0983 MDN1976 MDN2438	98.5%		
2004-078	7/19/2004 CVAFS-9	0.99989	0.024 ng/L	7.67 ng/mL 7.17 ng/mL	95.9% 89.6%	MDN0445 MDN1916 MDN2429	2.4% 1.9% 1.1%	MDN0445 MDN1916 MDN2429	85.2%	MDN0956 0.0	060 ng/Bottle
2004-079	7/13/2004 CVAFS-10	0.99999	0.085 ng/L	7.73 ng/mL 7.49 ng/mL	96.5% 93.6%	MDN0405 MDN0735 MDN2616	1.4% 0.4% 1.1%	MDN0405 MDN0735 MDN2616	99.6%		
2004-080	7/19/2004 CVAFS-10	1.00000	0.049 ng/L	7.62 ng/mL 7.48 ng/mL	95.2% 93.5%	MDN0421 MDN2507 MDN2602	5.4% 7.2% 0.9%	MDN0421 MDN2507 MDN2602	103.4%		
2004-081	7/20/2004 CVAFS-10	0.99998	0.059 ng/L	7.62 ng/mL 7.48 ng/mL	95.2% 93.4%	MDN0646 MDN2395 MDN2621	0.9% 2.5% 3.3%	MDN0646 MDN2395 MDN2621	99.3%	BB20 0.0	025 ng/Bottle
2004-082	7/24/2004 CVAFS-10	0.99977	0.056 ng/L	7.98 ng/mL 7.72 ng/mL	99.7% 96.4%	MDN0952 MDN1921 MDN2478	4.5% 0.7% 0.6%	MDN0952 MDN1921 MDN2478	95.5%	MDN2103 0.0	026 ng/Bottle
2004-083	7/20/2004 CVAFS-9	0.99989	0.041 ng/L	7.59 ng/mL 7.08 ng/mL	94.9% 88.5%	MDN0276 MDN2628 MDN2639	2.8% 2.2% 0.4%	MDN0276 MDN2628 MDN2639	110.5% 99.9%		
2004-084	7/28/2004 CVAFS-10	0.99988	0.033 ng/L	7.85 ng/mL 7.83 ng/mL	98.1% 97.8%	MDN0666 MDN0833	3.2%	MDN0666 MDN0833	94.9%		

						MDN2592	0.1%	MDN2592	102.6%	
2004-085	7/30/2004 CVAFS-9	0.99986	0.030 ng/L	7.84 ng/mL 7.77 ng/mL	97.9% 97.1%	MDN0827 MDN2170 MDN2470	0.3% 1.8% 0.7%	MDN0827 MDN2170 MDN2470	98.8%	
2004-086	7/30/2004 CVAFS-10	0.99988	0.009 ng/L	7.97 ng/mL 7.98 ng/mL	99.5% 99.7%	MDN2113 MDN2342 MDN2573	2.4% 0.7%	MDN2113 MDN2342 MDN2573	98.9%	MDN1984 0.028 ng/Bottle MDN0116 0.019 ng/Bottle
2004-087	7/31/2004 CVAFS-10	0.99995	0.050 ng/L	7.92 ng/mL 7.97 ng/mL	98.9% 99.5%	MDN0836 MDN2197 MDN2260	2.5% 2.7% 1.0%	MDN0836 MDN2197 MDN2260	100.5%	MDN1991 0.032 ng/Bottle
2004-088	8/3/2004 CVAFS-9	0.99966	0.043 ng/L	7.83 ng/mL 7.56 ng/mL	97.8% 94.4%	MDN2310 MDN2541 MDN2647	0.2% 0.9%	MDN2310 MDN2541 MDN2647	102.2%	
2004-089	8/3/2004 CVAFS-10	0.99998	0.058 ng/L	7.95 ng/mL 7.73 ng/mL	99.3% 96.5%	MDN1732 MDN2087 MDN3016	2.1% 1.7% 2.3%	MDN1732 MDN2087 MDN3016	99.4%	MDN2619 0.026 ng/Bottle
2004-090	8/4/2004 CVAFS-10	0.99997	-0.002 ng/L	7.87 ng/mL 7.88 ng/mL	98.3% 98.5%	MDN0126 MDN2289 MDN2435	0.2% 3.0% 0.9%	MDN0126 MDN2289 MDN2435	101.4%	MDN2233 0.017 ng/Bottle
2004-091	8/13/2004 CVAFS-10	0.99981	0.056 ng/L	7.96 ng/mL 8.01 ng/mL	99.4% 100.1%	MDN0678 MDN2349 MDN2509	0.2% 0.3% 5.6%	MDN0678 MDN2349 MDN2509	93.8%	
2004-092	8/17/2004 CVAFS-10	0.99994	0.043 ng/L	7.95 ng/mL 7.66 ng/mL	99.4% 95.7%	MDN0114 MDN2498 MDN2645	0.9% 2.8% 1.2%	MDN0114 MDN2498 MDN2645	100.6%	
2004-093	8/16/2004 CVAFS-10	0.99992	0.047 ng/L	7.96 ng/mL 7.70 ng/mL	99.5% 96.2%	MDN0075 MDN0492 MDN2436	2.7% 4.1% 1.2%	MDN0075 MDN0492 MDN2436		MDN2635 0.032 ng/Bottle MDN2234 0.036 ng/Bottle
2004-094	8/17/2004 CVAFS-9	0.99989	-0.048 ng/L	8.39 ng/mL 7.24 ng/mL	104.9% 90.5%	MDN0831 MDN2134 MDN3009	3.8% 1.2% 2.5%	MDN0831 MDN2134 MDN3009	123.1%	
2004-095	8/18/2004 CVAFS-10	0.99992	0.065 ng/L	7.82 ng/mL 7.76 ng/mL	97.6% 97.0%	MDN0297 MDN2026 MDN2615	3.5% 9.9% 10.3%	MDN0297 MDN2026 MDN2615	104.5%	
2004-096	8/25/2004 CVAFS-10	0.99986	0.075 ng/L	8.03 ng/mL 7.74 ng/mL	100.3% 96.7%	MDN0871 MDN1741 MDN2092	0.6% 7.1%	MDN0871 MDN1741 MDN2092	105.9%	
2004-097	8/26/2004 CVAFS-10	0.99975	0.031 ng/L	8.00 ng/mL 7.70 ng/mL	99.9% 96.1%	MDN2097 MDN2213 MDN2263	1.2% 2.7% 0.1%	MDN2097 MDN2213 MDN2263	109.9%	MDN0836 0.023 ng/Bottle MDN2342 0.033 ng/Bottle
2004-098	8/30/2004 CVAFS-10	0.99961	0.054 ng/L	8.24 ng/mL 8.11 ng/mL	102.9% 101.4%	MDN2069 MDN2077 MDN2451	1.6% 0.6% 1.5%	MDN2069 MDN2077 MDN2451	124.7%	MDN0102 0.024 ng/Bottle
2004-099	8/30/2004 CVAFS-9	0.99768	0.039 ng/L	7.46 ng/mL 6.92 ng/mL	93.1% 86.5%	MDN1924 MDN2501	10.3% 12.1%	MDN1924 MDN2501		MDN2330 0.017 ng/Bottle

						MDN2503	6.5%	MDN2503	118.7%	
2004-100	8/31/2004 CVAFS-10	0.99989	0.001 ng/L	7.33 ng/mL 8.14 ng/mL	91.6% 101.6%	MDN0183 MDN0439 MDN0934	0.4% 1.4% 2.9%	MDN0183 MDN0439 MDN0934	103.1% 106.8%	
2004-101	9/3/2004 CVAFS-10	0.99989	0.031 ng/L	6.69 ng/mL 7.58 ng/mL	83.5% 94.7%	MDN0144 MDN1958 MDN2372	5.6% 1.9% 1.9%	MDN0144 MDN1958 MDN2372	107.2%	
2004-102	9/7/2004 CVAFS-10	0.99990	0.029 ng/L	8.03 ng/mL 8.06 ng/mL	100.3% 100.7%	MDN0481 MDN0925 MDN2206	0.9% 0.3% 2.0%	MDN0481 MDN0925 MDN2206	102.4%	
2004-103	9/9/2004 CVAFS-9	0.99795	0.015 ng/L		102.7% 101.0%	MDN2059 MDN2317 MDN2397	1.4% 1.3% 0.6%	MDN2059 MDN2317 MDN2397	103.8%	MDN0896 0.037 ng/Bottle MDN2310 0.017 ng/Bottle
2004-104	9/13/2004 CVAFS-10	0.99961	0.056 ng/L	7.97 ng/mL 7.77 ng/mL	99.5% 97.0%	MDN0751 MDN0845 MDN2561	2.9% 2.9%	MDN0751 MDN0845 MDN2561	98.1%	MDN0155 0.049 ng/Bottle
2004-105	9/13/2004 CVAFS-9	0.99642	-0.024 ng/L	8.25 ng/mL	103.1%	MDN0843	1.9%	MDN0843	107.1%	
2004-106	9/17/2004 CVAFS-9	0.99885	-0.014 ng/L	7.32 ng/mL 7.65 ng/mL	91.4% 95.6%	MDN1927 MDN2131 MDN2324	4.3% 9.6% 3.0%	MDN1927 MDN2131 MDN2324	114.5%	
2004-107	9/17/2004 CVAFS-10	0.99993	0.013 ng/L	7.85 ng/mL 7.85 ng/mL	98.0% 98.0%	MDN0398 MDN2358 MDN3000	1.6% 4.0% 3.1%	MDN0398 MDN2358 MDN3000	98.1%	
2004-108	9/22/2004 CVAFS-10	0.99997	0.020 ng/L	7.92 ng/mL 7.74 ng/mL	99.0% 96.7%	MDN0225 MDN0405 MDN2338	1.6% 3.1% 16.0%	MDN0225 MDN0405 MDN2338	92.5%	MDN2328 0.027 ng/Bottle MDN2168 0.018 ng/Bottle
2004-109	9/21/2004 CVAFS-9	0.99871	0.020 ng/L	7.92 ng/mL 7.90 ng/mL	98.9% 98.6%		15.0% 15.2%	MDN1736 MDN2578 MDN2646	102.2%	
2004-110	9/22/2004 CVAFS-9	0.99979	-0.039 ng/L	7.72 ng/mL 7.64 ng/mL	96.4% 95.4%	MDN1972 MDN2080 MDN2535	3.9% 9.4% 9.7%	MDN1972 MDN2080 MDN2535	116.9%	MDN3008 0.012 ng/Bottle
2004-111	9/23/2004 CVAFS-9	0.99999	0.005 ng/L	7.94 ng/mL 7.34 ng/mL	99.1% 91.7%	MDN0483 MDN1935 MDN2406	2.4% 8.3% 1.8%	MDN0483 MDN1935 MDN2406	102.4%	
2004-112	9/24/2004 CVAFS-9	0.99963	0.022 ng/L	7.60 ng/mL 7.39 ng/mL	95.0% 92.3%	MDN0197 MDN2223 MDN2608	12.9% 5.1% 2.3%	MDN0197 MDN2223 MDN2608	92.0%	
2004-113	9/24/2004 CVAFS-10	0.99959	0.024 ng/L	7.95 ng/mL 7.45 ng/mL	99.3% 93.0%	MDN0487 MDN2160 MDN2468	0.7% 0.1% 3.8%	MDN0487 MDN2160 MDN2468	94.5%	
2004-115	9/28/2004 CVAFS-9	0.99994	0.040 ng/L	8.06 ng/mL 7.35 ng/mL	100.6% 91.9%	MDN0799 MDN0816	6.2% 2.7%	MDN0799 MDN0816		

				MDN0848 3.0%	MDN0848 94.6%	
Quarterly Mean:	0.99964	0.036 ng/L	96.3%	3.0%	102.9%	0.028 ng/Bottle
Std Dev:	±0.00070	±0.031	±4.1%	±3.4%	±21.9%	±0.011

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MDN Quarterly Analysis QC Summary, Quarter 4 of 2004

<u>Analysis</u>	<u>Calibration</u> R	BrCl Blk Conc	SRM (Nist 164 TV=8.005 ng/mL		<u>Duplic</u> Bottle ID	ates RPD	<u>Spik</u> Bottle ID	<u>es</u> Rec.	<u>Bottle Bl</u> Bottle ID	anks Conc
2004-114	10/5/2004 0.99909 CVAFS-9	0.010 ng/L		95.9% 90.1%	MDN0699 MDN1913 MDN2143	4.3% 1.5% 10.7%	MDN0699 MDN1913 MDN2143	89.7%		
2004-116	10/5/2004 0.99993 CVAFS-10	0.044 ng/L	•	97.5% 97.6%	MDN2336 MDN2385 MDN2445	3.0% 2.0% 2.1%	MDN2336 MDN2385 MDN2445	98.2%		
2004-117	10/14/2004 0.99995 CVAFS-10	0.046 ng/L		99.1% 93.9%	MDN0954 MDN1755 MDN2071	2.9% 1.5% 2.0%	MDN0954 MDN1755 MDN2071	97.3%		
2004-118	10/14/2004 0.99936 CVAFS-9	0.030 ng/L		98.5% 90.7%	MDN0640 MDN2027 MDN2129	1.7% 8.0% 6.9%	MDN0640 MDN2027 MDN2129	87.3%		
2004-119	10/15/2004 0.99968 CVAFS-9	0.040 ng/L		99.9% 96.4%	MDN0492 MDN2058 MDN2505	1.2% 4.8% 6.0%	MDN0492 MDN2058 MDN2505	100.4%		
2004-120	10/18/2004 0.99995 CVAFS-10	0.056 ng/L	6.00 ng/mL	96.6% 74.9% 94.9%	MDN0734 MDN2272 MDN2449	1.6% 0.9% 1.2%	MDN0734 MDN2272 MDN2449	97.2%	MDN0283 0.02	24 ng/Bottle
2004-121	10/21/2004 0.99984 CVAFS-10	0.035 ng/L		100.1% 96.7%	MDN2175 MDN2367 MDN2542	1.0% 7.2% 1.3%	MDN2175 MDN2367 MDN2542	94.8%		
2004-122	10/18/2004 0.99987 CVAFS-9	0.002 ng/L		95.0% 92.6%	MDN2064 MDN2117 MDN2548	3.9% 7.2% 9.6%	MDN2064 MDN2117 MDN2548	102.1%	MDN2470 0.01	14 ng/Bottle
2004-123	10/28/2004 0.99984 CVAFS-9	0.047 ng/L		97.1% 94.6%	MDN0796 MDN2049 MDN2331	4.7% 1.2% 2.5%	MDN0796 MDN2049 MDN2331	97.8%		
2004-124	10/27/2004 0.99985 CVAFS-9	0.033 ng/L	· ·	96.2% 89.8%	MDN0142 MDN0155 MDN3000	5.4% 7.4% 1.1%	MDN0142 MDN0155 MDN3000	92.5%		
2004-125	11/4/2004 0.99989 CVAFS-9	0.070 ng/L		95.6% 89.5%	MDN0419 MDN2190 MDN2539	3.5% 17.0% 5.7%	MDN0419 MDN2190 MDN2539	86.3%	MDN2690 0.01 MDN0739 0.01	
2004-126	11/4/2004 0.99985 CVAFS-10	0.042 ng/L		104.0% 93.9%	MDN0123 MDN1740 MDN2453	10.0% 3.9% 1.4%	MDN0123 MDN1740 MDN2453	113.5%		
2004-127	10/21/2004 0.99946 CVAFS-10	0.006 ng/L	7.57 ng/mL 9	94.6%	MDN2174 MDN2235	0.8% 6.2%	MDN2174 MDN2235			
2004-128	11/8/2004 0.99992 CVAFS-9	0.049 ng/L		97.0% 90.5%	MDN0397 MDN2413	4.8% 2.6%	MDN0397 MDN2413		MDN2152 0.02 MDN0199 0.01	•

					MDN2474	9.9%	MDN2474	96.3%	
2004-129	11/9/2004 0.99990 CVAFS-9	0.021 ng/L	7.82 ng/mL 7.49 ng/mL	97.7% 93.6%	MDN0494 MDN2378 MDN2393	6.3% 5.3% 8.5%	MDN0494 MDN2393		
2004-130	11/9/2004 0.99991 CVAFS-10	0.069 ng/L	8.28 ng/mL 8.06 ng/mL	103.4% 100.7%	MDN0811 MDN1975 MDN2577		MDN0811 MDN1975 MDN2577	91.1%	
2004-131	11/16/2004 0.99984 CVAFS-10	0.070 ng/L	8.46 ng/mL 7.44 ng/mL	105.7% 92.9%	MDN0141 MDN2276 MDN2553	1.5% 1.6% 13.7%	MDN0141 MDN2276 MDN2553	101.5%	
2004-132	11/10/2004 0.99993 CVAFS-9	0.006 ng/L	7.71 ng/mL 7.32 ng/mL	96.3% 91.5%	MDN2358 MDN2658 MDN2660	7.8% 3.1% 4.1%	MDN2358 MDN2658 MDN2660	100.2%	MDN2523 0.028 ng/Bottle
2004-133	11/16/2004 0.99991 CVAFS-9	0.038 ng/L	8.01 ng/mL 7.63 ng/mL	100.1% 95.3%	MDN2110 MDN2659 MDN2720	4.3% 7.4% 6.9%	MDN2110 MDN2659 MDN2720	97.3%	MDN0953 0.022 ng/Bottle
2004-134	11/11/2004 0.99993 CVAFS-9	0.032 ng/L	7.84 ng/mL 7.30 ng/mL	97.9% 91.1%	MDN0111 MDN0666 MDN1761	12.7% 3.7% 3.7%	MDN0111 MDN0666 MDN1761	92.7%	
2004-135	11/11/2004 0.99989 CVAFS-10	0.093 ng/L	8.39 ng/mL 7.56 ng/mL	104.8% 94.4%	MDN2391 MDN2439 MDN2666	2.4% 2.0% 1.3%	MDN2391 MDN2439 MDN2666	100.7%	
2004-136	11/12/2004 0.99925 CVAFS-9	0.029 ng/L	7.81 ng/mL 7.36 ng/mL	97.5% 92.0%	MDN0633 MDN0668 MDN0853	4.3% 2.5% 3.5%	MDN0633 MDN0668 MDN0853	96.0%	
2004-137	11/10/2004 0.99983 CVAFS-10	0.039 ng/L	8.32 ng/mL 7.46 ng/mL	104.0% 93.1%	MDN0146 MDN0823	0.3% 0.3%	MDN0146 MDN0823 MDN1954	106.3%	MDN2641 0.035 ng/Bottle
2004-138	11/18/2004 0.99988 CVAFS-9	0.032 ng/L	7.62 ng/mL 7.03 ng/mL	95.2% 87.8%	MDN1928 MDN2477 MDN2694	7.7% 0.5% 4.5%	MDN1928 MDN2477 MDN2694	101.6%	
2004-139	11/22/2004 0.99990 CVAFS-9	0.002 ng/L	7.70 ng/mL 7.53 ng/mL	96.2% 94.0%	MDN0799 MDN2635 MDN2676	5.1% 15.9%	MDN0799 MDN2635 MDN2676	105.5%	
2004-140	12/8/2004 0.99870 CVAFS-10	0.016 ng/L	7.93 ng/mL 8.14 ng/mL	99.0% 101.7%	MDN0678 MDN2395 MDN2582	1.3% 1.0% 0.7%	MDN0678 MDN2395 MDN2582	98.9%	MDN1914 0.047 ng/Bottle
2004-141	12/7/2004 0.99990 CVAFS-10	0.029 ng/L	7.80 ng/mL 7.85 ng/mL	97.4% 98.1%	MDN0949 MDN2583 MDN2606	5.1% 5.8% 2.2%	MDN0949 MDN2583 MDN2606		
2004-142	12/2/2004 0.99977 CVAFS-9	0.030 ng/L	7.80 ng/mL 7.48 ng/mL	97.4% 93.4%	MDN2600 MDN2685 MDN2701	1.4% 1.8% 0.5%	MDN2600 MDN2685 MDN2701		MDN1761 0.014 ng/Bottle MDN1970 0.016 ng/Bottle
2004-143	12/2/2004 0.99979 CVAFS-10	0.038 ng/L	7.82 ng/mL 7.67 ng/mL	97.7% 95.8%	MDN0757 MDN0772	1.3% 3.9%	MDN0757 MDN0772		

					MDN2308	1.0%	MDN2308	105.9%	
2004-144	12/13/2004 0.99995 CVAFS-10	0.034 ng/L	7.66 ng/mL 7.82 ng/mL	95.6% 97.7%	MDN2054 MDN2569 MDN2587	1.1% 0.7% 0.7%	MDN2054 MDN2569 MDN2587	102.3%	MDN0483 0.022 ng/Bottle MDN2080 0.013 ng/Bottle MDN2059 0.012 ng/Bottle
2004-145	12/15/2004 0.99983 CVAFS-9	0.049 ng/L	7.83 ng/mL 7.66 ng/mL	97.8% 95.6%	MDN2213 MDN2217	1.7% 3.8%	MDN2213 MDN2217		
2004-146	12/14/2004 0.99999 CVAFS-9	0.048 ng/L	7.65 ng/mL 7.64 ng/mL	95.6% 95.4%	MDN0761 MDN2487 MDN2608	2.1% 10.6% 0.8%	MDN0761 MDN2487 MDN2608	101.4%	
2004-147	12/14/2004 0.99985 CVAFS-10	0.042 ng/L	7.71 ng/mL 7.81 ng/mL	96.3% 97.5%	MDN0183 MDN0425 MDN2382	0.5% 0.6% 0.8%	MDN0183 MDN0425 MDN2382	101.1%	MDN0969 0.019 ng/Bottle
2004-148	12/15/2004 0.99981 CVAFS-10	0.038 ng/L	7.64 ng/mL 7.73 ng/mL	95.5% 96.6%	MDN0113 MDN0392 MDN2053	5.8% 1.3% 0.3%	MDN0113 MDN0392 MDN2053	98.4%	
2004-149	12/21/2004 0.99981 CVAFS-10	0.030 ng/L	7.78 ng/mL 7.76 ng/mL	97.1% 96.9%	MDN0123 MDN0923 MDN2130	1.9% 2.8% 1.8%	MDN0123 MDN0923 MDN2130	98.9%	MDN2093 0.025 ng/Bottle
2004-150	12/22/2004 0.99987 CVAFS-10	0.026 ng/L	7.71 ng/mL 7.81 ng/mL	96.3% 97.5%	MDN2148 MDN2498 MDN2524	0.5% 0.2% 0.2%	MDN2148 MDN2498 MDN2524	99.3%	
2004-151	12/30/2004 0.99996 CVAFS-9	0.046 ng/L	7.70 ng/mL 7.77 ng/mL	96.2% 97.1%	MDN0489 MDN0758 MDN2189	4.6% 1.8% 6.6%	MDN0489 MDN0758 MDN2189		MDN2365 0.022 ng/Bottle
2004-152	12/27/2004 0.99970 CVAFS-9	0.033 ng/L	7.96 ng/mL 7.70 ng/mL	99.4% 96.1%	MDN0283 MDN2262 MDN3011	6.7% 2.1% 0.8%	MDN0283 MDN2262 MDN3011		
2004-153	12/28/2004 0.99992 CVAFS-9	0.021 ng/L	7.82 ng/mL 7.38 ng/mL	97.7% 92.1%	MDN0125 MDN1933 MDN2725	5.9% 1.9% 4.1%	MDN0125 MDN1933 MDN2725	92.5%	
2004-154	12/28/2004 0.99993 CVAFS-10	0.026 ng/L	7.78 ng/mL 7.88 ng/mL	97.2% 98.4%	MDN2030 MDN2516 MDN2566	0.4% 7.6% 2.2%	MDN2030 MDN2516 MDN2566	109.9%	
2004-155	12/29/2004 0.99964 CVAFS-9	0.030 ng/L	7.62 ng/mL 7.45 ng/mL	95.2% 93.1%	MDN1927 MDN1959 MDN2555	3.9% 1.9% 4.7%	MDN1927 MDN1959 MDN2555	97.1%	MDN1931 0.006 ng/Bottle MDN0938 0.005 ng/Bottle
2004-156	12/27/2004 0.99991 CVAFS-10	0.041 ng/L	7.83 ng/mL 7.88 ng/mL	97.8% 98.4%	MDN1759 MDN2451 MDN2491	1.6% 4.4% 0.2%	MDN1759 MDN2451 MDN2491	97.4%	
2004-157	12/29/2004 0.99949 CVAFS-10	0.063 ng/L	8.05 ng/mL 7.49 ng/mL	100.6% 93.6%	MDN1973 MDN2011 MDN2657	9.2% 6.6% 0.3%	MDN1973 MDN2011 MDN2657	94.9%	MDN2413 0.014 ng/Bottle
	ly Mean: 0.99978 Std Dev: ±0.00024	0.037 ng/L ±0.019		96.1% ±4.1%		3.9% ±3.5%		103.0% ±18.6%	0.019 ng/Bottle ±0.009

Methylmercury Quarterly Analysis QC Summary, Quarter 1 of 2004

DataSetID		Calibration	Prep Blk	Dorm - 2		Duplicates		Spikes		
		R	Conc. (ng/L)	TV=4470 ng/L	%Rec	Comp ID	RPD	Comp ID	%Rec	RPD
MHG7-040106-1	1/6/2004	0.99848	0.050	3856.686	86.3	WA1820031209	23.3	NS0120031202 MS	78.21	3.0
CVAFS-7	Batch#100							NS0120031202 MSD	80.77	
MHG1-040108-1	1/8/2004	0.99937	0.040	3951.369	88.4	OR10 COMP 013	12.3	OR10 COMP 013 MS	84.29	7.8
CVAFS-1	Batch#101							OR10 COMP 013 MSD	92.99	
MHG7-040129-1	1/29/2004	0.99993	0.000	4385.717	98.1	OR10 COMP 014	15.6	OR10 COMP 014 MS	92.08	0.1
CVAFS-7	Batch#103							OR10 COMP 014 MSD	91.95	
MHG7-040212-1	2/12/2004	0.99999	0.050	4871.615	109.0	LA2320040203	5.4	LA2320040127 MS	103.19	4.3
CVAFS-7	Batch#104							LA2320040127 MSD	107.82	
MHG1-040302-1	3/2/2004	0.99985	0.060	4595.395	102.8	LA0520040217	30.0	LA1020040217 MS	94.26	2.2
CVAFS-1	Batch#105							LA1020040217 MSD	92.06	
MHG7-040309-1	3/9/2004	0.99943	0.030	4407.775	98.6	IN2120040203	4.9	OR10 COMP 015 MS	99.04	6.5
CVAFS-7	Batch#106							OR10 COMP 015 MSD	91.76	
MHG7-040316-1	3/16/2004	0.99989	0.030	4734.368	105.9	LA2320040302	6.1	LA2820040225 MS	105.23	4.2
CVAFS-7	Batch#107							LA2820040225 MSD	100.71	
MHG7-040324-1	3/24/2004	0.99893	0.120	4506.614	100.8	FL04 COMP 034	300.0	OR10 COMP 016 MS	102.33	16.9
CVAFS-7	Batch#108							OR10 COMP 016 MSD	83.85	
MHG7-040331-1	3/31/2004	0.99997	0.090	4770.290	106.7	LA1020040309	17.1	LA0520040316 MS	101.97	3.1
CVAFS-7	Batch#109							LA0520040316 MSD	98.74	

Methylmercury Quarterly Analysis QC Summary, Quarter 2 of 2004

DataSetID		Calibration	Prep Blk	Prep Blk Dorm - 2		Duplicates		Spikes			
		R	Conc (ng/L)	TV=4470 ng/L	%Rec	Comp ID	RPD	Comp ID	%Rec	RPD	
MHG7-040409-1	4/9/2004	0.99954	0.090	4464.019	99.9	IN3420040330	13.5	WA1820040330 MS	94.39	3.3	
CVAFS-7	Batch#110							WA1820040330 MSD	90.57		
MHG1-040414-1	4/14/2004	0.99981	0.000	4971.940	111.2	IN3920040406	8.2	NS0120040406 MS	97.70	4.2	
CVAFS-1	Batch#111							NS0120040406 MSD	93.08		
MHG7-040423-1	4/23/2004	0.99997	0.120	4687.644	104.9			LA0520040413 MSD	83.85	0.0	
CVAFS-7	Batch#112							LA0520040413 MS	83.85		
MHG7-040519-1	5/19/2004	0.99995	0.030	4417.574	98.8	NS0120040420	7.9	FL04 COMP 037 MS	95.77	6.1	
CVAFS-7	Batch#113							FL04 COMP 037 MSD	102.01		
MHG7-040521-1	5/21/2004	0.99999	0.070	4916.858	110.0	LA1020040505	13.6	LA2820040504 MS	101.29	0.0	
CVAFS-7	Batch#114							LA2820040504 MSD	101.29		
MHG1-040609-1	6/9/2004	0.99995	0.080	5183.158	116.0	WI22 COMP 016	8.0	WI22 COMP 016 MS	93.13	10.7	
CVAFS-1	Batch#115							WI22 COMP 016 MSD	82.56		
MHG1-040617-1	6/17/2004	0.99514	-0.010	4716.470	105.5	WI31 COMP 029	41.4	WI99 COMP 097 MS	80.86	7.2	
CVAFS-1	Batch#116							WI99 COMP 097 MSD	87.78		

Methylmercury Quarterly Analysis QC Summary, Quarter 3 of 2004

DataSe	etID	Calibration	Prep Blk	Dorm - 2	2	Duplicates		Spike	S	
		R	Conc (ng/L)	TV=4470 ng/L	%Rec	Comp ID	RPD	Comp ID	%Rec	RPD
MHG7-040709-1 CVAFS-7	7/9/2004 Batch#117	0.99969	0.000	4501.024	100.7	LA0520040622	30.7	NS0120040629 MS 101 NS0120040629 MSD	0.60 103.96	2.0
MHG7-040722-1 CVAFS-7	7/22/2004 Batch#118	0.99976	0.060	4617.126	103.3	FL32 COMP 010	20.2	GA09 COMP 022 MS GA09 COMP 022 MSD	98.68 98.68	0.0
MHG7-040805-1 CVAFS-7	8/5/2004 Batch#119	0.99840	0.070	4649.854	104.0	LA2820040706	2.5	LA2320040706 MS LA2320040706 MSD	88.90 84.70	4.7
MHG7-040820-1 CVAFS-7	8/20/2004 Batch#120	0.99986	0.000	4662.252	104.3	MD98 COMP 002	0.0	GA09 COMP 023 MS GA09 COMP 023 MSD	95.40 9.86	143.4
MHG7-040909-1 CVAFS-7	9/9/2004 Batch#121	0.99993	0.130	4029.792	90.2	FL3220040814	0.0			
MHG7-040916-1 CVAFS-7	9/16/2004 Batch#122	0.99982	0.080	4235.328	94.8	GA0920040813	100.0	SC0520040817 MS SC0520040817 MSD	107.40 85.12	22.2
MHG7-040930-1 CVAFS-7	9/30/2004 Batch#123	0.99989	0.070	4930.021	110.3	FL04 COMP 041	0.0	FL11 COMP 041 MS FL11 COMP 041 MSD	94.40	4.9
Methvlmercur	v Quarterly	Analvsis QC	Summarv. Q	uarter 4 of 200)4					
DataSe	•	Calibration	Prep Blk	Dorm - 2		Duplicates		Spike	S	
		R	Conc (ng/L)	TV=4470 ng/L	%Rec	Comp ID	RPD	Comp ID	%Rec	RPD
MHG7_0/1007_1	10/7/2004	0.00227	U U3U	E242 042	117 2	NSU12UUAUU21	33 U	ELUE COMP USE MG	11/1 2/	3 0

DataSetID		Calibration	Prep Blk	Dorm - 2		Duplicates		Spikes			
		R	Conc (ng/L)	TV=4470 ng/L	%Rec	Comp ID	RPD	Comp ID	%Rec	RPD	
MHG7-041007-1	10/7/2004	0.99837	0.030	5242.942	117.3	NS0120040921	33.0	FL05 COMP 025 MS	114.24	3.9	
CVAFS-7	Batch#124							FL05 COMP 025 MSD	109.82		
MHG7-041021-1	10/21/2004	0.99953	0.060	4368.177	97.7	MN23 COMP 104	30.1	FL32 COMP 013 MS	97.87	9.0	
CVAFS-7	Batch#125							FL32 COMP 013 MSD	89.35		
MHG1-041104-1	11/4/2004	0.99990	0.020	5240.390	117.2	NS0120041005	12.5	MN16 COMP 104 MS	119.89	13.9	
CVAFS-1	Batch#126							MN16 COMP 104 MSD	103.28		
MHG7-041111-1	11/11/2004	0.99974	0.090	4688.745	104.9	LA2820040831	8.7				
CVAFS-7	Batch#127										
MHG7-041202-1	12/2/2004	0.99577	0.040	4101.590	91.8	WA1820040914	7.3	NS0120041109 MS	95.10	11.2	
CVAFS-7	Batch#128							NS0120041109 MSD	84.60		
MHG1-041218-1	12/18/2004	0.99928	0.020	4870.871	109.0	FL04 COMP 044	0.0	LA232009411003 MS	97.42	1.8	
CVAFS-1	Batch#129							LA232009411003 MSD	99.16		