

CALFED Mercury Project Quality Assurance Oversight

Analysis and Evaluation of Sample Splits

Submitted: December 5, 2003

submitted to:

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1. Introduction

As outlined in the CALFED Mercury Project Quality Assurance Oversight Proposal, Frontier Geosciences, Inc. (Frontier) has conducted a quality assurance analysis of the samples provided by the five participating laboratories:

- ◆ Central Valley Regional Water Quality Control Board
- ◆ Moss Landing Marine Laboratories
- ◆ Texas A&M University at Galveston
- ◆ University of California at Davis
- ◆ United States Geological Survey

The purpose of this program is to assess the sampling procedures and analyses of each of the participating laboratories. This document outlines sample collection and submission; sample receipt, preservation, and storage; sample analyses method descriptions; analysis results comparison; recommendations and conclusions.



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2. Sample Collection and Submission

Each participating laboratory was required to collect and submit field sample splits for external quality assurance analysis by Frontier. The field sample splits were rotated among sites and events to achieve an overall rate of at least five percent sample submission. Participating laboratories collected and submitted the samples to Frontier between March 2000 and November 2001.



3. Sample Receipt, Preservation, and Storage

Frontier received all of the samples from the participating laboratories according to the strict guidelines of Frontier's Standard Operating Procedure: *Sample Receipt, Chain of Custody, Tracking, and Disposal* (FGS-005). All samples were received using ultra-clean sample handling techniques in a laboratory identified to be low in atmospheric mercury.

Frontier received all samples listed on the chain-of-custody forms in good condition unless otherwise noted. Upon receipt, Frontier recorded the temperature and properly labeled all of the samples. Frontier preserved and stored the samples based upon their type and required analysis in the following manner:

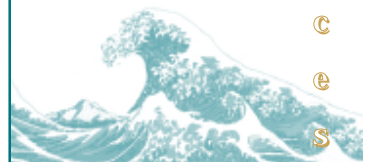
- ◆ Sediment samples for mercury and methyl mercury analysis that were shipped cold but not frozen were stored at approximately 4 °C.
- ◆ Sediment samples for mercury and methyl mercury analysis that were shipped frozen were stored at below 0 °C.
- ◆ Tissue samples for mercury and methyl mercury analysis were stored at below 0 °C.

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- ◆ Water samples for mercury analysis were oxidized to 1% (v/v) with 0.2 N BrCl and stored at approximately 20 °C.
- ◆ Water samples for methyl mercury analysis were preserved with to 0.4% (v/v) with 12 N HCl and stored at approximately 4 °C in a dark environment.



4. Sample Analysis Method Descriptions

All reagents, gases, and water used by Frontier to prepare and analyze samples are ultra-pure grade and pre-analyzed and routinely monitored to ensure sufficiently low concentrations of the analyte of interest in the preparation blanks and used during sample preparation and analysis.

Mercury analyses are performed using cold vapor-atomic fluorescence spectrometry (CV-AFS), with dual pen chart recorders or integrators as output devices. Total mercury (THg) and dissolved mercury (DHg) standards are prepared by the direct dilution of NIST certified NBS-3133 mercury standard solution. The results are independently verified by the analysis of NIST-1641d (water certified reference material).

Total monomethyl mercury (TMMHg) and dissolved monomethyl mercury (DMMHg) standards are made from pure powder and accurately calibrated for monomethyl mercury (equal to total mercury minus ionic mercury) against NSB-3133. The results are verified by daily analysis of NRCC DORM-2.

All daily analytical runs begin with a five-point standard curve spanning two orders of magnitude with additional



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standards analyzed every ten samples. The daily standard curve is calculated using the initial standards (blank corrected) of the day, with linear regression forced through zero. For each sample set, at least one matrix duplicate sample, two matrix spike samples, and three method blanks (preparation blanks) are co-processed and analyzed in exactly the same manner as the samples.

A. Mercury Analysis

Sediment samples for THg analysis are first digested in 10 mL of modified aqua regia, followed by dilution to 40 mL with reagent water. Tissue samples for THg analysis are first digested in 10 mL of hot refluxing 7:3 HNO₃/H₂SO₄, followed by dilution to 40 mL with 0.2 N BrCl. Water samples for THg analysis are oxidized to 1% (v/v) with 0.2 N BrCl and then allowed to digest overnight at room temperature. Digests are analyzed for total mercury in strict accordance with the Standard Operating Procedures outlined in the *Frontier Geosciences Quality Assurance Manual (Frontier QAM)* and *CALFED Mercury Project Quality Assurance Project Plan (CALFED QAPP)*.

Aliquots of each digest (up to 100 mL for waters, 0.01 to 5 mL for solids digests) are reduced in pre-purged reagent water to Hg⁰ with SnCl₂. The Hg⁰ is then purged onto gold traps as a pre-concentration process.

The mercury contained on the gold traps is then analyzed by thermal desorption into the CV-AFS using a dual amalgamation technique. Peak heights or peak areas are accessed by chart recorders or integrators respectively, and recorded on bench sheets in chart units to the nearest 0.2 unit.

Net mercury concentrations are calculated according to the following formula:

Sediments $[\text{THg}] \text{ (ng/g)} = \{[(\text{PH}-\text{b})/\text{S}] * (\text{V}/\text{v}) - \text{B}\} / \text{m}$

Tissues $[\text{THg}] \text{ (ng/g)} = \{[(\text{PH}-\text{b})/\text{S}] * (\text{V}/\text{v}) - \text{B}\} / \text{m}$

Waters $[\text{THg}] \text{ (ng/L)} = [(\text{PH}-\text{b})/\text{S}] / \text{V}-\text{B}$

- **PH** is the chart recorder peak height or integrator peak area in chart units
- **b** is the mean peak height or peak area of the bubbler blanks
- **S** is the calibration curve slope in units/ng
- **V** is the volume of digestate analyzed in L units
- **B** is the mean method blank in ng/L units
- **v** is the final volume of the digestate in L units
- **m** is the mass of solid sample analyzed in g units

B. Monomethyl Mercury Analysis

Sediments must be cold-extracted due to the potential for significant positive monomethyl mercury artifact-formation during the distillation of samples containing high levels of inorganic mercury. Aliquots of these samples are accurately weighed into 40-mL Teflon centrifuge tubes, and aliquots of H₂SO₄/KBr solution and CuSO₄ solution are added.

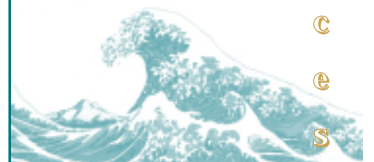
Following mixing, an aliquot of CH₂Cl₂ is added to each tube and the samples are shaken for one hour. The samples are then centrifuged to separate the solvent from the aqueous layer. Exactly 2.0 mL of CH₂Cl₂ are removed from each sample and inserted into a Teflon vial containing reagent water. The samples are heated to 45° C and purged with nitrogen to volatize the CH₂Cl₂, thus releasing the monomethyl mercury to the pure aqueous phase.

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Tissues, due to inherently higher monomethyl mercury concentrations, are digested with 10 mL of hot 25% KOH/MeOH for two hours and diluted to 40 mL with MeOH. The digestates are then analyzed directly for MMHg and Hg(II).

Water samples are distilled prior to analysis to liberate the MMHg. Using a Teflon distillation system, each sample is distilled in strict accordance to the Standard Operating Procedures outlined in the Frontier QAM and CALFED QAPP. The procedure requires 45 mL (for higher TMMHg samples, a smaller aliquot diluted to 45 mL) of acidified sample to be distilled using 60 mL Teflon distillation tubes. An aliquot of APDC solution is added to each sample prior to distillation to enhance reproducibility and recovery.

The distillate is received in a vessel containing 5 mL of reagent water and distilled to 40 mL. Thus, 35 mL out of 45 mL of sample is distilled for the analysis. The historic mean MMHg distillation recovery has been determined to be $89.4 \pm 10.6\%$ ($n = 136$ distillations in 2001). All net MMHg results for water samples are corrected for this empirically derived distillation efficiency.

Distilled, digested, or extracted samples are analyzed using aqueous phase ethylation, purging onto Carbotrap (iodated carbon), isothermal GC separation, and CV-AFS. Prior to ethylation, the distillate is diluted to 55 mL with reagent water, and the pH adjusted to 4.9 with the addition of an acetate buffer. Samples are ethylated by the addition of NaBEt_4 , and then the volatile ethyl analogs are purged with nitrogen onto Carbotrap.

Subsequent to a trap-drying step, the mercury ethyl analogs are thermally desorbed into a 1.3-m isothermal GC column (15% OV-3 on Chromasorb WAW-DMSC) heated at 100°C for separation. The column resolves the following peaks: elemental mercury, dimethyl mercury, methyl ethyl mercury, and diethyl mercury. Due to the wet chemistry used, only the methyl ethyl mercury and the monomethyl mercury analogs are quantified for this assay.

The organo-mercury compounds are pyrolytically broken down to Hg^0 prior to entering the CV-AFS detector for quantification.

Peak heights are accessed by chart recorder, and recorded on bench sheets in chart units to the nearest 0.2 unit. In the calculations below, 0.894 is the distillation recovery factor, and 5 is factored to account for the 2 out of 10 mL of the CH_2Cl_2 that was back extracted into the aqueous phase. The extraction procedure has no recovery factor, as it is essentially quantitative.

Net MMHg concentrations are calculated according to the following formula:

Sediments $[MMHg] \text{ (ng/g)} = \{[(PH-b)/S*5*(V/v)]-B\}/m$

Tissues $[MMHg] \text{ (ng/g)} = \{[(PH-b)/S*(V/v)]-B\}/m$

Waters $[MMHg] \text{ (ng/L)} = [(PH-b)/S/0.894/V]-B$

- **PH** is the recorder peak height in chart units
- **b** is the mean peak height or peak area of the bubbler blanks
- **S** is the calibration curve slope in units/ng
- **V** is the volume of digestate analyzed in L units
- **B** is the mean method blank in ng/L units
- **v** is the final volume of the digestate in L units
- **m** is the mass of solid sample analyzed in g units



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5. Analysis Results Comparison and Discussion

Each participating laboratory collected and submitted the following field sample splits for external quality assurance analysis by Frontier. Participating laboratories collected and submitted the samples to Frontier between March 2000 and November 2001.

The results of Frontier's analyses were compared against the participating laboratory's results and the relative percentage difference (RPD) calculated. Results that fell below either the participating laboratory's or Frontier's reporting limit have been noted below. Any instance of a sample's calculated RPD value being greater than 25% has also been noted below.

Please note that all THg results from samples analyzed between June 2001 and January 6, 2003 at Frontier are likely to have been affected by a bias in the calibration standards. In short, ignoring all other analytical variability, the results we initially reported were approximately 8% bias-low. All Frontier generated results included in this final report have been corrected for the low bias. Frontier prepares standards from a primary NIST reference material (NIST-3133, 10.00 ppm Hg in nitric acid), which we replace annually. In 2001, without specific notification, NIST began certifying this standard in mg/kg unit instead

of in mg/L units (the 10% HNO₃ matrix has a specific gravity of 1.08).

In many cases this bias is less significant than routine instrument variability and rounding of results. Because this bias was small, all our ongoing quality control parameters (calibration verifications, spike recoveries, other CRM recoveries) remained well within their limits and all data met acceptance criteria.

A. **Central Valley Regional Water Quality Control Board (CVRB)**

CVRB submitted ten water sample sets from three sites between March 2000 and October 2001. For a summary of the data, see Appendix A1.

1. **Waters**

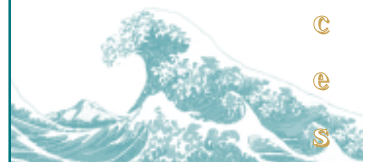
- ◆ **THg**—Quality Assurance Compliance: 80%. For the THg analyses, the RPD values of two of the ten samples were greater than 25%.
- ◆ **DHg**—Quality Assurance Compliance: 80%. For the DHg analyses, the RPD values of two of the ten samples were greater than 25%.
- ◆ **TMMHg**—Quality Assurance Compliance: 80%. For the TMMHg analyses, the RPD values of two of the ten samples were greater than 25%.
- ◆ **DMMHg**—Quality Assurance Compliance: 100%. For the DMMHg analyses, the RPD values of three of the six samples were greater than 25%; however, the values of the results from both laboratories were less than four times Frontier's reporting limit of 0.020 ng/L

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B. Moss Landing Marine Laboratories (MLML)

MLML submitted fifteen sediment samples on November 22, 2001, and forty-four tissue samples between May 2000 and September 2001. For a summary of the data, see Appendix A2.

1. Sediments

- ◆ **THg**—Quality Assurance Compliance: 100%. For the THg analyses, the RPD values of all thirteen of the samples analyzed were less than 25%.
- ◆ **MMHg**—Quality Assurance Compliance: 13%. For the MMHg analyses, the RPD values of thirteen of the fifteen samples were greater than 25%. Dr. Mark Stevens stated in the MLML final report that “further research is needed in the freezing and thawing process of the samples during long term storage”. Frontier agrees with this statement and would stress for all future 5% comparison samples received for analysis, a chart of the receipt temperature and the shipment temperature be reviewed by Frontier and MLML which may establish a possible trend that hindering reproducibility between labs.

2. Tissues

- ◆ **THg**—Quality Assurance Compliance: 95%. For the THg analyses, the RPD values of two of the forty-four samples were greater than 25%.
- ◆ **MMHg**—Quality Assurance Compliance: 100%. For the MMHg analyses, the RPD values of both samples were less than 25%.

C. Texas A&M University at Galveston (TAMUG)

TAMUG submitted nine water samples and three sediment samples between February and June 2001. For the complete data, see Appendix A4.

1. Waters

- ◆ **THg** – Quality Assurance Compliance: 33%. For the total mercury analyses, the RPD values of two of the three samples were greater than 25%.
- ◆ **DHg** – Quality Assurance Compliance: 50%. For the total mercury analyses, the RPD values of two of the three samples were greater than 25%; however, for one of these samples the results from both laboratories were less than the Frontier reporting limit of 0.15 ng/L.
- ◆ **TMMHg** – Quality Assurance Compliance: 100%. For the total methyl mercury analyses, the RPD values of two of the three samples were greater than 25%; however, for both of these samples the results from both laboratories were less than four times the Frontier reporting limit of 0.020 ng/L.
- ◆ **DMMHg** – Quality Assurance Compliance: 100%. For the dissolved methyl mercury analyses, the RPD values of all three of the samples were greater than 25% or not calculated; however, the values of the results from both laboratories were less than two times Frontier's reporting limit of 0.020 ng/L.

2. Sediments

- ◆ **TMMHg** – Quality Assurance Compliance: 33%. For the methyl mercury analyses, the

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RPD values of two of the three samples were greater than 25%.

D. University of California at Davis (UCD)

UCD submitted thirty-eight tissue samples between April and November 2001, and eight water samples sets between March and July 2000. For a summary of the data, see Appendix A4.

1. Tissues

- ◆ **THg**—Quality Assurance Compliance: 92%. For the THg analyses, the RPD values of three of the thirty-eight samples were greater than 25%.
- ◆ **MMHg**—Quality Assurance Compliance: 82%. For the MMHg analyses, the RPD values of seven of the thirty-eight samples were greater than 25%.

2. Waters

- ◆ **THg**—Quality Assurance Compliance: 50%. For the THg analyses, the RPD values of four of the eight samples were greater than 25%.
- ◆ **DHg**—Quality Assurance Compliance: 63%. For the DHg analyses, the RPD values of three of the eight samples were greater than 25%.
- ◆ **TMMHg**—Quality Assurance Compliance: 86%. For the TMMHg analyses, the RPD values of two of the eight samples were greater than 25%; however, for one of the samples the values of the results from both labs were less than four times Frontier's reporting limit of 0.020 ng/L.
- ◆ **DMMHg**—Quality Assurance Compliance: 60%. For the DMMHg analyses, the RPD values of five of the

eight samples were an issue. The RPD values for three of the samples were greater than 25%; however, for one of the samples, the values of the results from both laboratories were less than four times Frontier's reporting limit of 0.020 ng/L. The RPD values for two of the samples were not calculated because the values of Frontier's results were less than Frontier's reporting limit of 0.020 ng/L.

E. United States Geological Survey (USGS)

USGS submitted water sample sets from three sites between March 2000 and February 2001. For a summary of the data, see Appendix A5.

1. Waters

- ◆ **THg**—Quality Assurance Compliance: 0%. For the THg analyses, the RPD values of all three samples were greater than 25%.
- ◆ **DHg**—Quality Assurance Compliance: 100%. For the DHg analyses, the RPD values of all three samples were less than 25%.
- ◆ **TMMHg**—Quality Assurance Compliance: 33%. For the TMMHg analyses, the RPD values of two of the three samples were greater than 25%.
- ◆ **DMMHg**—Quality Assurance Compliance: 100%. For the DMMHg analyses, the RPD values of two of the three samples were not calculated because the values of USGS' results were less than USGS' reporting limit of 0.022 ng/L.

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V. Recommendations and Conclusions

Few conclusions can be suggested from this very limited set of data. Intercomparability of results for the following parameters should be investigated further: THg in waters (total and dissolved) and MMHg in sediments. These are the same matrix/analyte combinations that raised concern during the Intercomparison Study (reported by Frontier Geosciences March 2000 and May 2001); therefore, it is strongly recommended that continued QA oversight effort be expended for specific research groups prior to commencing on the next phase of research.

One of the most important aspects of the QA oversight effort is the analysis and interpretation of the five-percent QA field splits. For future CALFED Mercury Project research, it is strongly recommended that a database be funded which would allow the “real time” entry of not only the five percent splits but all analytical run QC, in turn allowing the program manager, project manager, and all participating researchers the ability to enter and generate comparative results. The immediate generation of comparative results would allow any patterns between duplicate samples to be reviewed and corrective action instigated sooner.

For the research groups where one or more of the applicable matrix/analyte combinations exhibited a QA Compliance rating of less than 75%, a QA audit (as described in the *Frontier Geosciences Proposal for Programmatic QA Oversight for the CALFED Mercury Project* dated June 18, 2003) should be performed prior to further research for this project.

Some discrepancies were seen in the total mercury/methyl mercury ratios of the fish data from the oversight laboratory. The antiquated method used at the time that these samples were analyzed has now been abandoned for a more current method, with which these discrepancies are not seen. Therefore, a QA Compliance rating of less than 75% for this parameter does not necessarily indicate a QC problem at the participating research group.

The CALFED Mercury Project QA Oversight effort and the analysis of the five-percent QA field splits demonstrate the dedication by program management to insure that data from all project sub-tasks and research groups will show consistency and intercomparability.

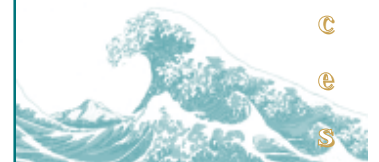


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Appendix A-1

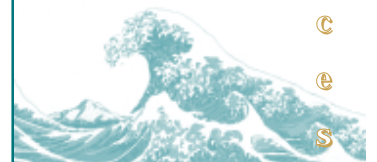
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Note: THg and DHg values from Frontier were adjusted +8% post-reporting

Water Samples

Receipt Date	Sample ID	Analysis	CVRB Result	Frontier Result	RPD (%)	Comments
3/29/00	Prospect Slough	THg (ng/L)	38.6	30.8	22.4	
3/29/00	Prospect Slough	DHg (ng/L)	1.89	1.52	21.5	
2/1/01	Sacramento River at Greene Landing	THg (ng/L)	22.89	26.95356	16.3	
2/1/01	Sacramento River at Greene Landing	DHg (ng/L)	2.55	2.66868	4.5	
3/1/01	Sacramento River at Greene Landing	THg (ng/L)	14.55	14.49792	0.4	
3/1/01	Sacramento River at Greene Landing	DHg (ng/L)	2.56	2.35872	8.2	
3/29/01	Sacramento River at Greene Landing	THg (ng/L)	3.42	4.1526	19.3	
3/29/01	Sacramento River at Greene Landing	DHg (ng/L)	0.75	1.03788	32.2	RPD > 25
5/3/01	Prospect Slough	THg (ng/L)	21.4	14.8	36.3	RPD > 25
5/3/01	Prospect Slough	DHg (ng/L)	0.79	0.71	10.3	
5/31/01	Prospect Slough	THg (ng/L)	44.8	32.2	32.7	RPD > 25
5/31/01	Prospect Slough	DHg (ng/L)	1.40	1.51	7.7	
6/28/01	Prospect Slough	THg (ng/L)	37.7	31.1	19.2	
6/28/01	Prospect Slough	DHg (ng/L)	1.23	2.86	79.7	RPD > 25
8/2/01	Molelumne-Consumnes Rivers	THg (ng/L)	6.96	6.40	8.3	
8/2/01	Molelumne-Consumnes Rivers	DHg (ng/L)	1.15	1.36	16.6	
8/30/01	Prospect Slough	THg (ng/L)	28.1	22.6	21.6	
8/30/01	Prospect Slough	DHg (ng/L)	1.36	1.27	6.5	
10/4/01	Prospect Slough	THg (ng/L)	18.0	14.8	19.7	
10/4/01	Prospect Slough	DHg (ng/L)	1.04	1.18	12.4	
3/29/00	Prospect Slough	TMMHg (ng/L)	0.701	1.02	36.9	RPD > 25
2/1/01	Sacramento River at Greene Landing	TMMHg (ng/L)	0.244	0.254	4.0	
2/1/01	Sacramento River at Greene Landing	DMMHg (ng/L)	0.058	0.057	1.7	
3/1/01	Sacramento River at Greene Landing	TMMHg (ng/L)	0.177	0.252	35.0	RPD > 25
3/1/01	Sacramento River at Greene Landing	DMMHg (ng/L)	0.083	0.095	13.5	

Receipt Date	Sample ID	Analysis	CVRB Result	Frontier Result	RPD (%)	Comments
3/29/01	Sacramento River at Greene Landing	TMMHg (ng/L)	0.084	0.097	14.4	
5/3/01	Prospect Slough	TMMHg (ng/L)	0.144	0.168	15.4	
5/3/01	Prospect Slough	DMMHg (ng/L)	< 0.014	0.030	N/C	
5/31/01	Prospect Slough	TMMHg (ng/L)	0.229	0.227	0.9	
5/31/01	Prospect Slough	DMMHg (ng/L)	0.069	0.018	117.2	RPD > 25; both values < 4x the Frontier RL of 0.020 ng/L
6/28/01	Prospect Slough	TMMHg (ng/L)	0.208	0.234	11.8	
8/2/01	Molelumne-Consumnes Rivers	TMMHg (ng/L)	0.167	0.186	10.8	
8/2/01	Molelumne-Consumnes Rivers	DMMHg (ng/L)	0.050	0.075	40.0	RPD > 25; both values < 4x the Frontier RL of 0.020 ng/L
8/30/01	Prospect Slough	TMMHg (ng/L)	0.141	0.165	15.7	
8/30/01	Prospect Slough	DMMHg (ng/L)	0.047	0.025	61.1	RPD > 25; both values < 3x the Frontier RL of 0.020 ng/L
10/4/01	Prospect Slough	TMMHg (ng/L)	0.122	0.103	16.9	



Appendix A-2

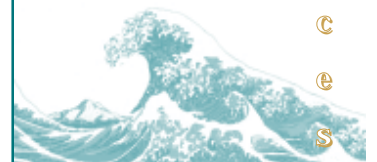
Moss Landing Marine Laboratories (MLML)

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**Analysis and
Evaluation
of Sample Splits**

December 2003

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Moss Landing Marine Laboratories (MLML)

Note: THg and DHg values from Frontier were adjusted +8% post-reporting

Sediment Samples

Receipt Date	Sample ID	Analysis	MLML Result	Frontier Result	RPD (%)	Comments	
11/22/00	L187	158 Petaluma Pt. Marsh	THg (ng/g)	322	345	6.9	
11/22/00	L194	130 Suisan Bay	THg (ng/g)	335	345	2.9	
11/22/00	L219	361 Cache Creek @ Conway Ranch	THg (ng/g)	575	580	0.9	
11/22/00	L236	214 Liberty Island	THg (ng/g)	266	234	12.8	
11/22/00	L294	152 SPB National Wildlife Refuge	THg (ng/g)	278	300	7.6	
11/22/00	L358	256 San Pablo Bay	THg (ng/g)	288	355	20.8	
11/22/00	L489	272 SFB near Brook Island	THg (ng/g)	534	541	1.3	
11/22/00	L522	111 Mallard Island	THg (ng/g)	287	353	20.6	
11/22/00	L555	64 Beaver Slough	THg (ng/g)	190	201	5.6	
11/22/00	L627	313 SFB	THg (ng/g)	240	269	11.4	
11/22/00	L679	153 Napa Slough	THg (ng/g)	347	366	5.3	
11/22/00	L819	131 Goodyear Slough	THg (ng/g)	340	399	16.0	
11/22/00	L822	306 SFB near SFO	THg (ng/g)	285	349	20.2	
11/22/00	L187	158 Petaluma Pt. Marsh	MMHg (ng/g)	0.101	0.214	71.7	RPD > 25
11/22/00	L194	130 Suisan Bay	MMHg (ng/g)	0.261	0.166	44.5	RPD > 25
11/22/00	L219	361 Cache Creek @ Conway Ranch	MMHg (ng/g)	0.810	10.8	172.2	RPD > 25
11/22/00	L236	214 Liberty Island	MMHg (ng/g)	0.643	0.952	38.7	RPD > 25
11/22/00	L294	152 SPB National Wildlife Refuge	MMHg (ng/g)	0.171	0.236	31.9	RPD > 25
11/22/00	L358	256 San Pablo Bay	MMHg (ng/g)	0.079	0.261	107.1	RPD > 25
11/22/00	L457	61 North Mokelumne River	MMHg (ng/g)	0.494	5.67	167.9	RPD > 25
11/22/00	L489	272 SFB near Brook Island	MMHg (ng/g)	0.467	0.750	46.5	RPD > 25
11/22/00	L522	111 Mallard Island	MMHg (ng/g)	0.290	0.743	87.7	RPD > 25
11/22/00	L555	64 Beaver Slough	MMHg (ng/g)	0.650	0.895	31.7	RPD > 25
11/22/00	L627	313 SFB	MMHg (ng/g)	0.218	0.411	61.4	RPD > 25
11/22/00	L679	153 Napa Slough	MMHg (ng/g)	0.259	0.470	57.9	RPD > 25
11/22/00	L819	131 Goodyear Slough	MMHg (ng/g)	0.502	0.433	14.8	
11/22/00	L822	306 SFB near SFO	MMHg (ng/g)	1.10	1.22	10.3	
11/22/00	L917	Seasonal Connection Slough	MMHg (ng/g)	0.950	2.84	99.8	RPD > 25

Moss Landing Marine Laboratories (MLML)

Note: THg and DHg values from Frontier were adjusted +8% post-reporting

Tissue Samples

Receipt Date	Sample ID	Analysis	MLML Result	Frontier Result	RPD (%)	Comments	
5/3/00	99-1143	Mokelumne downstream of Cosumnes	THg (ng/g)	752	647	15.0	
5/3/00	99-1164	Smith Canal by Yosemite Park	THg (ng/g)	486	466	4.2	
5/3/00	99-1169	Port of Stockton Turning Basin	THg (ng/g)	110	124	12.0	
5/3/00	99-1306	Paradise Cut	THg (ng/g)	51.7	54.9	6.0	
5/3/00	99-1410	Old River near Paradise Cut	THg (ng/g)	270	284	5.1	
5/3/00	99-1421	Darrel's Cosumnes River	THg (ng/g)	1000	980	2.0	
5/3/00	99-1428	SJR downstream of Vernalis	THg (ng/g)	511	610	17.7	
5/3/00	99-1432	Lake Nacimiento/Las Tablas Creek	THg (ng/g)	1310	1300	8.5	
5/3/00	99-1820	SJR around Turner's Cut	THg (ng/g)	96.7	94.2	2.6	
5/3/00	99-1831	SJR around Bowman Road	THg (ng/g)	1030	1240	11.4	
7/18/00	99-1054	Sacramento River @ RM47	THg (ng/g)	524	711	30.3	RPD > 25
7/18/00	99-1151	SJR North of Hwy 4	THg (ng/g)	147	140	4.9	
7/18/00	99-1158	Mokelumne between Beaver and Hog Sloughs	THg (ng/g)	205	264	25.2	RPD > 25
7/18/00	99-1221	Feather River @ Nicolaus	THg (ng/g)	667	606	9.6	
7/18/00	99-1293	Middle River @ Bullfrog	THg (ng/g)	170	140	19.4	
7/18/00	99-1494	Suisun Bay	THg (ng/g)	503	511	1.6	
7/18/00	99-1805	Sycamore Slough near Mokelumne River	THg (ng/g)	< 28.2	30.0	N/C	
7/18/00	99-1811	SJR near Potato Slough	THg (ng/g)	244	233	4.6	
7/18/00	99-1812	White Slough @ Lodi	THg (ng/g)	128	124	3.2	
7/18/00	99-1831	SJR around Bowman Road	THg (ng/g)	1030	1180	13.6	
7/18/00	99-2381	Wiest Lake	THg (ng/g)	< 28.2	21.3	N/C	
9/19/01	00-0951	Sacramento River @ River Marker 44	THg (ng/g)	256	287	11.4	
9/19/01	00-0956	Feather River	THg (ng/g)	342	373	8.7	
9/19/01	00-1477	Consumnes River	THg (ng/g)	2090	1970	5.9	

Receipt Date	Sample ID		Analysis	MLML Result	Frontier Result	RPD (%)	Comments
9/19/01	00-1480	Consumnes River	THg (ng/g)	428	414	3.3	
9/19/01	00-1481	Mokelumne below Cosumnes	THg (ng/g)	1240	1190	4.1	
9/19/01	00-1490	Sacramento River near Isleton	THg (ng/g)	411	384	6.8	
9/19/01	00-1492	Frank's Tract	THg (ng/g)	123	108	13.0	
9/19/01	00-1554	SJR @ Crow's Landing	THg (ng/g)	910	815	11.0	
9/19/01	00-1564	Little Holland Tract	THg (ng/g)	334	333	0.3	

Moss Landing Marine Laboratories (MLML)

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Tissue Samples

Receipt Date	Sample ID	Analysis	MLML Result	Frontier Result	RPD (%)	Comments	
9/19/01	00-1565	Sherman Lake	THg (ng/g)	347	345	0.6	
9/19/01	00-1573	Potato Slough	THg (ng/g)	110	105.0	4.7	
9/19/01	00-1579	Stanislaus River	THg (ng/g)	445	385	14.5	
9/19/01	00-1588	SJR @ Vernalis	THg (ng/g)	1100	1110	0.9	
9/19/01	00-1599	Big Break	THg (ng/g)	308	310	0.6	
9/19/01	00-1726	SJR @ Landers	THg (ng/g)	134	118	12.7	
9/19/01	00-1727	Feather River above Yuba	THg (ng/g)	1590	1780	11.3	
9/19/01	00-1734	Feather River between Yuba and Bear	THg (ng/g)	845	777	8.4	
9/19/01	00-1741	SJR @ Landers	THg (ng/g)	491	552	11.7	
9/19/01	00-1745	Feather River Suckers	THg (ng/g)	269	268	0.4	
9/19/01	00-1746	SJR @ Landers	THg (ng/g)	367	294	22.1	
5/3/00	99-1432	Lake Nacimiento/Las Tablas Creek	MMHg (ng/g)	1000	1130	12.2	
7/18/00	99-1805	Sycamore Slough near Mokelumne River	MMHg (ng/g)	35.0	36.4	3.8	



Appendix A-3

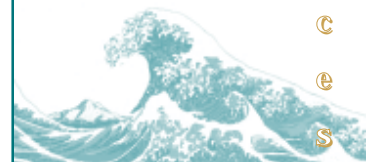
Texas A&M at Galveston (TAMUG)

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December 2003

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Texas A&M at Galveston (TAMUG)

Note: THg and DHg values from Frontier were adjusted +8% post-reporting

Water Samples

Receipt Date	Sample ID	Analysis	TAM Result	Frontier Result	RPD (%)	Comments
2/22/01	Station 4	DMMHg (ng/L)	0.007	0.025	112.5	RPD > 25; both results <= the Frontier RL of 0.025 ng/L
2/22/01	Station 19	TMMHg (ng/L)	0.081	0.044	59.2	RPD > 25; both results < 4x the Frontier RL of 0.025 ng/L
2/22/01	Station 11	THg (ng/L)	11.5	10.1	13.4	
2/22/01	Station 16	THg (ng/L)	8.72	6.45	30.0	RPD > 25
6/13/01	Station 3	DHg (ng/L)	0.92	2.36	87.8	RPD > 25
6/13/01	Station 8	DHg (ng/L)	0.65	0.74	12.9	
6/13/01	Station 8	TMMHg (ng/L)	0.035	0.030	15.4	
6/13/01	Station 4	DMMHg (ng/L)	0.008	< 0.005	N/C	
6/13/01	Frank's Tract	THg (ng/L)	4.38	5.78	27.6	RPD > 25
6/13/01	Frank's Tract	DHg (ng/L)	0.36	0.82	78.0	RPD > 25
6/13/01	Frank's Tract	TMMHg (ng/L)	0.057	0.037	42.6	RPD > 25
6/13/01	Frank's Tract	DMMHg (ng/L)	0.030	< 0.005	N/C	

Sediment Samples

Depth	Sample ID	Analysis	TAM Result	Frontier Result	RPD (%)	Comments
0-1 cm	Frank's Tract	MMHg (ng/g)	0.24	0.289	18.5	
1-2 cm	Frank's Tract	MMHg (ng/g)	0.34	0.442	26.1	RPD > 25
2-3 cm	Frank's Tract	MMHg (ng/g)	0.29	0.423	37.3	RPD > 25



Appendix A-4

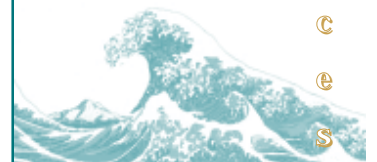
University of California at Davis (UCD)

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University of California at Davis (UCD)

Note: THg and DHg values from Frontier were adjusted +8% post-reporting

Tissue Samples

Receipt Date	Sample ID	Analysis	UCD Result	Frontier Result	RPD (%)	Comments	
4/23/01	505 MID	Aeshnidae	THg (ng/g)	64	63.8	0.3	
4/23/01	510 CLO	Hydropsyche	THg (ng/g)	100	103	3.0	
4/23/01	510 CLO	LMB-10	THg (ng/g)	1330	1160	13.7	
4/23/01	510 CLO	SSUC-5	THg (ng/g)	489	463	5.5	
4/23/01	520 NFC	Hydropsyche	THg (ng/g)	103	103	0.0	
4/23/01	520 NFC	SSUC-4	THg (ng/g)	1670	1490	11.4	
4/23/01	538 UBC	Tipulidae	THg (ng/g)	120	118	1.7	
4/23/01	538 UBC	SPM-6	THg (ng/g)	2160	2290	5.8	
4/23/01	538 UBC	SSUC-9	THg (ng/g)	1580	1330	17.2	
4/23/01	550 BRC	Hydropsyche	THg (ng/g)	1450	1560	7.3	
4/23/01	550 BRC	SSUC-6	THg (ng/g)	7890	7710	2.3	
4/23/01	560 RUM	Corydalidae	THg (ng/g)	125	121	3.3	
4/23/01	560 RUM	Sm Bass-1	THg (ng/g)	6950	6770	2.6	
4/23/01	560 RUM	Sm Bass-20	THg (ng/g)	3300	3090	6.6	
4/23/01	565 SOL	Libellulidae	THg (ng/g)	90	88.1	2.1	
4/23/01	565 SOL	Hydropsyche	THg (ng/g)	215	212	1.4	
4/23/01	565 SOL	SMB-9	THg (ng/g)	1750	1580	10.2	
4/23/01	565 SOL	SSUC-7	THg (ng/g)	1320	1240	6.3	
11/2/01	510 CLO	Hydropsyche-113000	THg (ng/g)	50	42.1	17.2	
11/2/01	510 CLO	Hydropsyche-050301	THg (ng/g)	110	84.3	26.5	RPD > 25
11/2/01	520 NFC	Perlodidae-051501	THg (ng/g)	50	50.2	0.4	
11/2/01	520 NFC	SPDA-1A-051501	THg (ng/g)	350	245	35.3	RPD > 25
11/2/01	530 HAR	Coenagrionidae-022001	THg (ng/g)	19100	15900	18.3	
11/2/01	538 UBC	Tipulidae-022001	THg (ng/g)	460	373	20.9	

Receipt Date	Sample ID	Analysis	UCD Result	Frontier Result	RPD (%)	Comments	
11/2/01	538 UBC	Naucoridae-082301	THg (ng/g)	230	208	10.0	
11/2/01	538 UBC	ROCH-2A-022001	THg (ng/g)	380	366	3.8	
11/2/01	538 UBC	ROACH-A-071201	THg (ng/g)	540	557	3.1	
11/2/01	550 BRC	Hydropsyche-121100	THg (ng/g)	2390	3600	40.4	RPD > 25
11/2/01	550 BRC	Naucoridae-071201	THg (ng/g)	3350	3100	7.8	
11/2/01	550 BRC	ROCH-2B-021501	THg (ng/g)	2590	2210	15.8	
11/2/01	550 BRC	ROACH-B-071201	THg (ng/g)	4110	3460	17.2	
11/2/01	560 RUM	Corydalidae-050301	THg (ng/g)	140	132	5.9	
11/2/01	560 RUM	SPDA-1B-111000	THg (ng/g)	230	201	13.5	
11/2/01	560 RUM	SSUC-1A-021700	THg (ng/g)	270	259	4.2	
11/2/01	565 SOL	Hydropsyche-111000	THg (ng/g)	150	131	13.5	
11/2/01	565 SOL	RDSH-2A-111000	THg (ng/g)	700	598	15.7	
11/2/01	565 SOL	SSUC-1A-080100	THg (ng/g)	360	345	4.3	
11/2/01	570 YSB	RDSH-2C-052200	THg (ng/g)	280	222	23.1	

University of California at Davis (UCD)

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Tissue Samples

Receipt Date	Sample ID	Analysis	UCD Result	Frontier Result	RPD (%)	Comments	
4/23/01	510 CLO	Hydropsyche	MMHg (ng/g)	92	93.7	1.8	
4/23/01	538 UBC	Tipulidae	MMHg (ng/g)	111	121	8.6	
4/23/01	550 BRC	Hydropsyche	MMHg (ng/g)	1220	1040	15.9	
4/23/01	560 RUM	Corydalidae	MMHg (ng/g)	111	98.4	12.0	
4/23/01	565 SOL	Libellulidae	MMHg (ng/g)	109	93.5	15.3	
11/2/01	510 CLO	Hydropsyche-113000	MMHg (ng/g)	22	30.7	33.0	RPD > 25
11/2/01	510 CLO	Hydropsyche-050301	MMHg (ng/g)	107	127	17.1	
11/2/01	520 NFC	Perlodidae-051501	MMHg (ng/g)	43	41.1	4.5	
11/2/01	520 NFC	SPDA-1A-051501	MMHg (ng/g)	347	415	17.8	
11/2/01	530 HAR	Coenagrionidae-022001	MMHg (ng/g)	8160	9220	12.2	
11/2/01	538 UBC	Tipulidae-022001	MMHg (ng/g)	423	411	2.9	
11/2/01	538 UBC	Naucoridae-082301	MMHg (ng/g)	198	248	22.4	
11/2/01	538 UBC	ROCH-2A-022001	MMHg (ng/g)	505	515	2.0	
11/2/01	538 UBC	ROACH-A-071201	MMHg (ng/g)	570	700	20.5	
11/2/01	550 BRC	Hydropsyche-121100	MMHg (ng/g)	759	854	11.8	
11/2/01	550 BRC	Naucoridae-071201	MMHg (ng/g)	3040	2860	6.1	
11/2/01	550 BRC	ROCH-2B-021501	MMHg (ng/g)	1120	2010	56.9	RPD > 25
11/2/01	550 BRC	ROACH-B-071201	MMHg (ng/g)	3060	4140	30.0	RPD > 25-
11/2/01	560 RUM	Corydalidae-050301	MMHg (ng/g)	129	113	13.2	
11/2/01	560 RUM	SPDA-1B-111000	MMHg (ng/g)	167	282	51.2	RPD > 25
11/2/01	560 RUM	SSUC-1A-021700	MMHg (ng/g)	284	335	16.5	
11/2/01	565 SOL	Hydropsyche-111000	MMHg (ng/g)	99	116	15.8	
11/2/01	565 SOL	RDSH-2A-111000	MMHg (ng/g)	695	896	25.3	RPD > 25
11/2/01	565 SOL	SSUC-1A-080100	MMHg (ng/g)	350	464	28.0	RPD > 25
11/2/01	570 YSB	RDSH-2C-052200	MMHg (ng/g)	225	372	49.2	RPD > 25

University of California at Davis (UCD)

Note: THg and DHg values from Frontier were adjusted +8% post-reporting

Water Samples

Receipt Date	Sample ID	Analysis	UCD Result	Frontier Result	RPD (%)	Comments
3/3/00	545 UBC	TMMHg (ng/L)	0.103	0.060	52.8	RPD > 25; both values <= 5x the RL
3/3/00	545 UBC	DMMHg (ng/L)	0.024	0.039	47.6	RPD > 25; both values <= 5x the RL
3/3/00	550 SUL	TMMHg (ng/L)	0.218	0.117	60.3	RPD > 25
3/3/00	550 SUL	DMMHg (ng/L)	0.108	0.134	21.5	
6/14/00	533 DC5	TMMHg (ng/L)	0.371	0.367	1.1	
6/14/00	533 DC5	DMMHg (ng/L)	0.180	0.223	21.3	
6/14/00	535 DAV	TMMHg (ng/L)	0.737	0.611	18.7	
6/14/00	535 DAV	DMMHg (ng/L)	0.607	0.546	10.6	
7/13/01	538 UBC	TMMHg (ng/L)	0.295	0.268	9.6	
7/13/01	538 UBC	DMMHg (ng/L)	0.170	0.070	83.3	RPD > 25
7/13/01	540 SUL	TMMHg (ng/L)	18.2	17.5	3.9	
7/13/01	540 SUL	DMMHg (ng/L)	1.93	< 0.020	N/C	Significant difference
7/13/01	550 BRC	TMMHg (ng/L)	1.09	0.974	11.2	
7/13/01	550 BRC	DMMHg (ng/L)	0.487	0.062	154.8	RPD > 25
7/13/01	555 BR3	TMMHg (ng/L)	0.818	0.130	145.1	RPD > 25
7/13/01	555 BR3	DMMHg (ng/L)	0.114	< 0.020	N/C	Significant difference
3/3/00	545 UBC	THg (ng/L)	5.38	9.71	57.4	RPD > 25
3/3/00	545 UBC	DHg (ng/L)	2.04	2.22	8.5	
3/3/00	550 SUL	THg (ng/L)	376	416	10.1	
3/3/00	550 SUL	DHg (ng/L)	135	160	16.9	
6/14/00	533 DC5	THg (ng/L)	49.7	44.3	11.5	
6/14/00	533 DC5	DHg (ng/L)	8.95	8.83	1.3	
6/14/00	535 DAV	THg (ng/L)	6.31	6.55	3.7	
6/14/00	535 DAV	DHg (ng/L)	4.73	4.54	4.1	

Receipt Date	Sample ID	Analysis	UCD Result	Frontier Result	RPD (%)	Comments
7/13/01	538 UBC	THg (ng/L)	1.04	1.34	25.2	RPD > 25
7/13/01	538 UBC	DHg (ng/L)	1.01	2.35	79.8	RPD > 25
7/13/01	540 SUL	THg (ng/L)	1180	1110	6.1	
7/13/01	540 SUL	DHg (ng/L)	163	86.0	61.8	RPD > 25
7/13/01	550 BRC	THg (ng/L)	20.3	15.1	29.4	RPD > 25
7/13/01	550 BRC	DHg (ng/L)	12.8	11.6	9.8	
7/13/01	555 BR3	THg (ng/L)	18.8	8.18	78.7	RPD > 25
7/13/01	555 BR3	DHg (ng/L)	3.84	6.11	45.6	RPD > 25



Appendix A-5

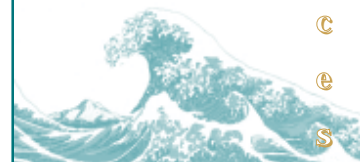
United States Geological Survey (USGS)

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United States Geology Survey (USGS)

Note: THg and DHg values from Frontier were adjusted +8% post-reporting

Water Samples

Receipt Date	Sample ID	Analysis	USGS Result	Frontier Result	RPD (%)	Comments
2/22/01	Cache Creek at Rumsey	THg (ng/L)	60.5	31.5	63.0	RPD > 25
2/22/01	Cache Creek at Rumsey	DHg (ng/L)	11.1	12.9	15.0	
3/1/00	North Fork Cache Creek	THg (ng/L)	23.7	34.4	36.8	RPD > 25
3/1/00	North Fork Cache Creek	DHg (ng/L)	1.9	1.63	15.3	
3/20/00	Cache Creek into Settling Basin	THg (ng/L)	24.3	15.2	45.9	RPD > 25
3/20/00	Cache Creek into Settling Basin	DHg (ng/L)	1.5	1.22	20.6	
2/22/01	Cache Creek at Rumsey	TMMHg (ng/L)	0.586	0.707	18.7	
2/22/01	Cache Creek at Rumsey	DMMHg (ng/L)	0.132	0.145	9.4	
3/1/00	North Fork Cache Creek	TMMHg (ng/L)	0.082	0.132	46.6	RPD > 25
3/1/00	North Fork Cache Creek	DMMHg (ng/L)	< 0.023	0.024	N/C	
3/20/00	Cache Creek into Settling Basin	TMMHg (ng/L)	0.088	0.208	81.1	RPD > 25
3/20/00	Cache Creek into Settling Basin	DMMHg (ng/L)	< 0.022	0.048	N/C	