The CALFED Mercury Project
Quality Assurance Oversight Final Report

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Submitted to:

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EXECUTIVE SUMMARY

This report addresses the quality assurance (QA) oversight work conducted by Frontier Geosciences (Frontier) as commissioned by the CALFED Mercury Project. The QA oversight study was part of the project's general QA program. This study was designed to help assess comparability of sub-task data and findings. The CALFED QA oversight components are:

1. Three intercomparison studies conducted for waters, sediments and tissues.
2. 197 analyses for 5% QA field splits to assess contract laboratory performance.
3. Two on-site assessments to help new or academic mercury laboratories.
4. Method detection limit studies for each analyte/matrix combination.
5. Third-party data set validation to objectively review QA/QC practices of data reporting.
6. Scientific and QA review of all methods used to ensure state-of-the-art procedures and good laboratory practices (GLP).

Major Findings:

- Sediment and tissue intercomparison studies showed good interlaboratory comparability while water studies revealed poor comparability.

- 5% QA field splits totaled 197 analyses for the period of 2000-2001. Comparisons of duplicate results are detailed in the QC section of each sub-task report.

- Method detection limit studies met pre-approved detection limits.

- QA/QC practices for each data set that went through third-party validation met control limits specified in the Quality Assurance Project Plan (QAPP) and followed good laboratory practices.

- Methods as shown in the QAPP are final copies with all required edits incorporated.

INTRODUCTION

The CALFED Mercury Project is one of the first multi-institutional research efforts to utilize comprehensive, quality assurance oversight. This is the final report for a two-year QA oversight study commissioned by the CALFED Mercury Project. The QA oversight study was designed to supplement the project's general QA program (see figure 1). Max Puckett from California Department of Fish and Game was the designated QA Manager and directed the project's QA program and adherence to the quality assurance project plan. Beverly van Buuren (Frontier Geosciences Inc.) was the External QA Officer who developed and conducted the QA oversight study. This report addresses the QA oversight work conducted by Frontier Geosciences. Quality assurance reports that summarize the results of the QA/QC assessments and evaluations, including precision, accuracy, comparability, representativeness, and completeness of the monitoring data were provided by each project investigator or the QA Manager and are not part of this report.

The CALFED Mercury Project assembled a diverse team of principal investigators and associates from state and federal resource and regulatory agencies, universities, and consulting firms. The general purpose was to find ways to reduce mercury concentrations in fish tissue to levels that do not pose a wildlife or human health hazard. It would determine which are the most bioavailable sources of mercury in the watersheds, where the most active methylation was taking place downstream, and what environmental factors accelerate the methylation of mercury in sediments. Targeted remediation could then be cost-effectively directed at sites contributing the majority of biologically available mercury to the system.

In common with many large-scale projects, the CALFED Mercury Project faced the following two quality assurance questions:

1. How do we establish confidence that data produced by multiple laboratories are comparable?
2. How do we guarantee that data are valid for future use and interpretation?

When data from multiple researchers is compiled, the outcome of QA oversight helps define the direction, and how far data interpretation can go. QA programs use many techniques to help establish interlaboratory comparability, but it is the right combination of techniques that provides the necessary, documented confidence that data is equivalent. The CALFED QA oversight components are: intercomparison studies, five percent QA field splits, on-site assessments, method detection limit studies, third-party data set validation, and a scientific and QA review of all methods used. Omission of any component lowers the confidence level and compromises the validity of the project.

Researchers working on large-scale projects often regret not sorting out QA issues at the start because this oversight can jeopardize later funding, project validity, and reputations. The CALFED QA effort was designed to help this project stand above others.

RESULTS AND DISCUSSION

Intercomparison Studies

Intercomparison studies are an ongoing process used to evaluate comparability of data and should be conducted initially, and biannually for the duration of a project. An intercomparison study can provide the necessary documentation to confirm interlaboratory precision. When an intercomparison study uses blind Certified Reference Materials (CRMs) as samples, it can show results on both precision and accuracy (bias).

In the CALFED project, intercomparison studies included tissues, sediments, and waters. The initial study, conducted in March 2000, was comprehensive, addressing multiple matrices and methods. Thereafter, single matrix studies were performed in July 2000 and July 2001. The study reports are presented as appendix A.

Samples were submitted to each laboratory dependent on the scope of work for the CALFED project. A z-score was calculated for each laboratory in each analyte and matrix. This is an expression of how far laboratory results are from the expected or true value. A bias estimate was calculated from the difference between the laboratory mean (x) and the expected or true value (y). The bias estimate was than divided by the study-determined, target standard deviation (σ_t). The target standard deviation for all analytes and matrices is 10%.

$$\text{z-score} = (x-y)/\sigma_t$$

Interlaboratory precision varied between matrices and analytes. The analyte with the highest variability was total mercury in waters (see figures 2-4). This is an issue that was not resolved by conducting subsequent studies. Waters sampled for the CALFED Mercury Project were often low-level, and a discrepancy of 0.5-1.0 ng/L could create an issue for data interpretation and validation. Researchers and the scientific advisory committee should scrutinize water data for this project along side results from the five percent QA splits and the intercomparison studies. The tissue and sediment studies indicate a rating of “good” while the water studies indicate a rating of “poor.” It is important to note that the intercomparison studies include limited data points and their impact on assessment of general project data is limited. In some cases, a better indicator of sub-task comparability is the five percent QA splits (this data comparison should be included in the reports from each project investigator or from the QA Manager).

Five Percent Field Sample Splits

All project investigators were required to collect and submit field splits (i.e., duplicates) for external analysis by Frontier. This part of the program was set up to assess sampling procedures and each contract laboratory's performance. The external QA samples were to be rotated among sites and events to achieve an overall rate of 5% field split samples. For example, if a project investigator collected a total of 100 water samples at four sites in two sampling events, then the sampling team would send 5 discrete field splits to Frontier (see figure 5). Table 1 shows how many samples were submitted for each matrix by organization and date.

This data should be compared side-by-side with the data from each contract laboratory. Project investigators should include a quality control section in their final report that details the results of these samples and makes conclusions based on the precision.

In order to comply with the requirement, water, tissue and sediment samples were sent to Frontier (FGS) by Texas A&M, Moss Landing Marine Laboratory, University of California, Davis, Central Valley Regional Water Quality Control Board, and the United States Geological Survey spanning a time period of February 2000 to November 2001. Samples were analyzed using high-level (litigation-level) quality assurance determination. The following narrative details how samples were handled upon receipt at Frontier.

Sample Receipt. All samples listed on the chain-of-custody forms were received in good condition. Upon receipt, cooler temperature was recorded for each shipment. Following sample receipt, water samples for methyl mercury analysis were preserved with 0.4% (v/v) 12N HCl and placed in refrigerated storage until sample preparation could take place. Water samples for total mercury analysis were oxidized with 1%, 2% or 5% (v/v) BrCl and placed in storage until analysis could take place. Tissue and soil/sediment samples, if frozen on arrival, were placed in freezer storage until sample preparation could take place. Soil/sediment samples that arrived chilled, but not frozen, were placed in refrigerated storage until sample preparation.

Analysis. *General.* All samples were received and logged in according to FGS protocols on the day of receipt. All samples identified on chain-of-custody forms were received in good condition. Samples were processed using ultra-clean sample handling techniques in a laboratory known to be low in atmospheric Hg. Reagents, gases, and DI water are all reagent or ultra-pure grade, and previously analyzed for Hg to ensure negligible blanks. All Hg analyses were performed using cold vapor atomic fluorescence spectrometry (CVAFS) as a detector (Bloom and Fitzgerald, 1988), with dual pen chart recorders or integrators as output devices. Total Hg (THg) standards are prepared by direct dilution of NIST certified NBS-3133 10.00 mg/mL Hg standard solution, and results independently verified by the analysis of NIST 1641d (water SRM 1.59 mg/L ± 0.018 mg/L THg). Monomethyl mercury (MMHg) standards were made up from the pure powder, and then

accurately calibrated for MMHg (equal to THg minus ionic Hg) against NBS-3133. MMHg results were also cross-verified by daily analysis of NRCC DORM-2 (4,470 ± 370 ng/g MMHg).

All daily analytical runs were begun with a 5 point standard curve, spanning two orders of magnitude, with additional standards run every 10 samples. The daily standard curve was calculated using the initial standards (blank corrected) of the day, using linear regression, forced through zero (Excel 97). All raw data and calculations have been supplied with this data package. Calculations were made using Excel spreadsheets, which illustrate each step. All summary data are appended with a code, which allows simple cross-referencing of the result with its appropriate full data package.

For each sample set (or 20 samples), at least one method replicate, two matrix spikes, and at least three method blanks were co-processed, and analyzed exactly as the ordinary samples.

Methyl Mercury Analysis. Prior to analysis, water samples were distilled to liberate the MMHg (US EPA Draft Method 1630; Horvat, et. al, 1993; Bloom and Von der Geest, 1995). Using an all Teflon distillation system, each sample was distilled according to published FGS protocols. For water samples, 45 mL (or, for higher total Hg samples, a smaller aliquot, diluted to 45 mL) of 0.4% (v/v) HCl acidified sample was distilled using 50 mL Teflon distillation tubes. To each sample, 0.2 mL of 1% APDC solution was added prior to distillation, to enhance reproducibility and recovery (Bloom, et. al., 1994). The distillate was received into a tube containing 5.0 mL of DDW to start, and distilled to an engraved line at 40.0 mL. Thus, 35 mL out of 45 mL of sample was distilled over for the analysis. The historic mean MMHg distillation recovery has been found to be 90.6 ± 9.4% (n= 164 distillations in 1994). All net MMHg results by distillation have been corrected for this empirically derived distillation efficiency

Due to their higher inherent methyl Hg concentrations, tissues were digested with 10 mL of hot 25% KOH/methanol for 2 hours (Bloom, 1989), and then diluted to 40.0 mL with methanol. A ratio of 1 gram tissue to 40 mL solution was utilized, and the digestates were then analyzed directly for methyl Hg and Hg(II) as described below.

Because of the potential for significant positive MMHg artifact formation during the distillation of samples containing high levels of inorganic Hg (Bloom, et. al, 1997), sediments were cold extracted rather than distilled. Aliquots of these samples (0.5 grams) were accurately weighed into 40 mL Teflon centrifuge tubes, and 5 mL of H_2SO_4/KBr solution plus 1 mL of 1 M $CuSO_4$ were added. After mixing, 10.0 mL of methylene chloride (CH_2Cl_2) was added to each tube, and the samples shaken for 1 hour. The samples were then centrifuged at 3000 RPM for 30 minutes to separate the solvent from the aqueous layer. Exactly 2.0 mL of CH_2Cl_2 was removed from each sample and pipetted into a Teflon vial containing 57.6 mL of deionized water. The samples were heated to 45^{o}C and purged with N_2 to volatilize the CH_2Cl_2, thus releasing the MMHg to the pure aqueous phase.

Distilled, digested, or extracted samples were analyzed using aqueous phase ethylation, purging onto Carbotrap, isothermal GC separation, and cold vapor atomic fluorescence spectrometry (CVAFS) detection (Bloom, 1989; Liang, et. al, 1994; Bloom and Fitzgerald, 1987). The method detection limit (3 σ of the method blank) is approximately 1.5 pg MMHg, as Hg. Prior to ethylation, the distillate was diluted to 55 mL with DI water, and the pH brought to 4.9 with the addition of acetate buffer. Samples were ethylated by the addition of sodium tetraethyl borate, and then the volatile ethyl analogs purged with N_2 onto Carbotrap. After a trap drying step, the mercury ethyl analogs were thermally desorbed into a 1 m isothermal GC column (15% OV-3 on Chromasorb WAW-DMSC) held at 100°C for separation. The column resolves the following peaks: elemental Hg, dimethyl Hg, methyl ethyl Hg, and diethyl Hg. Because of the wet chemistry used, only methyl ethyl Hg, the MMHg analog is quantified for this assay. The organo-Hg compounds are pyrolytically broken down to Hg^o prior to entering the CVAFS detector for quantification. Peak heights are accessed by chart recorder, and recorded on bench sheets in "chart units" to the nearest 0.2 unit. Net MMHg concentrations were calculated according to the following formulae, where **PH** is the chart recorder peak height, **V** is the aliquot size of water sample distilled, **bb** is the instrument (bubbler) blank, **B** is the mean method blank, in the same units as the sample, **V** is the total volume of sediment extract or distillate, **v** is the aliquot volume of sediment extract or distillate analyzed, **m** is the mass of sediment distilled or extracted, and **S** is the calibration curve slope in units/ng, for the set of samples. In the calculations below, 0.906 is the distillation recovery factor (the extraction procedure has no recovery factor, as it is essentially quantitative), and 5 is a factor to account for the fact that 2 out of 10 mL of the CH_2Cl_2 was back extracted into the aqueous phase.

[MMHg] (ng/L) = {[((**PH-bb)**/**S**)/0.906]/**V**} - **B** (distillation)

[MMHg] (ng/g) = {[((**PH-bb**)/**S**)*(**V**/**v**))]-**B**}/**m** (KOH digestion)

[MMHg] (ng/g) = {[(((**PH-bb**)/**S**)*5*(**V**/**v**))] - **B**}/**m** (extraction)

Total Hg analysis. For water samples, BrCl was added to an aliquot of the sample at a level of 1 mL per 100 mL of sample. The samples were then allowed to digest overnight at room temperature. Sediment and tissue samples (1 gram) were first digested in 10 mLs of hot refluxing 7:3 HNO_3/H_2SO_4 digestion, followed by dilution to 40 mL with 0.02 N BrCl.

Digests were analyzed for total Hg in accordance with the SOPs described in the Frontier Geosciences QA manual. Aliquots of each digest (1 to 100 mL for whole water, 0.01 to 5 mL for solids digests) were reduced in pre-purged DDW to Hg^o with $SnCl_2$, and then the Hg^o purged onto gold traps as a preconcentration step. The Hg contained on the gold traps was then analyzed by thermal desorption into a cold vapor atomic fluorescence detector (CVAFS), using the dual amalgamation technique. Peak heights are accessed by chart recorder, and recorded on bench sheets in "chart units" to the nearest 0.2 unit. Net THg concentrations were calculated according to the following formulae,

where **PH** is the chart recorder peak height, **b** is the mean bubbler blank, **V** is the digest, **B** is the mean method blank and **S** is the calibration curve slope in units/ng:

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

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

Table 1

Organization and Date	Total Hg Sediment	Methyl Hg Sediment	Total Hg Water	Methyl Hg Water	Total Hg Tissue	Methyl Hg Tissue
Texas A&M						
June 13, 2001		3	4	4		
MLML						
May 3, 2000					10	10
Sept 12, 2000	15	15				
Sept 19, 2001					20	20
UC Davis						
March 2, 2000			4	4		
June 13, 2000			4	4		
July 13, 2001			5	5		
Nov 2, 2001					20	20
CVRWB						
March 28, 2000			3	2		
May 3, 2001			2	2		
June 26, 2001			2	1		
July 31, 2001			1	1		
August 27, 2001			2	2		
October 1, 2001			2	2		
USGS						
Feb 29, 2000			2	2		
March 18, 2000			2	2		
TOTAL = 197	**15**	**18**	**33**	**31**	**50**	**50**

On-site Assessments (Audits)

Most of the laboratories utilized in the CALFED project have long-standing reputations for high-quality mercury analyses and are audited by certified organizations (i.e., state and federal environmental laboratory accreditation boards). Two of the academic laboratories did not hold any accreditation for analysis. Therefore, the project management determined that these two laboratories would benefit from an on-site assessment by the External QA Officer (B. van Buuren).

Ms. van Buuren and Paulette Jones (QA Chemist II, Frontier) conducted an audit of mercury capabilities at Moss Landing Marine Laboratory and Dr. Darell Slotton's laboratory at University of California, Davis in June 2000. Audit scope consisted of organization and personnel, sample receipt and storage areas, sample vessel/media preparation, sample preparation, sample analysis and instrumentation, documentation (logbooks, reporting practices and data packages), QA, performance test samples, and methodology. The most important aspect of the visits was to help labs comply with the QAPP and ultra-clean mercury practices. The audit team spent about 6 hours at each laboratory and followed a sample from receipt of log-in all the way through to analyses, data review and validation.

Method Detection Limit (MDL) Studies

All participating laboratories performed MDL studies following the protocols in EPA document 40 CFR part 136. Studies were conducted at the onset of the project. In some cases, historical data or previous studies were allowed as substitutes. MDL studies covered each analyte/matrix combination. All studies are located in appendix B. Table 2 shows studies by organization, analyte and matrix.

Studies are necessary to provide documented and intercomparable results for data interpreters. For example, consider a lab is performing mercury analysis by purge and trap with CVAFS for sediment, water and tissue samples. Three different MDLs on each CVAFS instrument in the lab need to be done. MDLs should be performed using the protocols set out in EPA document 40 CFR part 136. This is a relatively simple plan, with the analyst performing 7 replicates (6 degrees of freedom) of a clean matrix spike (examples of "clean" matrices for low-level mercury analysis are DIW, Ottawa River Sand, or supermarket chicken meat). The results are put through some simple statistical analysis and an MDL is established.

Table 2

Laboratory	Analyte	Matrix	MDL
Batelle	THg	water	0.203 ng/L
	MMHg	water	0.087 ng/L
	THg	sediment	0.009 ng/g
	MMHg	sediment	0.058 ng/g
	THg	tissue	0.013 ng/g
	MMHg	tissue	0.005 ng/g
USGS	THg	water	0.3 ng/L
	THg	sediment	0.8 ng/g
UC Davis	THg	tissue	0.01 ug/g
MLML	THg	water	0.22 ng/L
	THg	sediment	15.6 ng/g
	MMHg	sediment	0.019 ng/g
	THg	tissue	25.1 ng/g
	MMHg	tissue	3.19 ng/g
Texas A&M	THg	fresh water	0.031 ng/L
	THg	salt water	0.014 ng/L
	MMHg	estuarine water	0.009 ng/L
	MMHg	sediment	0.032 ng/g

Dataset Review and Validation

Frontier reviewed and validated a portion of data sets from each laboratory at the onset of the project. Items analyzed in data-set validation were documentation issues, consistency of calculations, how QC samples are utilized, whether general QA protocols are met, scientific coherence and usability of the data. All data sets that were submitted met the QA criterion as specified in the CALFED QAPP. Table 3 shows the reports submitted to Frontier by organization and date.

Table 3 *(continued on following page)*

Organization	Date of Report* or Analytical Run
Batelle	May 11, 2000
	July 20, 2000
	June 22, 2000
	March 2000 Set 2
	March 2000
	July 20, 2000

Organization	Date of Report* or Analytical Run
USGS	October 3, 2000
	August 17, 2000
	September 29, 2000
UC Davis	October 25, 2000
	October 14, 2000
	October 20, 2000
	July 27, 2000
MLML	June 19, 2000
	June 27, 2000
	October 10, 2000
	July 14, 2000
	July 19, 2000
	July 26, 2000
	September 7, 2000
	September 18, 2000
	October 9, 2000
	September 21, 2000
	September 19, 2000
	August 23, 2000

*Some reports contain multiple data sets.

Written Methods Evaluation

Evaluations were performed on each organization's standard operating procedures (SOP) to ensure it met the most recent capabilities (e.g., methyl mercury preparation for sediments). The evaluation assessed each method on scientific and quality control criteria (by Nicolas S Bloom of Frontier and B. van Buuren respectively). A list of the methods is shown in table 4 and each may be located in appendix D of the QAPP.

Table 4 *(continued on following page)*

Organization	SOP/Document	Designated CALFED ID
Batelle	SOP MSL-I-003-00 TAMU Sediment and Tissue Digestion	SOP-CALFED.D01
Batelle	SOP MSL-I-016-02 Total Mercury in Tissues and Sediments	SOP-CALFED.D02
	by Cold Vapor Atomic Absorption (CVAA)	
Batelle	SOP MSL-I-015-03 Methyl Mercury in Tissues and Sediments	SOP-CALFED.D03
	by Cold Vapor Atomic Flourescence (CVAF)	
Batelle	SOP MSL-I-024-01 Mixed Acid Tissue Digestion	SOP-CALFED.D04
Batelle	SOP MSL-I-014-01 Methyl Mercury in Aqueous Samples	SOP-CALFED.D05
	by Cold Vapor Atomic Fluorescence (CVAF)	
Batelle	SOP MSL-I-013-02 Total Mercury in Aqueous Samples by Cold Vapor Atomic Fluorescence	SOP-CALFED.D06
MLML	Analysis of Mercury in Sediments by Flow Injection Mercury System (FIMS) DFG-103	SOP-CALFED.D16
MLML	Digestion and Analysis of Trace Elements in Tissue and Sediment	SOP-CALFED.D17
	Using Teflon Vessels	
Sacramento (USFWS)	Avian Egg Harvest, Embryo Examination and Shell Thickness Determination	SOP-CALFED.D18
	with Intent to Save Contents for Chemical Analysis	
Texas A&M	Aqua Regia Digestion of Solid Materials for the Determination of Total Mercury	SOP-CALFED.D19
	LOER Procedure-0003	
Texas A&M	Determination of Total Hg in Aqueous Samples by Sodium Borohydride	SOP-CALFED.D20
	Reduction and Cold Vapor Atomic Fluorescence LOER Procedure-0001	
UCDavis	Dry Weight Sample Preparation Techniques for Aquatic Invertebrate	SOP-CALFED.D21
	and Fish Sample, Prior to Mercury and Other Analyses. UC Davis SOP #2	
UCDavis	Laboratory Sediment Slurry Mercury Methylation Experiments UC Davis SOP #4	SOP-CALFED.D22
UCDavis	Analysis of Total Mercury in Biological Tissues Using the Perkin-Elmer FIMS UC Davis 1	SOP-CALFED.D23

Organization	SOP/Document	Designated CALFED ID
UCDavis	Laboratory Stable Isotope Analysis for Plant and Animal Tissue UC Davis SOP #5	SOP-CALFED.D24
USGS/Boulder	Determination of Total Mercury in Environmental Water Samples	SOP-CALFED.D25
USGS/Boulder	Determination of Total Mercury in Environmental Sediment Samples	SOP-CALFED.D26
USGS/Boulder	Determination of Selected Major Cations, Dissolved Iron and Silica in	SOP-CALFED.D27
	Aqueous Media by Inductively-Coupled Plasma Atomic Emmision Spectroscopy	
USGS/Boulder	Determination of Selected Trace Metals in Aqueous Media by	SOP-CALFED.D28
	Inductively-Coupled Plasma Mass Spectroscopy	
USGS/Patuxent	Analysis of Mercury by Cold Vapor Atomic Absorption SOP 9024	SOP-CALFED.D29
USGS/Patuxent	Digestion of Water, Sediment, and Biological Tissue for Mercury Analysis SOP ST16	SOP-CALFED.D30
USGS/Patuxent	Determination of Methyl Mercury in Sediments and Tissues SOP 9712	SOP-CALFED.D31

CONCLUSIONS

The CALFED QA oversight components summarized in this report are: intercomparison studies, five percent QA field splits, on-site assessments, method detection limit studies, third-party data set validation, and a scientific and QA review of all methods used. These components should be used in conjunction with the general QA program to help assess comparability of intra-project sub-tasks.

The most useful parts of the QA oversight effort are the intercomparison studies and the five percent QA field splits. The intercomparison study reports are located in appendix A. The project QC data base (not part of the QA oversight effort) should show a side-by-side comparison of the five percent QA field split results from the contract laboratory and Frontier. Relative percent differences between duplicates that are greater than 25% need to be investigated for trends. Another helpful tool in data assessment will be the QC control charts detailing recoveries on certified reference materials, matrix duplicates, matrix spikes and concentration of method blanks.

The two questions asked at the beginning of this report can be answered by utilizing the data contained in this report and the reports provided by the QA Manager (as part of the general QA program).

1. How do we establish confidence that data produced by multiple laboratories are comparable?

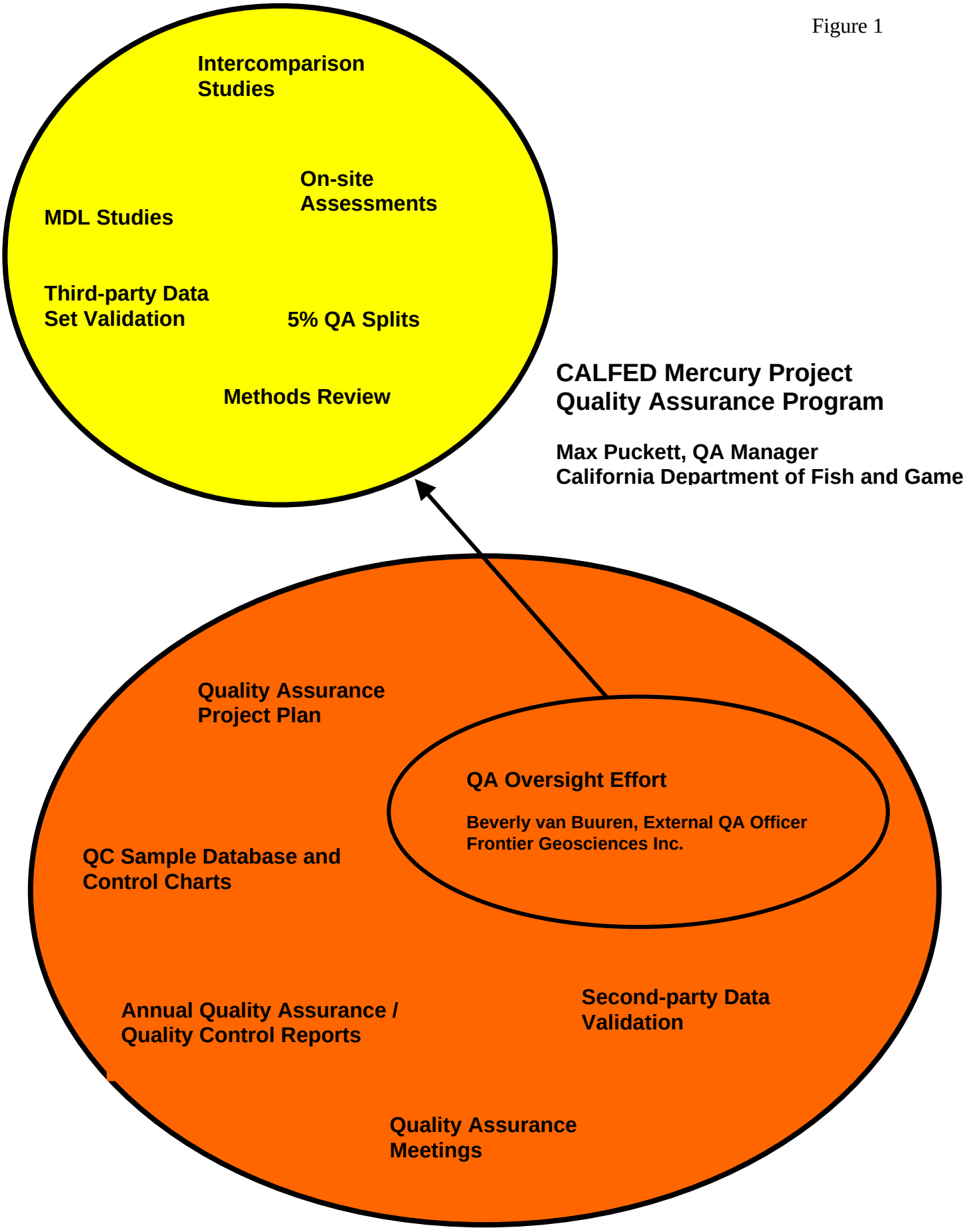
a) Intercomparison study results
b) Five percent QA field splits
c) Control charts of analytical run QC (e.g., certified reference materials, matrix spikes)
d) Report validation to ensure adherence to QAPP

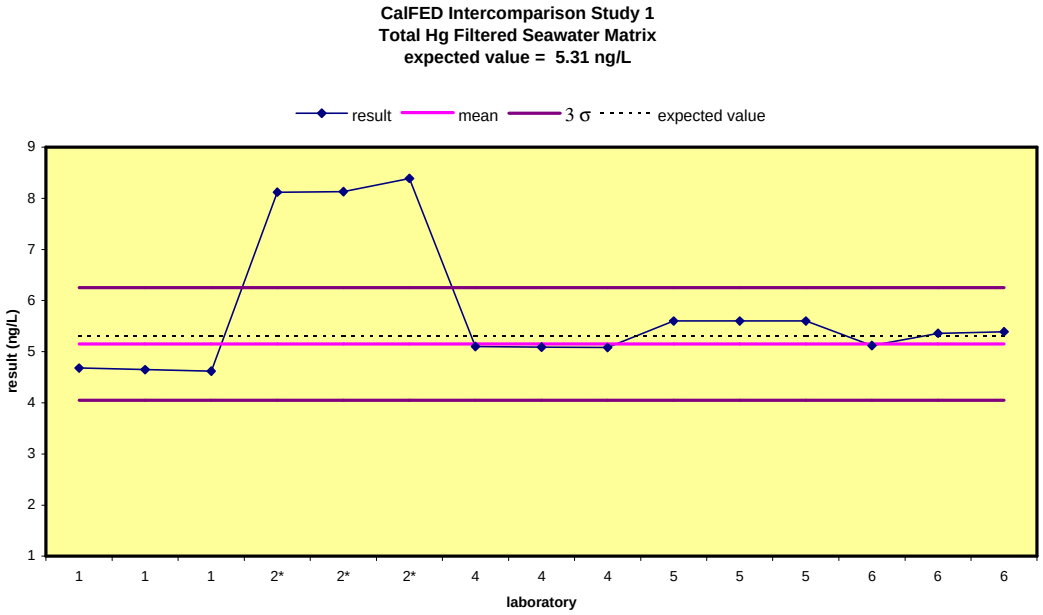
2. How do we guarantee that data are valid for future use and interpretation?

a) Consistent practices as spelled out in SOPs and QAPP
b) All QC data validated in “real time” and acted upon if trends or non-compliant results are found
c) QC criterion set prior to project start and adhered to by project investigators
d) Appropriate methods used (as determined on both a scientific and QA level)
e) Consistent and easy-to-read reporting formats
f) Second and third-party data validation

The CALFED Mercury Project QA oversight effort accomplished its goal to provide project management with tools for answering these two, important questions. Project management is commended for realizing the need to create consistent practices at the on-set of this project. This report, when utilized with reports from the general QA program, can help provide consistency and accountability when bringing all sub-tasks together into one study.

Figure 1


Intercomparison Studies
On-site Assessments
MDL Studies
Third-party Data Set Validation
5% QA Splits
Methods Review
CALFED Mercury Project Quality Assurance Program
Max Puckett, QA Manager
California Department of Fish and Game
Quality Assurance Project Plan
QA Oversight Effort
Beverly van Buuren, External QA Officer
Frontier Geosciences Inc.
QC Sample Database and Control Charts
Annual Quality Assurance / Quality Control Reports
Second-party Data Validation
Quality Assurance Meetings


CalFED Intercomparison Study 1
Total Hg Filtered Seawater Matrix
expected value = 5.31 ng/L
result
mean
3 σ
expected value
result (ng/L)
laboratory
1 1 1 2* 2* 2* 4 4 4 5 5 5 6 6 6

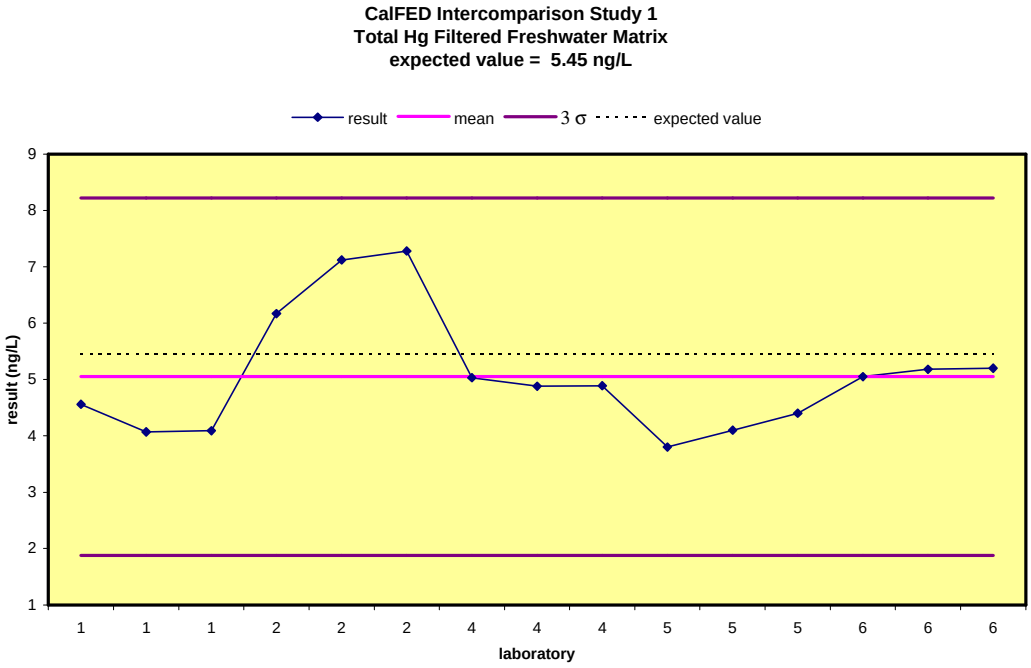
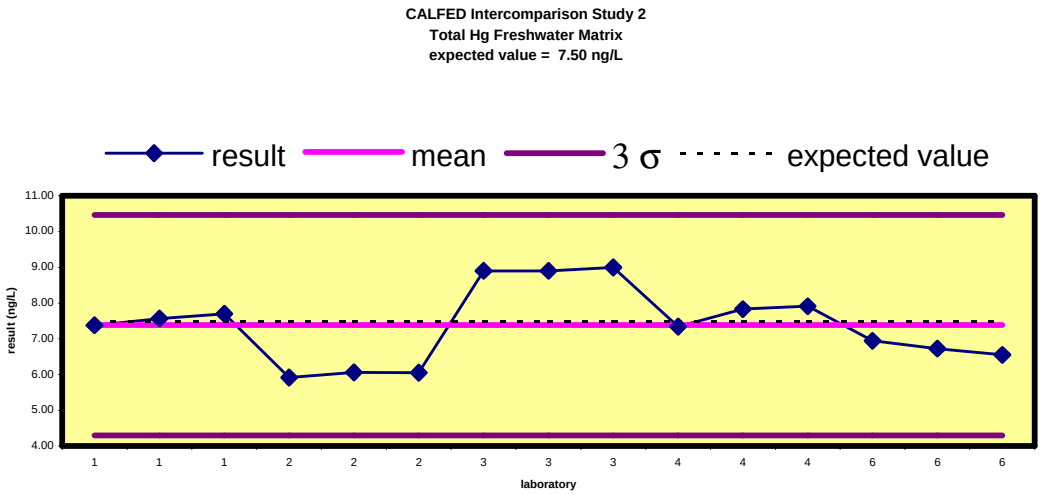

CalFED Intercomparison Study 1
Total Hg Filtered Freshwater Matrix
expected value = 5.45 ng/L
result
mean
3 σ
expected value
result (ng/L)
laboratory
1 1 1 2 2 2 4 4 4 5 5 5 6 6 6

Figure 3


CALFED Intercomparison Study 2
Total Hg Freshwater Matrix
expected value = 7.50 ng/L
result
mean
3 σ
expected value
result (ng/L)
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10.00
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laboratory

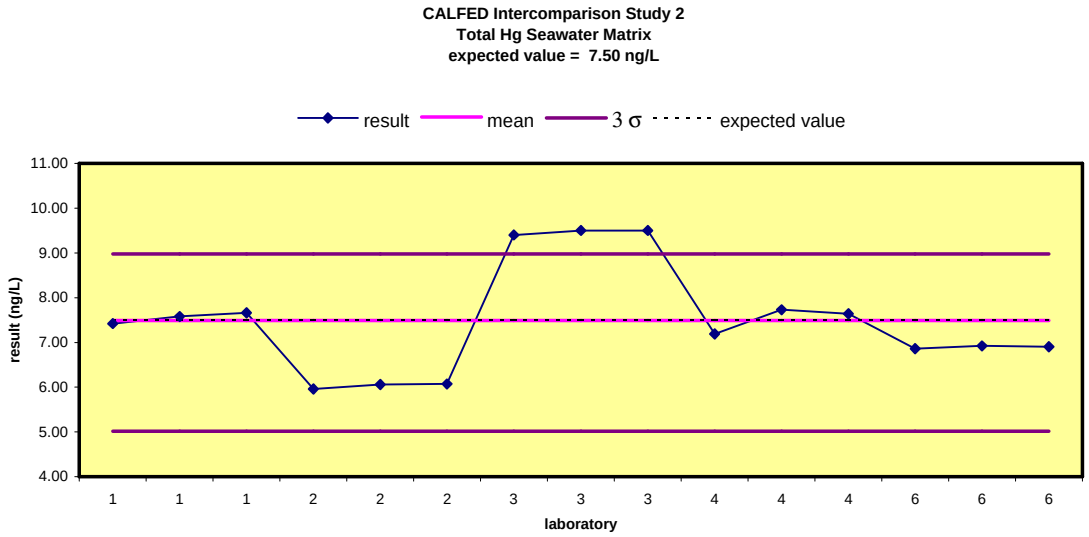
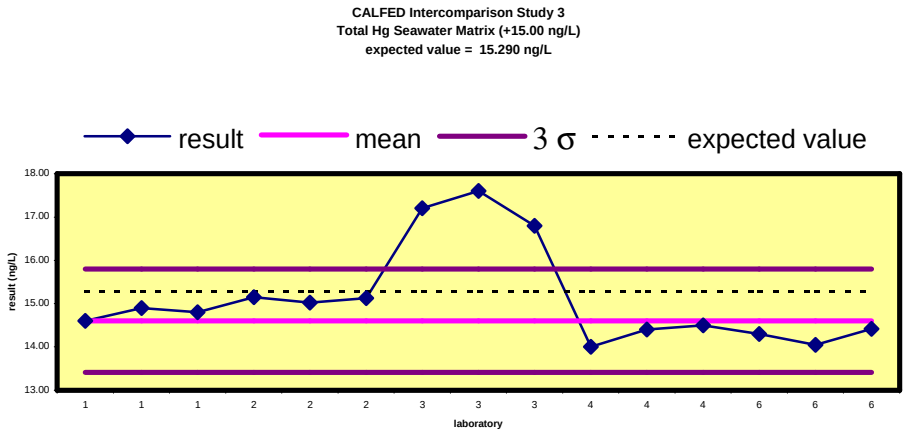
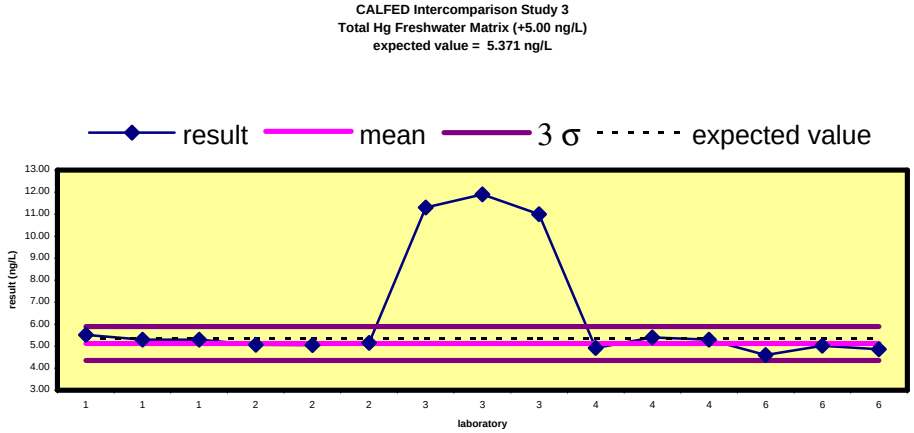
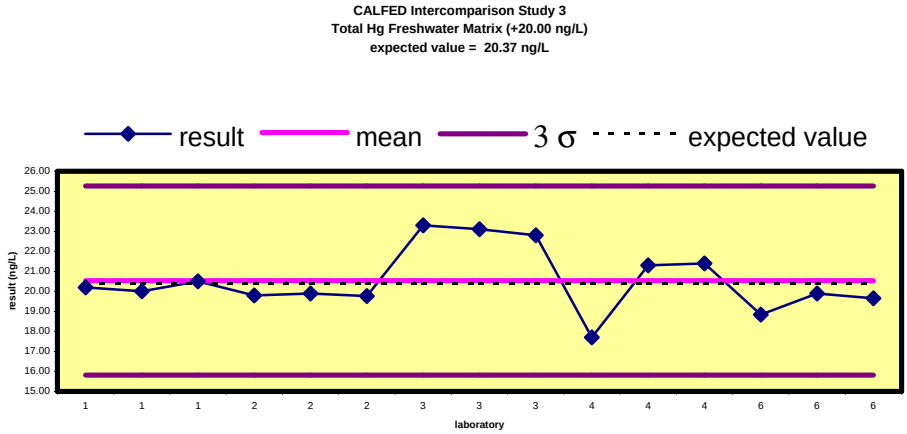
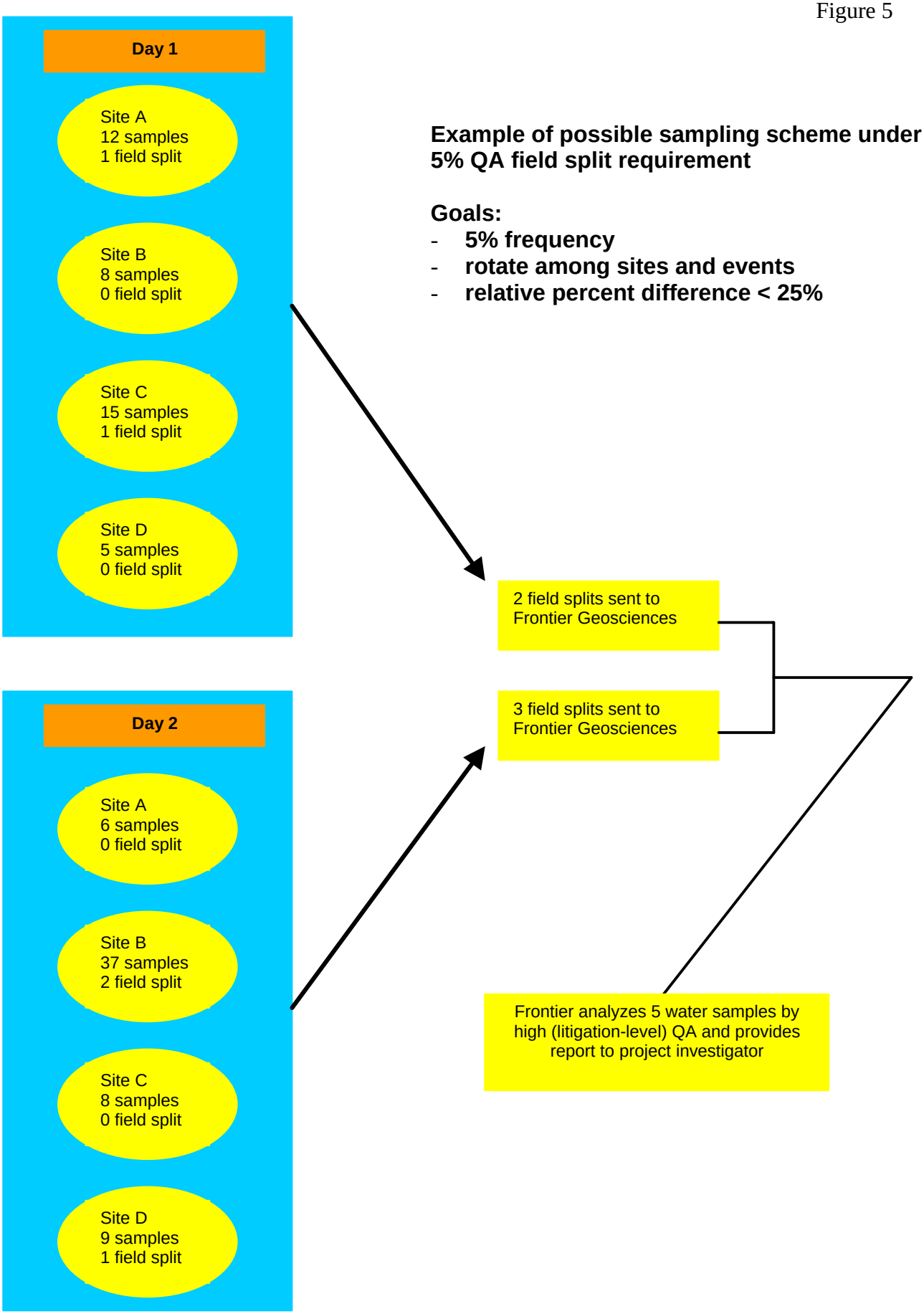

CALFED Intercomparison Study 2
Total Hg Seawater Matrix
expected value = 7.50 ng/L
result
mean
3 σ
expected value
result (ng/L)
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
1 1 1 2 2 2 3 3 3 4 4 4 6 6 6
laboratory

Figure 4


CALFED Intercomparison Study 3
Total Hg Seawater Matrix (+15.00 ng/L)
expected value = 15.290 ng/L
result
mean
3 σ
expected value
result (ng/L)
laboratory


CALFED Intercomparison Study 3
Total Hg Freshwater Matrix (+5.00 ng/L)
expected value = 5.371 ng/L
result
mean
3 σ
expected value
result (ng/L)
laboratory


CALFED Intercomparison Study 3
Total Hg Freshwater Matrix (+20.00 ng/L)
expected value = 20.37 ng/L
result
mean
3 σ
expected value
result (ng/L)
laboratory


Day 1
Site A
12 samples
1 field split
Site B
8 samples
0 field split
Site C
15 samples
1 field split
Site D
5 samples
0 field split
Example of possible sampling scheme under 5% QA field split requirement
Goals:
- 5% frequency
- rotate among sites and events
- relative percent difference < 25%
2 field splits sent to Frontier Geosciences
3 field splits sent to Frontier Geosciences
Day 2
Site A
6 samples
0 field split
Site B
37 samples
2 field split
Site C
8 samples
0 field split
Site D
9 samples
1 field split
Frontier analyzes 5 water samples by high (litigation-level) QA and provides report to project investigator

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RESULTING PRESENTATION/PUBLICATION

Van Buuren, B.H. and Puckett, H. M. 2001, "Quality Assurance Consulting in Mercury Research: The Quality Assurance Oversight Effort for the CALFED Mercury Project," 6th International Conference on Mercury as a Global Pollutant, Minamata, Japan (in press).

APPENDIX A

Provided as a separate, electronic appendix in PDF format.

APPENDIX B

Provided as a separate, electronic appendix in PDF format.