



A. Project Management

A.1 Project Organization and Responsibility

The CALFED Mercury Project has assembled a diverse multi-agency, multi-organization team of Principal Investigators and associates. These entities include state and federal resource and regulatory agencies, universities, and technical consultants.

Principal Investigator Mark Stephenson, of the California Department of Fish and Game (DFG) manages the CALFED Mercury Project at Moss Landing Marine Laboratories in Moss Landing, CA. The project coordinator is Max Puckett, of DFG at Granite Canyon Marine Laboratory, Monterey, CA. Mr. Puckett also serves as the project internal quality assurance manager. Beverly van Buuren, Frontier Geosciences, Inc. (Seattle, WA) serves as the project external quality assurance manager. San Jose State University Foundation (SJSUF San Jose, CA) administers the contract with the U.S. Bureau of Reclamation for the project, with Carol Sooter being the primary contract administrator and Bill Yabamoto being the fiscal administrator.

The following agencies and subcontractors will perform sample collection, analysis, and interpretive reporting:

- Battelle Marine Sciences Laboratory, Sequim, WA
- California Department of Conservation, Division of Mines and Geology, Sacramento, CA
- California Department of Fish and Game (Moss Landing Marine Lab, Moss Landing, CA and Granite Canyon Marine Lab, Monterey, CA)
- California Office of Environmental Health and Hazard Assessment, Sacramento, CA



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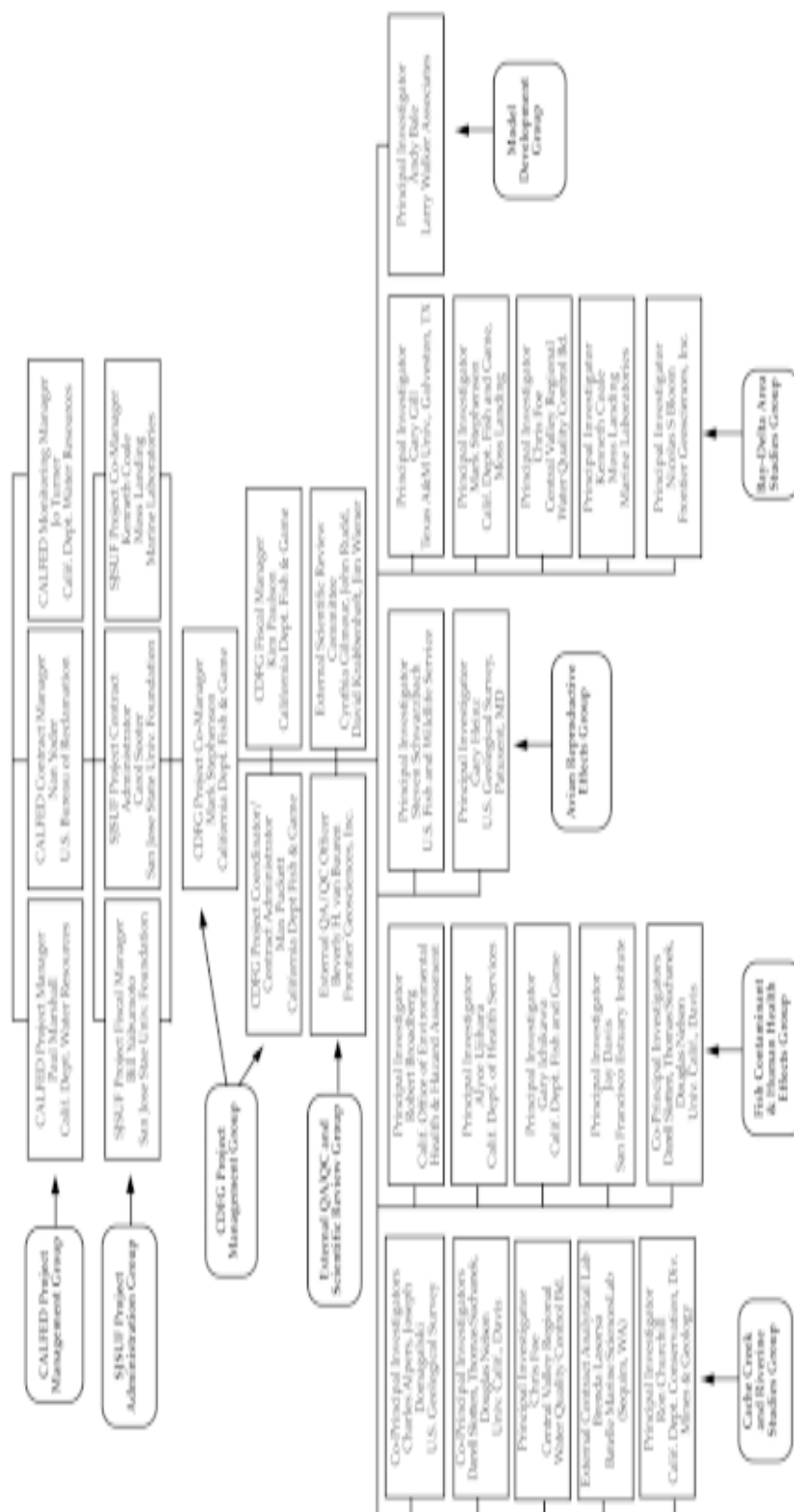
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- Calif. Regional Water Quality Control Bd., Central Valley Reg., Sacramento, CA
- California State University/Moss Landing Marine Lab, Moss Landing, CA
- Frontier Geosciences, Inc., Seattle, WA
- Larry Walker Associates, Davis, CA
- San Francisco Estuary Institute, Richmond, CA
- Texas A&M University, Galveston, TX
- University of California, Davis, CA
- U.S. Fish and Wildlife Service, Sacramento, CA
- U.S. Geological Survey, Sacramento, CA
- U.S. Geological Survey, Patuxent, MD

For the parameters measured by the CALFED Mercury Project, the agencies selected to perform sampling, laboratory analyses, and subsequent interpretive reporting, provide the precision, accuracy, detection and reporting limits. They also meet the quality control criteria necessary to satisfy the data quality objectives described in this document.

Sampling and analytical responsibilities are listed in Appendix A. The organizational structure of the CALFED Mercury Project is illustrated in Figure A-1.

Organizational Chart for the CALFED Project:
"An Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed"



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A.2 Goal Statement/Problem Definition

The goal statement for the CALFED Mercury Project developed by the participating investigators is as follows:

To provide information that will lead to a reduction of mercury in resident fish tissues to levels that are not harmful to humans and wildlife.

A.3 CALFED Project Description

A.3.1 Overall Program Background

- (a) CALFED Bay-Delta Program. The Bay-Delta Program is a consortium of State and Federal agencies with management and regulatory responsibilities in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary. The Bay-Delta Program's mission is to develop a long-term comprehensive plan that will restore ecological health and improve water management for beneficial uses of the Bay-Delta system.

The Bay-Delta Program has developed several implementation alternatives through the Federal/State environmental planning process which contain common programs to address ecosystem health, levee system integrity, water use efficiency, water transfers, water quality and watershed management. The common program to address ecosystem health is described in the Ecosystem Restoration Program (ERP). The ERP is a long-term ecosystem restoration program that will be implemented in phases over several decades.

- (b) CALFED Restoration Coordination Program. The December 15, 1994, Bay-Delta Accord included a commitment to develop and fund ecosystem restoration activities to improve the health of the Bay-Delta ecosystem. This funding source is commonly referred to as Category III. The CALFED Restoration Coordination Program is designed as a short-term program to allow implementation of ecosystem restoration actions while the programmatic environmental documents are being revised and finalized.

A process to guide allocation of Category III funds was developed by CALFED agencies with input from stakeholders. Ecosystem restoration projects may be selected through identification of various means such as directed programs and public solicitation processes.

The Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed Project was identified as a directed program and selected and recommended for funding by CALFED on February 4, 1999, and approved by the Secretary of the Interior on March 5, 1999, to benefit the ecosystem restoration category of "Water Quality and Temperature Improvement." Increased contaminant loads caused by urban runoff, agricultural runoff, mine drainage, wastewater treatment plants, and other point and non-point sources can stress the ecosystem at both an acute and chronic level. High water temperatures can also act as a stressor on cold water aquatic species such as salmon and steelhead. Numerous entities are collaborating on this project that are being subcontracted by SJSUF in order to accomplish the objectives and benefits of the project.

A.3.2 Project Objectives and Benefits

The objective of the Project is to provide information that will lead to a reduction of mercury in resident fish tissues to levels that are not harmful to humans and wildlife.

Eighty-eight percent of the mercury produced in the United States between 1850-1980 was mined in the Coast Range of California. Most of the mercury was transported across the Central Valley and lost in Sierra Nevada placer gold mining activities. As a result widespread mercury contamination has occurred in the Coast Range and Sierra Nevada waterways and downstream in the Central Valley Rivers and the Sacramento-San Joaquin Delta Estuary. Recent studies have determined that large amounts of mercury are still being transported annually into the Bay-Delta from both the Coast range and from the Sierra Nevadas. Not all the sources of this mercury have yet been identified, though Cache Creek in the Coast Range appears to be a major source.

Methyl mercury is a potent human neurotoxin, with developing fetuses and small children being most at risk. The principal route of human exposure is through consumption of mercury contaminated fish. Health advisories and interim health advisories have been posted in the Bay-Delta recommending no consumption of large striped bass and limited consumption of other sportfish species, with even lower consumption rates recommended for pregnant women and small children. More recent sampling has demonstrated high concentrations in other species suggesting that the contamination is more widespread than previously thought and that additional advisories may be warranted. Elevated concentrations of mercury in fish tissue may also represent a hazard to fish-eating birds and mammals.

An objective of the CALFED ERP is to restore aquatic habitat and increase fish abundance in the Central Valley and Bay-Delta. However, unless there is a successful mercury control program, some of the new fish are likely to have the same body burden as organisms already present in the estuary. Increased fish stocks would likely result in an increase in fish catches and an increase in mercury consumption by the California angling public. And, because restoration activities involving reflooding wetlands may result in a higher production of methyl mercury, this may increase the bioaccumulation of mercury in fishes. As a result, a successful CALFED ERP may exacerbate an already significant human health problem.

A.3.3 General Project Description

The general purpose of the overall Project is to determine ways to reduce mercury concentrations in fish tissue to levels that do not pose a wildlife or human hazard. This Project will determine what are the most bioavailable sources of mercury in the watersheds, where the most active methylation is taking place downstream, and what environmental factors accelerate the methylation of mercury in sediments. Future targeted remediation can then be directed in a cost-effective fashion at sites that contribute the majority of biologically available mercury to the system. The result of remediation should be a relatively rapid decrease in mercury concentrations in fish tissue close to the sources and a slow, gradual reduction (on the order of several decades) in mercury stocks throughout the rivers and Bay-Delta system. Unfortunately, so much mercury is present in sediment of the main stem rivers and in the Bay-Delta that fish tissue concentrations may only be affected by identifying and managing sites with high methylation potential. This could minimize mercury conversion to an organic form while allowing clean sediment to gradually bury and reduce the bioavailability of the material already present. The result should be a gradual reduction in Bay-Delta fish tissue concentrations. A series of studies are to be conducted to determine the information needed to begin implementing this strategy.

The overall project plan is fourfold. First: Determine the primary sources of mercury and methyl mercury to the Bay-Delta system. Second: Obtain data on mercury levels in fish to better evaluate the health risk posed to humans and wildlife by local fish consumption. Third: Determine the bioavailability of mercury from various sources and at various points along the watershed. Fourth: Conduct pilot mine remediation feasibility studies in Cache Creek. Finally: Integrate the loading, health risk, bioavailability, and mine remediation studies into

a cohesive research program, to determine many of the impacts of mercury, where mercury is coming from, and how to remediate it.

The monitoring program will augment and coordinate with a number of other monitoring efforts that are ongoing in the watershed, including the USGS National Water Quality Assessment Program, the Sacramento Coordinated Water Quality Monitoring Program, and monitoring efforts by the Department of Water Resources, US Bureau of Reclamation. The CALFED Mercury Project includes chemical, physical, biological and toxicological monitoring elements.

A.3.4 Measurements to be Taken in Project

The following environmental monitoring elements are included in the CALFED Mercury Project:

- mercury and methyl mercury in fish, invertebrate, and avian egg tissue
- mercury and methyl mercury in water
- mercury and methyl mercury in sediment

To a lesser extent, in some of the subprojects, the following constituents will be measured:

- dissolved and total organic carbon in water
- other trace metals, in addition to mercury, in water and sediment
- general constituents (minerals, nutrients, solids, turbidity, hardness) in water. Specific individual parameters measured by the CALFED Mercury Project are listed in Table A-1.

Table A-1
Parameters Measured for the CALFED Mercury Project

Chemical and Physical Water Quality Characteristics

Primary measurements of concern

Mercury, total and dissolved
Monomethyl mercury, total and dissolved

Secondary measurements made infrequently for ancillary information

Trace Metals

Arsenic, total and dissolved
Boron, total and dissolved
Cadmium, total and dissolved
Chromium (III), total
Conductivity
Copper, total and dissolved
Lead, total and dissolved
Nickel, total and dissolved
Selenium, total
Temperature
Zinc, total and dissolved

Nutrients

Ammonia, dissolved
Ammonia plus organic nitrogen, total and dissolved
Nitrite, dissolved
Nitrite & Nitrate, dissolved
Orthophosphate
Phosphorous (total), total and dissolved

General Constituents

Alkalinity
Calcium
Chloride
Dissolved Organic Carbon
Hardness
Iron
Magnesium
Manganese
Potassium
Silica
Sodium
Sulfate
Suspended Organic Carbon
Total Dissolved Solids
Total Organic Carbon
Total Suspended Solids
Turbidity

Field Parameters

Nitrate & Nitrite
Ortho-Phosphate
pH
Phosphate
Specific Conductance
Total Ammonia
Total Kjeldahl Nitrogen

Assessment Tools—The QAPP and any amendments to QAPP elements will be first reviewed and approved by project Quality Assurance Officers (as listed on the Approvals page of this QAPP) and by the U.S. Bureau of Reclamation Quality Assurance Manager prior to the initiation of monitoring.

Project Schedule—The proposed schedule for CALFED Mercury Project monitoring is summarized in Table A-2.

Sampling Schedules and Maps—Sampling schedules and sampling site location maps are available for review from each Principal Investigator.

Table A-2
Project Implementation Schedule for 2000-2002 Monitoring

Submit QAPP to USBR for Review	May-00
Receive Comments on QAPP	May-00
Make revisions to respond to comments on QAPP	May-00
Final Approval for QAPP for 2000-2001 Monitoring	May-00
Finalize and Execute Contracts for -2000-2001 Monitoring	May-00
Conduct field sampling and lab analyses	Feb-00 – Nov-00
Present draft data to Scientific Review Committee	Nov-00
Prepare Year One (Annual) Report	Jan-01
Conduct field sampling and lab analyses for Year Two	Nov-00 – Nov-01
Present draft Year Two data and total project data to Scientific Review Committee	Jan-02
Prepare Draft Project Final Report, including Year Two data	Mar-02
Prepare Project Final Report	May-02

A.4 Quality Objectives and Criteria for Measurement Data

Data Quality Objectives (DQO) ensure production of the highest quality, useable and coherent data. Project DQO consist of five components: precision, accuracy (bias), representativeness, comparability and completeness (PARCC).

- Precision is concerned with the ability to repeat results. To demonstrate the precision of a method, sample replicates may be analyzed and their results compared.
- Accuracy, or bias, is a measure of how close a result is with the true or expected value of the target analyte in a sample. Accuracy, or bias, may be determined by the analysis of certified reference materials, blank spikes, and matrix spikes, where the result can be compared with a true or expected value.
- Representativeness judges how well a single sample can describe the conditions of an entire sample population. Accurate, artifact-free sampling procedures and appropriate sample homogenization achieve representativeness.
- Comparability looks at ongoing projects and how variable one set of data is to another. Comparability helps to measure the scientific coherence and validity of a project.
- Completeness is a measure of how many data points collected are usable; this Project considers 85-90%, depending on monitoring element, of usable data to be an acceptable value for completeness.

The objective of data collection for this Project is to produce data that represent as closely as possible, *in situ* conditions of the Bay-Delta watershed. This objective will be achieved by using accepted methods to collect and analyze water, sediment, and biota. Assessing the program's ability to meet this objective will be accomplished by evaluating the resulting laboratory measurements in terms of detection limits, precision, accuracy, comparability, representativeness, and completeness, as outlined above and as presented in Section B of this document.

A.5 Documentation and Records

A.5.1 Data To Be Included In Data Reports

For each sample event, the field crew or monitoring agency shall provide the Quality Assurance Manager with copies of relevant pages of the field logs and copies of the chain-of-custody forms for all samples submitted for analysis. At a minimum, the following sample-specific information will be provided for each sample collected:

- sample ID number (unique for each sample and replicate)
- CALFED Mercury Project name
- sample location (latitude, longitude, and GIS coordinates available)
- sample type (matrices such as sediment, surface water, subsurface water, tissue, etc.)
- sample depth (if appropriate)
- sample collection method, e.g. grab or composite type (cross-sectional, flow-proportional, etc.)
- number of sub-samples in composite (if appropriate)
- QC sample type (if appropriate)
- date and time(s) of collection
- requested analyses (specific parameters or method references).

For each sample analyzed, the analyzing laboratory shall provide the Quality Assurance Manager with the following information:

- sample ID
- date of sample receipt
- dates of analysis
- analytical method(s)
- method detection limit (if appropriate)
- reporting limit (if appropriate)
- measured value of the analyte or parameter

In addition, the analyzing laboratory shall provide results from all laboratory QC procedures (blanks, duplicates, spikes, reference materials, etc.) and the sample IDs associated with each analytical sample batch.

A.5.2 Reporting Format

In addition to the laboratory's standard reporting format, all results meeting data quality objectives and results having satisfactory explanations for deviations from objectives shall be reported in tabular format on electronic media.



B. Data Acquisition

B.1 Sampling Design

The CALFED Mercury Project includes sample collection at numerous and varied locations in the Bay-Delta watershed. Due to the specific and varied nature of each of the substudies within this project, repetitive monitoring is not necessarily the objective for data collection, and thus, specific monitoring sites and methods may vary through time.

B.2 Sampling Methods Requirements

Samples will be collected from three environmental media: water, sediment, and biota. Sampling of biota will include methods specific for fish, benthic macroinvertebrates, and avian eggs. For each of these methods, described or referenced, it is the combined responsibility of all members of the sampling crew to determine if the performance requirements of the specific sampling method have been met, and to collect an additional sample if required. Descriptions of specific sampling methods and requirements (Field Sampling SOP's) are provided in the Appendices attached herein.

The primary constituents of concern for this project for measurement from environmental samples in water, sediment, and tissue are mercury (total and dissolved) and monomethyl mercury. Secondary information will be gathered by some participants on a sporadic basis as possible, but this information is deemed to be ancillary and not required as a part of this project. These secondary measurements

(primarily by USGS) will include sampling for trace metals, total suspended solids, hardness, turbidity, total dissolved solids, alkalinity, total organic carbon, dissolved organic carbon, general minerals (chloride, iron, manganese, calcium, magnesium, silica, sodium, sulfate, and potassium), and nutrients (nitrite, nitrate, ammonia, organic nitrogen, orthophosphate, and total phosphorus). See Table A-1.

Sampling SOPs have passed outside review and validation for quality assurance measures and ultra-clean sampling techniques. All sampling SOPs are provided in the Appendices attached herein.

B.2.1 Water Sampling

Water quality samples will be collected using ultra-clean techniques that minimize sample contamination. Sampling methods will generally conform to EPA “clean” sampling methodology described in *Method 1669: Sampling Ambient Water for Trace Metals* (USEPA 1995a). Samples shall be either cross-sectional composite samples or mid-depth grab samples, depending on location and flow conditions. After collection, samples will be stored at 4°C and dark until arrival at the contract laboratory. Field crews must rigorously follow ultra-clean sampling procedures and complete all necessary documentation according to the SOP.

B.2.2 Fish Sampling

Fish tissue samples will be collected using protocols detailed in *Contaminant Levels in Fish Tissue from San Francisco Bay* (SFRWQCB 1995). Details of the protocols are documented in Appendix C and summarized below.

Collection of fish for analysis of mercury and monomethyl mercury in tissue may be accomplished by a variety of methods, including hook and line, seines, gill nets, and electroshocking. Species collected will be non-migratory species that are most representative of a given location. Efforts will be made to collect fish of a similar (medium) size for each composite. Collection, handling and storage of whole fish and tissue samples will be performed in a manner consistent with Regional Monitoring Program (RMP)/UC Davis protocols

(SFEI 1999, SFRWQCB 1995) to assure the collection of representative, uncontaminated tissue chemistry samples. Field crews must rigorously follow sampling procedures and complete all necessary documentation according to the SOPs.

B.2.3 Egg Sampling

Procedures for the collection of wild bird eggs will vary by location and species to be sampled. However, here are the general guidelines that should be followed. All wild bird eggs must be collected under appropriate federal and state collecting permits. Visits to bird colonies to collect eggs should be done to minimize disturbance to the colony. Only fresh, unincubated eggs should be collected. This can be done by candling or floating the eggs. Ideally, one fresh egg should be collected from each nest to minimize any influence of sibling eggs in the egg injection studies. However, we recognize that it may be more practical in some cases to collect the entire clutch of eggs from each nest. Eggs should be kept at room temperature, avoiding extremes of heat or cold. The packaging of eggs may vary depending on species and number of eggs to be shipped, but, in general, the eggs should be packed with adequate protection to avoid breakage in shipping. Field crews must rigorously follow sampling procedures and complete all necessary documentation according to the SOPs.

B.2.4 Macro-invertebrate Sampling

Macro-invertebrate samples for mercury will be collected from riffle habitat at each of the sites where they are present. Sites may include rapids or cobble bottomed stretches with maximal flow, where aquatic insects tend to be most concentrated among the rock interstices. Stream invertebrates are collected primarily with the use of a research kick screen. Efforts will be made to collect a sufficient sample size (as available) of each taxon of interest to permit analysis for mercury. Samples are separated by taxa in the field and placed into clean, glass jars with Teflon™-lined lids. Samples are maintained live in sample bottles, on ice, between field and analytical laboratory. Field crews must rigorously follow sampling procedures and complete all necessary documentation according to the SOP.

B.2.5 Sediment Sampling

Collection of sediment samples will be accomplished by various methods described in detail in SOPs. Each method employs ultra-clean sampling techniques that minimize sample contamination and analyte degradation. Aqueous sediment samples are generally taken from the top centimeter of superficial sediment at the sediment/water surface. Terrestrial sediments at the mine sites will be collected directly into sample jars. Sediment-water exchange flux of Hg and MMHg will be measured with benthic flux chambers. Sediment pore water gradients will be obtained using a nonmetallic whole core squeezer. After collection, samples will be stored at 1-4°C, or frozen, until arrival at the contract laboratory. Field crews must rigorously follow ultra-clean sampling procedures and complete all necessary documentation according to the SOP.

B.2.6 Data Evaluation

Project Investigators are responsible for evaluating field sampling data for completeness and representativeness. Additionally, Project Investigators will evaluate sampling events to ensure field crews collected all QC samples, followed SOPs, and completed all necessary documentation.

Table B-2a

Sampling SOPs and their corresponding CALFED project
SOP Identification

<u>Agency Responsible for Sampling</u>	<u>Matrix</u>	<u>Analyte(s) of interest*</u>	<u>SOP Title</u>	<u>CALFED SOP Identification</u>
UC Davis	water	THg, MMHg	UC DAVIS-preliminary sop: field/sample prep/analytical	SOP.CALFED.C09
UC Davis	sediment	THg, MMHg	UC DAVIS SOP #4	SOP.CALFED.C09
UC Davis	fish	THg, MMHg	UC DAVIS SOP #3	SOP.CALFED.C10
UC Davis	macro-invertebrates	THg, MMHg	UC DAVIS SOP #3	SOP.CALFED.C10
MLML	water	THg	DFG SOP 100	SOP.CALFED.C03
MLML	sediment	THg, MMHg	DFG SOP 107.1	SOP.CALFED.C04
MLML	fish	THg, MMHg	Sample Collection and Prep	SOP.CALFED.C05
Texas A&M	water	THg, MMHg	LOER Procedure-0002	SOP.CALFED.C08
Texas A&M	sediment	THg, MMHg	LOER Procedure-0003	SOP.CALFED.C08
USFWS Sacramento	egg	THg, MMHg	Field collection of Avian eggs	SOP.CALFED.C07
USGS Patuxent	egg	THg, MMHg	Eggs for lab use	SOP.CALFED.C11
USGS Sacramento	water	THg, MMHg	USGS Field Sampling and Cleaning SOP	SOP.CALFED.C13
USGS Sacramento	sediment	THg, MMHg	USGS Field Sampling and Cleaning SOP	SOP.CALFED.C13

*No ancillary measurements are noted, only mercury measurements.



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Table B-2b
Sample Handling Requirements

<u>Parameter</u>	<u>Sample Container</u>	<u>Sample Volume¹</u>	<u>Immediate Processing and Storage</u>	<u>Holding Time²</u>
<i>Waters</i>				
Filtered Mercury, total	glass	125-250mL	Store between 4°C; Preserve with 0.5% HCl or 0.04% K ₂ Cr ₂ O ₇ with 4% HNO ₃	6 months
Filtered Monomethyl Mercury, total	glass	250mL	Store between 4°C (darkness); Preserve with 0.5% HCl	6 months
Unfiltered Mercury, total	glass	125-250mL	Store between 4°C; Preserve with 0.5% HCl or 0.04% K ₂ Cr ₂ O ₇ with 4% HNO ₃	6 months
Filtered Metals and major cations	Polyethylene or Teflon™	250mL	Field-filtered; Store at 4°C until preservation; If samples are not field-filtered, the laboratory must receive and filter within 36 hours of collection. Preserve with 0.8% HNO ₃	1 year
Unfiltered Metals and major cations	Polyethylene or Teflon™	250mL	Store at 4°C until preservation; Preserve with 0.8% HNO ₃	1 year
<i>General Constituents</i>				
Total Suspended Solids	Polyethylene	1000mL	Store at 4°C	60 days
Hardness	Polyethylene	125mL	Store at 4°C; Preserve to ≤pH 2 with HNO ₃	6 months
Turbidity	Polyethylene	500mL	Store in the dark at 4°C;	48 hours
Total Dissolved Solids	Polyethylene	500mL	Filtered; Store at 4°C	7 days
Alkalinity	Polyethylene	250mL	Field-filtered; Store at 4°C	14 days

Dissolved and suspended Organic Carbon	Amber Glass	125mL	Field-filtered; Store at 4°C	14 days
Major anions (unpreserved)	Polyethylene	250mL	Field-filtered; Store at 4°C	60 days
Total Ammonia, Nitrate & Nitrite, and Total Kjeldahl Nitrogen	Polyethylene	2L	Preserve to \leq pH 2 with H_2SO_4 ; Store at 4°C	28 days
Ortho-Phosphate	Brown Polyethylene	125mL	Filtered; Store at 4°C	14 days
Phosphorous (total)	Polyethylene	125mL	Unfiltered; Preserve to \leq pH 2 with H_2SO_4 ; Store at 4°C	14 days

Biota

Fish Tissue	Polyethylene (zip lock bags) or Glass (with a Teflon™ Lid)	200g	Refrigerate up to 7 days or Freeze until processing	1 year
Benthic Invertebrates	Polyethylene or Glass (with a Teflon™ Lid)	.10g	Refrigerate up to 7 days or Freeze until processing	1 year

Sediments

Sediment/Soils	Teflon™ or Glass (with a Teflon™ Lid)	250-500mL	Refrigerate up to 7 days or Freeze until processing	1 year
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¹Additional volumes may be required for QC analyses; NA = Not Applicable

²Holding time after initial preservation or extraction

B.3 Sample Handling and Custody

All samples will be handled, prepared, transported and stored in a manner so as to minimize bulk loss, analyte loss, contamination or biological degradation. Sample containers will be clearly labeled with an indelible marker. A completed chain-of-custody form will accompany all sample sets.

All samples remaining after successful completion of analyses will be disposed of properly. It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals.

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Samples will be kept for a minimum of 28 days after collection. The QA officer for each laboratory will evaluate the data before the end of the 28-day period. After this period, samples may be disposed of properly when all analyses have been completed, and data quality objectives have been met.

B.3.1 Mercury Specific Sample Handling

For low-level (ambient) mercury analyses, only rigorously acid-cleaned Teflon™ containers (or borosilicate glass or quartz containers with Teflon™-lined lids) may be used for water samples. Borosilicate glass I-Chem 200 Series bottles with Teflon™-lined lids may be used off-the-shelf for mercury collection. Equipment blanks will provide evidence that glass bottles are clean. Tissues, sediments, and contaminated water samples should be stored in glass containers with Teflon™-lined lids. Egg tissue samples may be stored in polypropylene jars. Potential sample contamination may result from the use of polyethylene, polypropylene, or other plastics not approved for mercury work. Samples may not be packed in vermiculite, as the dust from this material represents a contamination risk. Bubble wrap or foam should be used as packing materials.

Samples may be stored in refrigeration/freezer units or in insulated shipping containers with frozen blue ice packs or bags of ice. Frozen tissue and sediment samples may be stored with dry ice. Water samples must be stored at 4°C. Water samples for speciation analyses are to be stored between 0-4°C and in complete darkness. Water samples must always be handled and stored in an upright position.

Aqueous samples are shipped to analytical laboratories unpreserved by overnight courier (unless specified otherwise in the SOP). Solid samples are preserved in the field by freezing (unless specifically requested otherwise due to analyte requirements). Each sample container may be sealed inside a Ziplock™ bag labeled with a unique sample number. Samples must be packed securely to avoid leakage and breakage in transit. The completed chain-of-custody form will always accompany sample sets.

B.3.2 Trace Metals Specific Sample Handling

For low-level (ambient) trace metals analyses, only rigorously acid-cleaned, high-density polyethylene, polycarbonate, or Teflon™ may be used. Samples may not be sent packed in vermiculite, as the dust from this material represents a contamination risk. Bubble wrap or foam should be used as packing materials.

Samples may be stored in refrigeration/freezer units or in insulated shipping containers with frozen blue ice packs or bags of ice. Frozen tissue and sediment samples may be stored with dry ice. Water samples must be stored at 4°C until preservation. Water samples must always be handled and stored in an upright position.

Aqueous samples should be preserved within 36 hours of collection and shipped to the laboratory using a courier or other traceable method. Freezing in the field preserves solid samples (unless specifically requested otherwise due to analyte requirements). Each sample container may be sealed inside a Ziplock™ bag that is labeled with a unique sample number. Samples must be packed securely to avoid leakage and breakage in transit. The completed chain-of-custody form will always accompany sample sets.

B.3.3 Chain-of-custody

Chain-of-custody procedures require that possession of samples be traceable from the time the samples are collected until completion and submittal of analytical results. A complete chain-of-custody form is to accompany the transfer of samples to the analyzing laboratory. A typical chain-of-custody form is illustrated in Appendix B.

A sample is considered under custody if:

- it is in actual possession;
- it is in view after in physical possession;
- it is placed in a secure area (accessible by or under the scrutiny of authorized personnel only after in possession).

B.3.4 Sample Holding Times

Data quality objectives for sample holding times conform to recommendations documented in the analytical methods for individual parameters. All samples will be analyzed by the contract laboratory before the maximum allowable holding time for any sample is exceeded. Holding times for specific parameters are presented in Table B-2b.

B.3.5 Field Log

Field crews shall be required to keep a field log for each sampling event, which should be recorded and documented in a Field Event Report for each unique field sampling event. The following items should be recorded in the field log for each sampling event:

- time of sample collection;
- sample ID numbers, including etched bottle ID numbers for Teflon™ mercury sample containers and unique IDs for any replicate or blank samples;
- the results of any field measurements (temperature, D.O., pH, conductivity, turbidity) and the time that measurements were made;
- qualitative descriptions of relevant water conditions (e.g. color, flow level, clarity) or weather (e.g. wind, rain) at the time of sample collection;
- a description of any unusual occurrences associated with the sampling event, particularly those that may affect sample or data quality;
- sample collection location (latitude, longitude, and GPS coordinates available);
- sample collection depth, matrix collected, collection method;
- digital photograph of sampling location, if appropriate and possible;
- analyses to be conducted on sample(s);
- reference to QA/QC samples taken.

Appropriate pages from the sampling log will be photocopied and transmitted to the Quality Assurance Manager on a regular basis in the form of a Field Event Report.

The field crews shall have custody of samples during field sampling. Chain-of-custody forms will accompany all samples during shipment to contract laboratories. The field crew will transport all water quality samples to the analytical laboratory, by overnight courier, or by other traceable method.

B.3.6 Laboratory Custody Log

Laboratories shall maintain custody logs sufficient to track each sample from the point of submission to the laboratory through to the point of disposal. Laboratories must be able to track a sample's preservation and analysis date to ensure samples are processed within specified holding times.

B.4 Analytical Methods Requirements

Prior to analysis of any environmental samples for total mercury or monomethyl mercury analyses, the laboratory must have demonstrated the ability to meet minimum performance requirements for each analytical method. Requirements for initial demonstration of laboratory capability are listed below. Undoing capability will be demonstrated through on-site audits, participation in CALFED intercomparison studies, and data validation audits by the QA Management Team.

- SOPs will be submitted for approval by the QA Management Team for each analytical and sample preparation method. SOPs will be reviewed for scientific and quality assurance interest.
- MDL studies following protocols in 40 CFR part 136 initially and annually throughout the scope of the project. MDL studies will be conducted for each matrix and analyte. Reports will be submitted for approval by the QA Management Team.
- Laboratories will participate in the initial CALFED intercomparison study.

B.5 Quality Control Requirements

The types of quality control assessments used in the CALFED Mercury Project are discussed below. Quality control requirements and schedules are summarized in Table 5a-c. Detailed procedures for preparation and analysis of quality control samples are provided in the analytical method documents.

The following quality control requirements pertain to waters, sediments, and tissue samples. Not all sample types provide enough volume to satisfy the quality control requirements listed below (for example, pore waters). Therefore, the Quality Assurance Officer will judge quality control requirements for other sample types on a case-by-case basis.

B.5.1 Qualitative Objectives

Comparability—Comparability of the data can be defined as the similarity of data generated by different monitoring programs. For the purpose of the CALFED Mercury Project, this objective is addressed primarily by using standard sampling and analytical procedures where possible. Additionally, comparability of analytical data is addressed by analysis of standard reference materials (discussed subsequently in this document).

Representativeness—Representativeness can be defined as the degree to which the environmental data generated by the monitoring program accurately and precisely represent actual environmental conditions. For the CALFED Mercury Project, this objective is addressed by the overall design of the monitoring program. Specifically, assuring the representativeness of the data is addressed primarily by selecting appropriate locations, methods, times, and frequencies of sampling for each environmental parameter, and by maintaining the integrity of the sample after collection. Each of these is addressed elsewhere in this document.

B.5.2 Completeness

Data completeness is a measure of the amount of successfully collected and validated data relative to the amount of planned data to be collected for the project. Completeness is usually ex-

pressed as a percentage value. A project objective for percent completeness is typically based on the percentage of the data needed for the program or study to reach valid conclusions. Because the CALFED Mercury Project is intended to be a long term monitoring program, data that are not successfully collected for a specific sample event or site can typically be recollected at a later sampling event. For this reason, most of the data planned for collection can not be considered absolutely critical, and it is difficult to set a meaningful objective for data completeness. However, some reasonable objectives for data are desirable, if only to measure the effectiveness of the Monitoring Program. The following program goals for data completeness are based on the planned sampling frequency and a subjective determination of the relative importance of the monitoring element within the Monitoring Program:

<u>Monitoring Element</u>	<u>Completeness Objective</u>
Trace Metals	90%
General Water Quality Constituents	90%
Fish Tissue	85%

B.5.3 Field Procedures

For basic water quality analyses, quality control samples to be prepared in the field will consist of field blanks and field duplicates. This allows the number of field duplicates and field blanks as a total to achieve an overall rate of 10% for all analyses for a particular parameter. The external QA samples are rotated among sites and events to achieve an overall rate of 5% field duplicate samples.

Field Blanks—The purpose of analyzing field blanks is to demonstrate that sampling procedures do not result in contamination of the environmental samples. Field blanks will be prepared and analyzed for all analytes of interest at the rate of one per sample event, along with the associated environmental samples. Field blanks will consist of laboratory-prepared blank water processed through the sampling equipment using the same procedures used for environmental samples. If any analytes of interest are detected at levels greater than the Reporting Limit (RL) for the parameter, the sampling crew should be notified so that the source of contamination can be identified (if possible) and corrective measures taken prior to the next sampling event.

Field Duplicates—The purpose of analyzing field duplicates is to demonstrate the precision of sampling. Field duplicates will be prepared at the rate of one per sampling event, and analyzed along with the associated environmental samples. Field duplicates will consist of two aliquots from the same composite sample, or of two grab samples collected in rapid succession. If the relative Percent Difference (RPD) of field duplicate results is greater than 25% and the absolute difference is greater than the RL, both samples should be reanalyzed. If an RPD greater than 25% (35% for sediment/soil), for sample results greater than ten times the MDL, is confirmed by reanalysis, environmental results will be flagged “*field variability*”. The sampling crew should be notified so that the source of sampling variability can be identified (if possible) and corrective measures taken prior to the next sampling event.

B.5.4 Laboratory Analyses

For basic water quality analyses, quality control samples prepared in the contract laboratory(s) will typically consist of equipment blanks, method blanks, standard reference materials, laboratory duplicates, matrix spikes, and matrix spike duplicates.

Equipment Blanks—The purpose of analyzing equipment blanks is to demonstrate that sampling equipment is free from contamination. Prior to using sampling equipment for the collection of environmental samples, the laboratory responsible for cleaning and preparation of the equipment will prepare a subset of bottle blanks and sampler blanks.

The blanks will be analyzed using the same analytical methods specified for environmental samples. If any analytes of interest are detected at levels greater than the established control limit (as specified in the cleaning SOPs or laboratory QAP), the source(s) of contamination should be identified and corrected. The affected batch of bottles or equipment should be recleaned, and new equipment blanks should be prepared and analyzed.

Bottle blanks will consist of one of each type of sample container required for water quality analyses, selected randomly from the set of available bottles. The bottles will be filled with laboratory-prepared blank water, preserved like a regular sample for the analyte of interest, and allowed to stand for a minimum of 24 hours before analysis.

Sampler blanks will consist of laboratory-prepared blank water processed through the sampling equipment using the same procedures used for environmental samples.

Laboratories are encouraged to have an equipment-testing program that monitors random testing on a monthly basis. Control limits should be established and corrective actions documented. As part of good laboratory practices, equipment testing should be part of an SOP and addressed in the QAP.

Method Blanks—The purpose of analyzing method blanks is to demonstrate that the analytical procedures do not result in sample contamination. Method blanks will be prepared and analyzed by the contract laboratory at a rate of at least three for each analytical batch. Method blanks will consist of laboratory-prepared blank water processed along with the batch of environmental samples. The method blank should be prepared and analyzed before analysis of the associated environmental samples. If the result of the mean of the three method blanks run with a batch of samples is greater than the established control limit (as specified in the individual, analytical SOP), the source(s) of contamination should be corrected, and the associated samples should be reanalyzed. Additionally, the standard deviation must be within control limits as specified in the analytical SOP for the particular method. If reanalysis is not possible, the associated sample results should be qualified as *below detection* at the reported value.

Laboratory Control Samples (Certified Reference Materials)—The purpose of analyzing laboratory control samples (LCS) is to demonstrate the accuracy of the analytical method. Laboratory control samples will be analyzed at the rate of one per sample batch. Laboratory control samples will consist of a certified reference material of the sample matrix as the sample set. The LCS will be prepared along with the sample batch using the same preparation method. If recovery of any analyte is outside the acceptable range for accuracy, the analytical process is not being performed adequately for that analyte. In this case, the sample batch should be prepared again, and the laboratory control sample should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as *low or high biased*.

Certified reference materials will be supplied to all laboratories for sediment and tissues analysis. All analytical laboratories must use the CRM that has been designated for use on the CALFED project.

Matrix Spikes and Matrix Spike Duplicates—The purpose of analyzing matrix spikes (MS) and matrix spike duplicates (MSD) is to demonstrate the performance of the analytical method in a particular sample matrix and to demonstrate precision. Matrix spikes and matrix spike duplicates will be analyzed at the rate of one pair per sample batch for primary measurements of concern. Each matrix spike and matrix spike duplicate will consist of an aliquot of laboratory-fortified environmental sample. Matrix spike samples will be spiked during the preparation phase. Spiking the sample after the preparation phase is an analytical spike and must be recorded as such. In some analytical methods, it is not effective to spike the sample at the preparation phase. In these cases, the sample should be spiked at the analytical phase and reported as an analytical spike.

The analyst's goal should be to spike samples at two to five times native sample concentration. If the sample is spiked too high (>5X native sample concentration), and its percent recovery is within the control limits, the data is considered valid. If the sample is mistakenly spiked too low (<2X native sample concentration), or the native sample is too variable, but the LCS and other QC criteria are in compliance, then only the MS/MSD require reanalysis. The MS/MSD will be reanalyzed with the next batch of samples at a higher spiking level. If the MS/MSD is in compliance when reanalyzed, the previous data set is considered valid. If the MS/MSD is not within the control limits when reanalyzed, matrix interferences need to be investigated and all data flagged. Data will be flagged with a “*high*” or “*low*” bias.

If matrix spike duplicate RPD for any analyte is greater than the precision criterion, the results for that analyte have failed the acceptance criteria. Attempt to correct the problem (by homogenization, dilution, concentration, etc.) and reanalyze the samples and the matrix spike duplicates. If the matrix problem can't be corrected, qualify the results for that analyte as “*not reproducible*”.

Matrix (Digestion) Duplicates—The purpose of analyzing matrix duplicates is to demonstrate the precision of preparation and analytical method. Matrix duplicates will be prepared at the rate of one per analytical batch. Matrix duplicates will consist of two aliquots from the same sample. If an RPD greater than 25% (35% for sediment/soil), for sample results greater than ten times the MDL, is confirmed by reanalysis, environmental results will be flagged.

Table B-5a

Project Quality Control Requirements for Analysis of
Water Quality Samples: Frequency¹ of Field Quality
Assurance Samples for Trace Metals, Organic Carbon,
and General Water Quality Constituents.

<u>Parameter(s)</u>	<u>Field Duplicates</u>	<u>Field Blanks</u>
Mercury	1 per event*	1 per event**
Boron	1 per 2 events	1 per 2 events
Copper	1 per 2 events	1 per event
Cadmium	1 per 2 events	1 per 2 events
Zinc	1 per 2 events	1 per 2 events
Arsenic	1 per 2 events	1 per 2 events
Lead	1 per 2 events	1 per 2 events
Chromium	1 per event	1 per event
Nickel	1 per event	1 per event
Selenium	1 per event	1 per event
Silver	1 per event	1 per event
TSS	1 per event	0
Hardness	1 per event	0
Turbidity	1 per event	0
Alkalinity	1 per 2 events	0
TOC and DOC	1 per 2 events	1 per 2 events
TDS	1 per event	0
Nutrients	1 per event	0
Major Cations and Anions	1 per event	0

* 1 per event with a minimum frequency of 10% and a maximum of 1 in 5.

** For THg: 1 per event with a minimum frequency of 10% and a maximum of 1 in 5.

For MMHg: For the first 6 months of sampling 1 per event with a minimum frequency of 10% and a maximum of 1 in 5.
After the first 6 months of sampling, blanks are only required every six months.

¹An analytical batch is defined as 20 or less samples.

Table B-5b

Project Quality Control Requirements for Analysis of Total Mercury (THg) and Mono-Methyl Mercury (MMHg) in Waters.

<u>QA Procedure</u>	<u>QA Parameter</u>	<u>Frequency¹</u>	<u>Criterion</u>
Equipment Blanks: • bottle blanks • sampler blanks	Contamination	Random statistical testing. See specifics in Section B.5 of QAPP.	< 1/5 Sample Results or < MDL for Sample Concentrations Close to MDL
Field Blanks	Contamination	Various, see Table B-3a	< 1/5 Sample Results or ≤MDL for low-level samples
Field Duplicate	Field Precision	Various, see Table B-3a	RPD ≤ 25% if the sample result is >10X the MDL
Method Blank	Contamination	3 per analytical batch	THg < 0.5 ng/L MMHg < 0.1 ng/L
LCS (CRM)	Accuracy	1 per analytical batch	THg 75–125% Rec. MMHg 70–130% Rec.
Digestion Duplicate	Analytical Precision	1 per analytical batch	RPD ≤ 25% if the sample results is >10X the MDL
Matrix Spike	Matrix Interference	1 per analytical batch	THg 75–125% Rec. MMHg 70–130% Rec.
Matrix Spike Duplicate	Precision	1 per batch	RPD ≤ 25%
Continuing Calibration	Analytical Control	1 per 10 sample runs (including QC samples)	80–120% of initial slope
Assess percent of data successfully collected	Data Completeness	1 per event	90%

Notes:

MDL = Method Detection Limit; RPD = Relative Percent Difference;

RSD = Relative Standard Deviation; REC = Recovery; LCS = Laboratory Control Sample;

CRM = Certified Reference Material

¹An analytical batch is defined as 20 or less samples.

Table B-5c

Project Quality Control Requirements for Analysis of Total Mercury (THg) and Mono-Methyl Mercury (MMHg) in Sediments and Tissues.

<u>QA Procedure</u>	<u>QA Parameter</u>	<u>Frequency¹</u>	<u>Criterion</u>
Equipment Blanks: • bottle blanks • sampler blanks	Contamination	Random statistical testing. See specifics in Section B.5 of QAPP.	< 5X Sample Results or < MDL for Sample Concentrations Close to MDL
Field Blanks	Contamination	Various, see Table B-5a	< 5X Sample Results or ≤MDL for low-level samples
Field Duplicate	Field Precision and Sample Homogeneity	Various, see Table B-5a	RPD ≤ 25% if the sample result is >10X the MDL
Method Blank	Contamination	3 per analytical batch	THg < 0.10 ng/g MMHg Sediments < 0.02 ng/g Tissues < 2 ng/g
LCS (CRM)	Accuracy	1 per analytical batch	THg 75–125% Rec. MMHg 70–130% Rec.
Digestion Duplicate	Analytical Precision and Sample Homogeneity	1 per analytical batch	RPD ≤ 25% if the sample results is L >10X the MD
Matrix Spike	Matrix Interference	1 per analytical batch	THg 75–125% Rec. MMHg 70–130% Rec.
Matrix Spike Duplicate	Precision	1 per batch	RPD ≤ 25%
Continuing Calibration	Analytical Control	1 per 10 sample runs (including QC samples)	80–120% of initial slope
Assess percent of data successfully collected	Data Completeness	1 per event	90%

Notes:

MDL = Method Detection Limit; RPD = Relative Percent Difference;

RSD = Relative Standard Deviation; REC = Recovery; LCS = Laboratory Control Sample;

CRM = Certified Reference Material

¹An analytical batch is defined as 20 or less samples.

B.6 Instrument and Equipment Preventative Maintenance

B.6.1 Sample Equipment Cleaning Procedures

Equipment used for sample collection (peristaltic pump tubing, carboys and carboy caps, sample bottles, etc.) will be cleaned according to the specific procedures documented for each analytical method. The cleaning procedures for equipment used to collect water quality, sediment, and fish tissue samples is documented in Appendix C.

At least one equipment blank will be generated and analyzed prior to initiating monitoring for the current program year, and additional equipment blanks will be analyzed for new lots of critical cleaning reagents. In addition, for all analytes where contamination is considered a significant concern, field blanks will be collected and analyzed as directed in Section B-5 of this document. If the results of these analyses indicate any contamination, the source will be identified and corrected, and the equipment will be re-cleaned and re-tested. The combined regimen of equipment blanks and field blanks is considered to provide adequate control against potential systematic equipment contamination problems.

B.6.2 Analytical Instrument and Equipment Testing Procedures and Corrective Actions

Testing, inspection, maintenance of analytical equipment used by the contract laboratory, and corrective actions are documented in the Quality Assurance manuals for each analyzing laboratory. Laboratory QA Manuals are made available for review at the analyzing laboratory.

B.7 Calibration Procedures and Frequency

B.7.1 Laboratory Analytical Equipment

Frequency and procedures for calibration of analytical equipment used by each contract laboratory is documented in the Quality Assurance Manual for each contract laboratory. Laboratory QA Manuals are made available for review at the analyzing laboratory.

B.7.2 Field Instruments

Calibration of all instruments used for measurement of field parameters (temperature, pH, dissolved oxygen, and electroconductivity) is performed as described in the owner's manuals for individual instruments. Instruments used to measure pH, dissolved oxygen, and electroconductivity should be calibrated prior to taking field measurements at each site for each event. Typical field instrument calibration procedures are as follows:

- Temperature calibration is factory-set and requires no subsequent calibration.
- Calibration for pH measurement is accomplished using standard buffer solutions.
- Calibration for dissolved oxygen measurements is accomplished using an oxygen-saturated water sample.
- Calibration for electroconductivity measurements is generally accomplished using potassium chloride standard solutions.

B.8 Inspection/Acceptance Requirements for Supplies and Consumables

Gloves, sample containers, and any other consumable equipment used for sampling will be inspected by the sampling crew on receipt and will be rejected/returned if any obvious signs of contamination (torn packages, etc.) are observed. Inspection protocols and acceptance criteria for laboratory analytical reagents and other consumables are documented in the Quality Assurance Manuals for individual laboratories. Laboratory QA Manuals are made available for review at the analyzing laboratory.

B.9 General Laboratory Operations for All Participating Labs

B.9.1 Laboratory Operations

This section addresses only general laboratory operations, while participating laboratories will have their respective Laboratory Quality Assurance Manuals for their respective field and laboratory

analytical QA/QC requirements and procedures associated with the processing of their specific samples for their respective Project tasks/subtasks. All laboratories providing analytical support for chemical or biological analyses will have the appropriate facilities to store, prepare, and process samples as well as appropriate instrumentation and staff to provide data of the required quality within the time period dictated by the project. Laboratories are expected to conduct operations using good laboratory practices, including:

- A program of scheduled maintenance of analytical balances, microscopes, laboratory equipment and instrumentation.
- Routine checking of analytical balances using a set of standard reference weights (ASTM Class 3, NIST Class S-1, or equivalents).
- Checking and recording the composition of fresh calibration standards against the previous lot. Acceptable comparisons are < 5 percent of the previous value.
- Recording all analytical data in bound (where possible) logbooks, with all entries in ink.
- Monitoring and documenting the temperatures of cold storage areas and freezer units once per week.
- Verifying the efficiency of fume hoods.
- Having a source of reagent water meeting American Society of Testing and Materials (ASTM) Type I specifications (ASTM 1984) available in sufficient quantity to support analytical operations. The conductivity of the reagent water will not exceed 18 megohm at 25°C.
- Labeling all containers used in the laboratory with date prepared, contents, and initials of the individual who prepared the contents; other information as appropriate.
- Dating and storing all chemicals safely upon receipt. Chemicals are disposed of properly when the expiration date has expired.
- Using a laboratory information management system to track the location and status of any sample received for analysis.
- QAPP, SOPs, analytical methods manuals, safety plans readily available to staff.

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Laboratories will be able to provide information documenting their ability to conduct the analyses with the required level of data quality. Such information might include results from interlaboratory comparison studies, control charts and summary data of internal QA/QC checks, and results from certified reference material analyses. Laboratories will also be able to provide analytical data and associ-

ated QA/QC information in a format and time frame agreed upon with the Project QA Managers or Project Manager or their designee.

B.9.2 Laboratory Personnel, Training and Safety

To ensure that the samples are analyzed in a consistent manner throughout the duration of the project, key laboratory personnel will participate in an orientation session conducted during an initial site visit or via communications with Project QA staff. The purpose of the orientation session is to familiarize key laboratory personnel with the QAPP and the QA/QC program. Participating laboratories may be required to demonstrate acceptable performance before analysis of samples can proceed, as described for each indicator in subsequent sections. Laboratory operations will be evaluated on a continuous basis through technical systems audits, and by participation in interlaboratory round-robin programs. Meetings shall be held with all participating laboratories at regular intervals to continually review QA/QC procedures, and to revise/update the QAPP.

Personnel in any laboratory performing analyses for this Project will be well versed in good laboratory practices, including standard safety procedures. It is the responsibility of the particular participating laboratory QA Officer, laboratory manager and/or supervisor to ensure that safety training is mandatory for all laboratory personnel. Each laboratory is responsible for maintaining a current safety manual in compliance with the Occupational Safety and Health Administration (OSHA), or equivalent state or local regulations. The safety manual will be readily available to laboratory personnel, including all appropriate MSDS materials. Proper procedures for safe storage, handling and disposal of chemicals will be followed at all times; each chemical will be treated as a potential health hazard and good laboratory practices will be implemented accordingly.

B.9.3 Quality Assurance Documentation

All laboratories will have readily available for all staff the latest revision of the overall Project QAPP. In addition, the following documents and information will be current, and they will be available to all laboratory personnel participating in the processing of Project samples, as well as to Project QA and Project Management officials:

- Laboratory QA Plan: Clearly defined policies and protocols specific to a particular laboratory including personnel

responsibilities, laboratory acceptance criteria for release of data, and procedures for determining the acceptability of results.

- Laboratory Standard Operating Procedures (SOPs): Contains instructions for performing routine laboratory procedures, such as freezer logs, equipment and instrument instruction information, etc.
- Laboratory Analytical Methods Manual (Analytical SOPs): Step-by-step instructions describing exactly how a method is implemented in the laboratory for a particular analytical procedure. Contains all analytical methods utilized in the particular lab for the Project.
- Field Sampling Methods Manual (Sampling SOPs): Step-by-step instructions describing exactly how a method is implemented in the field for the collection of a sample for a particular analytical procedure. Contains all field methods utilized by the particular lab for the Project.
- Instrument performance information: Information on instrument baseline noise, calibration standard response, analytical precision and bias data, detection limits, etc. This information usually is recorded in logbooks or laboratory notebooks.
- Control charts: As part of good laboratory practices, all analytical laboratories are encouraged to maintain up-to-date control charts.

B.9.4 Analytical Procedures

Complete and detailed procedures for processing and analysis of samples in the field have been noted in Field Sampling SOPs attached in Appendix C, as well as in the respective laboratory's Field Methods Manual. Detailed procedures for processing and analysis of samples in the laboratory are provided in the attached Appendix D, as well as in the respective laboratory's Analytical Methods Manual.

B.9.5 Laboratory Performance Audits/Corrective Action

Initially, a QA performance "audit" or "visit" will be performed by Project QA staff to determine if each laboratory effort is in compliance with the procedures outlined in the this QAPP and to assist the laboratory where needed. Additionally, technical systems audits

may be conducted by a team composed of the Project QA Officer or designee, and his/her technical assistants. Reviews may be conducted at any time during the scope of the study. Results will be reviewed with participating laboratory staffs and corrective action recommended and implemented, where necessary. Furthermore, laboratory performance will be assessed on a continuous basis through the use of laboratory intercomparison studies (round robins).

B.9.6 Preparation and Use of Control Charts

Control charts are a graphical tool to demonstrate and monitor statistical control of a measurement process. A control chart basically is a sequential plot of some sample attribute (measured value or statistic). The type of control chart used primarily by laboratory analysts is a “property” chart of individual measurements (termed an X chart).

Measured values are plotted in their sequence of measurement. Three sets of limits are superimposed on the chart: 1) the “central line”, 2) the upper and lower “warning limits”, and 3) the upper and lower “control limits”.

As part of good laboratory practices, all analytical laboratories are encouraged to maintain up-to-date control charts.

B.10. Data Management

Copies of field logs, copies of chain of custody forms, original preliminary and final lab reports, and electronic media reports will be sent to the Quality Assurance Manager. Each type of report will be stored separately and ordered chronologically. The field crew will retain original field logs. The contract laboratory will retain original chain of custody forms. Copies of the preliminary and final data reports will be retained by the contract laboratory(s).

Concentrations of chemicals, and all numerical biological parameters will be calculated as described in the laboratory Standard Operating Procedures or referenced method document for each analyte or parameter.

The various data and information generated from the CALFED Mercury Project will be stored and maintained at the Program Manager’s offices. The data generated from the monitoring program will be transmitted to the Quality Assurance Manager in various formats and converted to a standard database format maintained on personal computers in the Program Manager’s offices. After data

entry or data transfer procedures are completed for each sample event, data will be inspected for data transcription errors, and corrected as appropriate. After the final QA checks for errors are completed, the data are added to the final database. The production of data tables is generated from this database.

In cases where environmental results are less than the reporting limit for a parameter, the results will be reported as “less than” the reporting limit; e.g. an analytical result of 4µg/L for an analyte with a reporting limit of 5µg/L will be reported as <5µg/L.



C. Assessment and Oversight

C.1. Assessments and Response Actions

Assessments of compliance with quality control procedures will be undertaken on a routine basis during the data collection phase of the project:

- The field sampling crews will perform performance assessments of sampling procedures. Corrective actions shall be carried out by the field sampling crew and reported to the Quality Assurance Manager.
- Assessment of laboratory QC results and implementation of corrective actions will be the responsibility of the QA officer at each laboratory and shall be reported to the Quality Assurance Manager as part of any data reports.
- Assessment of field QC results and implementation of corrective actions shall be the responsibility of the Quality Assurance Manager.

Routine procedures to assess precision and accuracy, criteria for success, and corrective actions have been discussed previously (Section B) and are summarized in Tables 5a-c.

Quarterly status reports will be produced by the participating project Principal Investigators, and compiled and submitted to CALFED by the DFG QA Manager and the External QA Officer to document project status, results of performance evaluations, data quality assessments, and any significant QA problems and recommended solutions.



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C.2. Quality Assurance Reports to Management

A quality assurance report will be prepared by the Quality Assurance Manager following each year of monitoring, as part of the annual report produced for the CALFED Mercury Project. The quality assurance report will summarize the results of QA/QC assessments and evaluations, including precision, accuracy, comparability, representativeness, and completeness of the monitoring data. The annual report will be distributed to the project managers, as well as to all other program participants and interested parties.



D. Data Validation and Usability

D.1. Data Review, Validation, and Verification

In addition to the data quality objectives presented in Tables 5a-c, the standard data validation procedures documented in the contract laboratory's Quality Assurance Manuals will be used to accept, reject, or qualify the data generated by the laboratory. Each laboratory's QA officer will be responsible for validating data generated by the laboratory. The Project's Principal Investigator will be responsible for validating and qualifying all data based on the evaluation of field and laboratory quality control samples.

D.2. Data Reporting

Laboratory personnel will verify that the measurement process was "in control" (i.e., all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with the analysis of a subsequent batch. In addition, each laboratory will establish a system for detecting and reducing transcription and/or calculation errors prior to reporting data.

Only data, which have met data quality objectives, or data which have acceptable deviations explained, will be submitted by the laboratory. When QA requirements have not been met, the samples will be reanalyzed when possible and only the results of the reanalysis will be submitted, provided they are acceptable.



E. Utilizing Subcontractors

E.1. Subcontracting Services

Project Investigators may subcontract services from analytical laboratories not covered by this QAPP if the following procedures are followed. Subcontracting services may only be used for ancillary measurements and not for any mercury or mercury speciation analyses. The CALFED Quality Assurance Manager, Max Puckett must approve subcontracting services, prior to submission of samples to the subcontracted laboratory.

Project Investigators will supply subcontract laboratories with the “Subcontract Laboratory Approval Form” (Appendix F). The subcontract laboratory must complete the form and return it to the CALFED Quality Assurance Manager along with any required supporting documentation (i.e. QAP, SOP, state accreditation certificates).

The CALFED Quality Assurance Manager will review the application and complete the form by indicating approval status, signing and dating in the appropriate section. A copy of the form will be submitted to the Project Investigator. The CALFED Quality Assurance Manager will maintain a file titled “Approved Subcontract Laboratories.” This file will contain all completed applications and supporting documentation.

Please note that the “Subcontract Laboratory Approval Form” is analyte and matrix specific. One form may be used for several different analytes and matrices, but approval in one area does not guarantee approval in additional areas. An additional form must be submitted each time an approved subcontract laboratory wants to upgrade their status to include more analytes and matrices.



F. Revisions to the Quality Assurance Project Plan

The purpose of this section is to document significant additions, deletions, and revisions to the approved QAPP for this project, and to provide the rationale for these changes. As revisions are made and approved/implemented, they will be documented in this section. Currently there are no revisions, since this is the first edition of the QAPP for this project.



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