

**GUADALUPE RIVER WATERSHED MERCURY TMDL PROJECT**  
*AGREEMENT NO. A2643G*

**TECHNICAL MEMORANDUM 7.4.2**  
**QUALITY ASSURANCE PLAN**

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We would like to thank the following individual for providing the SOPs to be used in the mercury analyses for the project, which are included in the appendix of this quality assurance plan document.

Nicolas Bloom, Frontier Geosciences

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# QUALITY ASSURANCE PLAN

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## 1.0 PROJECT MANAGEMENT

### 1.1 PROJECT TASK/ORGANIZATION AND RESPONSIBILITIES

The project manager of the Guadalupe TMDL Project is Dr. Tom Grieb. Dr. Grieb is a senior scientist and will utilize a hands-on approach to the management tasks. He will participate in all technical aspects of the project, and he will be the lead scientist in the monitoring-design and data analysis tasks. He has experience managing cooperative projects involving the Santa Clara Basin Watershed Management Initiative (WMI) that will serve in this project as the primary vehicle for public and stakeholder participation. Dr. Grieb will be the point-of-contact and chief spokesperson for the Tetra Tech project team. In addition to the project manager, the Tetra Tech project management team will consist of a project administrator, Rhonda Carlisle, and the quality assurance officer, Gary Wortham.

Mr. Gary Wortham, QA officer, will report directly to the Project Manager, as shown in the Project Organization Diagram included in the separate Project Management Plan. Mr. Wortham will be responsible for preparing the QA/QC sections of the individual sampling plans for this project, interfacing with the laboratories used to insure that all QA/QC requirements are understood and can be satisfied, validating the data from the field and laboratories, and preparing the QA reports for the various sampling efforts. Mr. Wortham is a senior environmental scientist with more than 13 years of field sampling and analytical chemical laboratory management and QA/QC experience. Mr. Wortham served as General Manager of a combined analytical chemistry and aquatic toxicology laboratory for seven years. In that capacity, he generated project specific QAPP documents and reviewed all work products to ensure that they met the QA/QC requirements of the project. While at Tetra Tech, he has served as QA Officer for the City of San Jose Streamflow Augmentation Project and is trained in ultra-clean mercury sampling procedures.

### 1.2 PROBLEM DEFINITION AND BACKGROUND

The Santa Clara Valley Water District has been designated as the lead agency on behalf of the Santa Clara Basin Watershed Management Initiative (WMI) for the development

of a Total Maximum Daily Load (TMDL) for mercury in the entire Guadalupe River Watershed.

Former mercury mines are located in the upper Guadalupe River Watershed, which have contributed mercury to downstream surface waters and San Francisco Bay. The New Almaden Mining District in the Guadalupe Creek and Alamitos subwatershed was the largest producer of mercury in North America. Mercury in the mining district is primarily present as the mineral cinnabar. Mercury in downgradient water and sediment can be present in dissolved or particulate forms. Under appropriate conditions, bacteria can convert inorganic mercury to the organic form, methylmercury, which is the form of primary concern from a human health and ecological perspective due to its greater toxicity and ability to bioaccumulate.

Other sources of mercury to the watershed include atmospheric deposition from global and local sources, stormwater runoff, and seepage from contaminated sites and landfills.

### 1.3 PROJECT/TASK DESCRIPTION

The overall objective of this project is to provide information to be used in development of a TMDL for mercury for the Guadalupe River Watershed, which includes the Guadalupe River, several smaller tributaries, and four reservoirs in the Upper Guadalupe watershed. The major tasks supported by this QAPP include the following:

- **Task 2: Synoptic Survey** - A sampling program will be designed and conducted to measure current total and methylmercury concentrations in water and sediment; determine extent and type of wetlands that may serve as potential methylation sites; identify sections along the creeks and rivers where fine sediment is accumulating or bank soils are actively being eroded; and where mine wastes are present in or near the waterbodies. A report will be prepared documenting the results and QA/QC information.
- **Task 3: Project Database** - Existing and new project data and QA/QC information will be incorporated into an electronic GIS-linked database with accompanying maps. The types of data will include: mercury sources, water quality data for mercury and ancillary parameters, watershed characteristics, sediment removal data, reservoir data, and biological receptor information.
- **Task 5: Data Collection** - Detailed sampling will be conducted to provide data to be used to determine the TMDL and to fill in key data gaps based on the results of the previous tasks such as sedimentation rates in the reservoirs and methylation rates in wetlands and deeper stream reaches. Laboratory studies may be conducted to evaluate hypotheses regarding the mercury cycle in water, sediment, or biota. Reports will be prepared describing the field sampling and laboratory programs and the associated QA/QC data.

Field sampling plans will be prepared prior to conducting sampling activities. The sampling plans will include sampling objectives, data quality objectives, sampling

locations, specific parameters, number and type of samples to be collected, QA/QC procedures, data analysis procedures, and data reporting procedures.

The planned sampling is expected to include the following types of activities:

- Water samples will be collected using ultra-clean techniques (EPA method 1669 – Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, US EPA, 1976) and analyzed for four forms of mercury (total mercury and methylmercury in filtered and unfiltered samples) using ultra-clean techniques.
- Water samples will be collected and analyzed for suspended solids, sulfate, sulfide, chloride, DOC, nitrate, nitrite, ammonia, total phosphorus, chlorophyll-a, pH, alkalinity, dissolved and total iron, temperature, specific conductivity, and dissolved oxygen.
- Sediment samples will be collected and analyzed for total and methylmercury, sulfide, sulfate, pH, total iron, moisture content, total organic carbon, and total phosphorus. Sediment samples will be described with respect to grain-size distribution, color, and any odors.
- Fish sampling and analysis for total mercury may be conducted under Task 5.
- Flows will be measured at the river/creek locations at the time of sampling for use in estimating mercury loads.
- A survey will be conducted to identify reaches of the Guadalupe River and tributaries with wetlands or abundant aquatic vegetation.
- A survey will be conducted to identify areas with high fine sediment accumulation and active erosion along the Guadalupe River and tributaries.
- A survey will be conducted to identify areas where calcines and other mine wastes are present in or near waterbodies.
- Planned laboratory methods are listed in Table 1.
- Table 2 shows where field and QA/QC procedures are located in this document.
- This QAPP can be amended to cover additional sampling and laboratory activities.

**Table 1  
Planned Laboratory and Field Measurement Methods**

<b>Parameter</b>	<b>EPA Method No.</b>	<b>Units</b>	<b>Reporting Limit</b>
<b>Water</b>			
Total Mercury	1631	ng/L	0.2 ng/L
Dissolved Mercury	1631	ng/L	0.2 ng/L
Methylmercury	1630	ng/L	0.05ng/L
Filtered Methylmercury	1630	ng/L	0.05ng/L
Suspended Solids Concentration	ASTM D3977-97 (2002)	mg/L	1 mg/L
Dissolved Organic Carbon	415.1	mg/L	1 mg/L
Sulfate	300	mg/L	5 mg/L
Sulfide	376.2	mg/L	0.04 mg/L
Chloride	300	mg/L	0.2 mg/L
Total and Dissolved Iron	6010	mg/L	0.2 mg/L
Total Phosphorus	365.1	mg/L	0.03 mg/L
Alkalinity	310.3	mg/L	1 mg/L
Nitrate	300.0	mg/L	0.1 mg/L
Nitrite	300.0	mg/L	0.1 mg/L
Ammonia	350.3	mg/L	0.1 mg/L
Chlorophyll-a	SM 10200-H	ug/L	0.5 ug/L
<b>Sediment Samples</b>			
Total Mercury	1631	ng/g	0.5 ng/g
Methylmercury	1630	ng/g	0.2 ng/g
Sulfide	SMWW 4500-S2	mg/kg	10 mg/kg
Sulfate	300	mg/kg	10 mg/kg
pH	9045C	Std. pH units (SU)	0.1 SU
Total Fe	6010	mg/kg	0.5 mg/kg
Moisture Content	ASTM D2216	% by wt	0.01% by wt
Grain Size Distribution	ASTM D422/4464	% by wt	0.1% by wt
Total Organic Carbon	9060	mg/kg	5 mg/kg
Total Phosphorus	365.1	Mg/kg	0.3 mg/kg
<b>Fish Samples</b>			
Total Mercury	1631	ng/g	0.1 ng/g



**Table 1 (continued)**

<b>Parameter</b>	<b>Units</b>	<b>Range</b>	<b>Resolution</b>	<b>Accuracy</b>
<b>Field Parameters</b>				
Specific Conductivity	mS/cm	0 to 100 mS/cm	0.001 to 0.1 mS/cm	±0.5% of reading or 0.001 mS/cm
Temperature	°C	-5 to +45 °C	0.01°C	±0.15°C
Dissolved Oxygen	mg/L	0 to 50 mg/L	0.01 mg/L	±0.2 - ±0.6 mg/L (range dependent)
	% Sat	0 to 500%	0.1%	±2 - ±6% air sat. (range dependent)
pH	SU	0 to 14 SU	0.01 SU	±0.2 SU
Turbidity	NTU	0 to 1,000 NTU	0.1 NTU	±0.5% of reading or 2 NTU (greater value)

Specific conductivity, temperature, dissolved oxygen, pH, and turbidity will be measured in the water samples in the field and as depth profiles in the reservoirs and lakes.

**Table 2  
Summary of Identified SOPs and QA/QC Procedures**

<b>Parameter</b>	<b>Field Procedures</b>	<b>Quality Control Criteria Procedure</b>
<b>General</b>		
Temperature	See Section 2.2	Section 2.5/2.6
DO	See Section 2.2	Section 2.5/2.6
pH	See Section 2.2	Section 2.5/2.6
Conductivity	See Section 2.2	Section 2.5/2.6
Turbidity	See Section 2.2	Section 2.5/2.6
TOC/DOC	See Section 2.2	Section 3.3/3.4
SSC	See Section 2.2	Section 3.3/3.4
Chloride	See Section 2.2	Section 3.3/3.4
Sulfide	See Section 2.2	Section 3.3/3.4
Sulfate	See Section 2.2	Section 3.3/3.4
Nutrients	See Section 2.2	Section 3.3/3.4
Chlorophyll-a	See Section 2.2	Section 3.3/3.4
Moisture Content	See Section 2.2	Section 3.3/3.4
Grain Size	See Section 2.2	Section 3.3/3.4
<b>Metals (total &amp; dissolved)</b>		
Mercury	Section 2.2/SOPs	Section 3.3/3.4 & SOPs
Methylmercury	Section 2.2/SOPs	Section 3.3/3.4 & SOPs
Iron	See Section 3.0	Section 3.3/3.4

Ultra-clean mercury methods are provided in the Appendix for handling and analyzing water, sediment, and tissue samples.

**1.4 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA**

Quality Assurance is a management function. It deals with setting policy and running an administrative system of management controls that cover planning, implementation, and review of data collection activities. Quality control is technical in nature and is implemented at the project level. It includes all the scientific precautions, such as calibration and duplication, that are needed to acquire data of known and adequate quality.

This project will include a synoptic survey and detailed field and laboratory studies to be determined following completion of Tasks 1 through 4. The data quality objectives for the field sampling programs are:

- To obtain valid data that meet requested reporting limits for total, dissolved, and methylmercury in water and total and methylmercury in sediment at all sampling locations.
- To obtain valid data that meet requested reporting limits for listed ancillary parameters in water and sediment at all sampling locations.

The data quality objectives for the laboratory experiments will be included in the specific plans for those experiments. In general, the purpose will be to obtain necessary data to conclusively test proposed hypotheses.

The chemical concentration data from field surveys and laboratory experiments will be evaluated based on accuracy, precision, representativeness, comparability, and completeness, as discussed in Section 3.4 of this QAPP. Other information from the field surveys will be reviewed for representativeness, comparability, and completeness.

### **1.5 DOCUMENTATION AND RECORDS**

This document presents the Guadalupe TMDL Mercury Study Project's quality assurance and quality control (QA/QC) protocols, requirements for laboratories associated with the project, and protocols for field documentation of sampling activities.

Field documentation will include: field equipment calibration logs, unique sample labeling, preparation of a field log book, preparation and maintenance of chain of custody records, request for laboratory analysis forms, and shipping papers. The specific information to be collected and noted on each of these documents is discussed in Section 2.3 on Sample Handling and Custody.

Laboratory documentation will include: sample results, case narratives, instrument calibration results, and laboratory QA/QC data. The specific information to be collected is discussed in Section 3.0 on Laboratory Protocols.

## **2.0 MEASUREMENT/DATA ACQUISITION**

### **2.1 SAMPLING PROGRAM DESIGN**

Field sampling plans will be prepared for the synoptic survey and the data collection effort to be designed under Task 5. QA/QC procedures will be included in these plans.

Laboratory experiments may be planned as part of Task 5 to address specific hypotheses regarding the form of mercury or its bioavailability. Detailed sampling plans with QA/QC procedures will be prepared for each of these experiments.

### **2.2 SAMPLING METHODS REQUIREMENTS**

The environmental media to be sampled will include water and sediment. The planned laboratory analytical methods are listed in Table 1. The methods have been selected to

provide the required precision, accuracy, and detection limits necessary to meet the information needs of the project. The required type of container for each planned laboratory method is listed in Table 3. The required preservatives and holding times for the chemical parameters are listed in Table 4.

**Table 3**  
**Sample Containers Used for Various Chemical Parameters in Water and Sediment**

<b>Container</b>	<b>Parameters</b>	<b>Requirements</b>
1 Liter HDPE	Chloride, Sulfate, Ammonia, Nitrate, Nitrite	Clean Bulk Pack Containers
2 Liter HDPE	Total Suspended Solids, Total Dissolved Solids, Total Organic Carbon, Dissolved Organic Carbon, Total Phosphorus	Clean Bulk Pack Containers
1 Liter HDPE	Total and Dissolved Iron	Certified by vendor for trace metals analyses
1 Liter PTFE	Total and Dissolved Mercury, Methylmercury (unfiltered & filtered)	Ultra clean prep. (See SOP for bottle washing)
250 mL HDPE	Sulfide	Clean Bulk Pack Containers
125 mL PTFE	Total Mercury and Moisture Content in Sediment	Ultra clean prep. (See SOP for bottle washing)
20 mL glass vial	Methylmercury in Sediment	Ultra clean prep. (See SOP for bottle washing)
125 mL HDPE	Total Iron, Total Phosphorus, and TOC in Sediment	Clean Bulk Pack Containers
250 mL HDPE	Grain-size Distribution in Sediment	Clean Bulk Pack Containers
125 mL HDPE	Total Mercury in Fish	Clean Bulk Pack Containers

**Table 4**  
**Chemical Parameters and Preservatives and Holding Times**

<b>Matrix</b>	<b>Parameter</b>	<b>Preservative</b>	<b>Laboratory Preparation</b>	<b>Holding Time</b>
<b>Water</b>	Total Hg	None	Acidify in lab 0.5% HCl	28 days after preservation
	Dissolved Mercury	None	Filter then acidify in lab 0.5% HCl	28 days after preservation
	Methylmercury	Nitric acid	Acidify in lab 0.5% HCl	28 days after preservation
	Dissolved Methylmercury	Nitric acid	Filter then acidify in lab 0.5% HCl	28 days after preservation
	Total Iron	Nitric acid	None	6 months
	Dissolved Iron	Filter in field then acidity with nitric acid	None	6 months
	DOC	Filter in field then acidify – HCl	None	28 days
	Chloride	Cool to < 4 °C	None	28 days
	Alkalinity	Cool to < 4 °C	None	28 days
	Nitrate	Cool to < 4 °C	None	2 days
	Nitrite	Cool to < 4 °C	None	2 days
	Ammonia	Acidify with H <sub>2</sub> SO <sub>4</sub> to pH<2	None	28 days
	Total Phosphorus	Acidify with H <sub>2</sub> SO <sub>4</sub> to pH<2	None	28 days
	Sulfate	Cool to < 4 °C	None	28 days
	Sulfide	Zinc Acetate & NaOH	None	7 days
	<b>Sediment</b>	SSC	Cool to < 4 °C	Separation
Chlorophyll-a		Cool to < 4 °C	Filter	6 months after filtering
Total Mercury		Cool to < 4 °C	See SOP in appendix	6 months
Methylmercury		Cool to < 4 °C	See SOP in appendix	6 months
Total Iron		Cool to < 4 °C	Digestion	6 months
Sulfate		Cool to < 4 °C	Digestion	6 months
Sulfide		Cool to < 4 °C	Digestion	6 months
pH		Cool to < 4 °C	None	7 days
Total Organic Carbon		Cool to < 4 °C	Extraction	7 days
Moisture Content		Cool to < 4 °C	None	2 days
<b>Fish</b>	Grain Size	None	None	6 months
	Total Mercury	Freeze at <-20 °C	Digestion	1 year after

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upon receipt at lab

processing, if  
frozen

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Filters to be used include: 0.45 $\mu$  nitrocellulose membrane for dissolved mercury and methylmercury; 0.45 $\mu$  cellulose acetate filter for dissolved iron; either a 0.45 $\mu$  nucleopore filter for low suspended solids (<10 mg/L) and a 62 $\mu$  cellulose acetate filter for high suspended solids.

### **2.2.1 Ultra-clean Water Sampling for Mercury**

Field personnel will follow strict procedures to ensure the collection of uncontaminated water samples. Field personnel are trained in EPA Method 1669 sampling procedures and techniques. SOPs for collection of trace-level mercury water samples and filtering are included in the appendix. The filtering of the mercury samples will be conducted in the laboratory. The following procedure is a summary of EPA Method 1669 for manual collection of samples directly into the sample bottle for collecting surface samples. Pumping will be used to collect deeper water samples.

1. At the site, all sampling personnel must put on a pair of clean room PVC gloves before commencing sample collection activity. Note that “clean hands” should put on shoulder-length polyethylene gloves prior to donning short PVC gloves. The “dirty hands” person only puts on the PVC gloves.
2. “Dirty hands” must open the storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.
3. Next, “clean hands” opens the inside bag containing the sample bottle and removes the bottle.
4. “Clean hands” unscrews the cap and, while holding the cap upside down, discards the reagent water directly into the water body.
5. “Clean hands” then submerges the sample bottle, and allows the bottle to partially fill with sample. “Clean hands” screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, “clean hands” holds the bottle just under the surface of the water and allows bottle to fill with sample. After the bottle is filled and while the bottle is inverted so that the mouth of the bottle is underwater, “clean hands” replaces the cap of the bottle. In this way, the sample has never contacted the air.
6. Once the bottle lid is replaced, “dirty hands” reopens the outer plastic bag, and “clean hands” opens the inside bag, places the bottle inside it, and zips the inner bag.
7. “Dirty hands” zips the outer bag.
8. Documentation – after each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

To ensure the collection of uncontaminated samples, only “clean hands” enters the water body. “Clean hands” walks upstream to the sample location and remains in the same location during the entire sample collection to avoid disturbing the stream sediments. In the event that “dirty hands” steps into the water body, the turbid water must be allowed to flow downstream before samples can be collected.

If the sampling is under high flow conditions where the person cannot safely enter the river, a container mounted on a pole will be used to collect water samples for filling the containers. A new container would be used for each location.

The procedure for collecting deep water samples for mercury using a peristaltic pump with specially-cleaned Teflon tubing are included in the SOP for Ultra-clean Aqueous Sample Collection and Preservation.

### **2.2.2 Water Sampling for Ancillary Water Quality Parameters**

To ensure the collection of uncontaminated samples, the bottles for the ancillary parameters are passed to the “clean hands” person, after collecting the mercury samples. In the event that “dirty hands” steps into the water body, the turbid water must be allowed to flow downstream before samples can be collected. Water samples will be collected using three distinct procedures:

**Unpreserved samples** – Sample bottles that do not contain preservative (e.g., TDS, SSC) will be rinsed out three times with sample water prior to sample collection. The rinse procedure will be as follows: (1) fill sample bottle with sample until it is approximately 25% filled, (2) close cap, (3) shake vigorously, (4) discard, (5) repeat two additional times, and (6) collect sample from just below water surface. All water sample bottles will be completely filled and have no head-space (the space between the surface of the sample and the cap).

**Preserved samples** – In shallow streams, a clean bottle will be filled after rinsing it three times, as described above, by facing it in the upstream direction just below the edge of the water. This bottle will then be used to fill the container with the preservative to the brim, but without overtopping it.

**Deep water samples** – In locations such as reservoirs where deep water samples are desired, the water samples will be collected by pumping through clean Teflon and/or silicone-based tubing. The first 4-liters of sample water collected through the tubing will be discarded. This assures that the distilled water that was pumped through the tubing for the first set of field blanks will be completely flushed out of the system and replaced with sample water. Sample bottles that contain preservative will be filled by carefully inserting the end of the tubing into the bottle (being careful to prevent the tubing from coming into contact with the preserved sample). The bottles will be filled in such a manner as to minimize sample agitation (e.g., filling the bottle slowly while it is slightly tilted). The preservatives used for each sample type are listed in Table 4. Dissolved metals samples will be collected by pumping the sample through an in-line pre-cleaned cellulose acetate filter (0.45  $\mu$ ) into a poly bottle that contains nitric acid preservative.

**Field/Equipment blanks** – If tubing is used, prior to collecting any sample, the tubing will be flushed with approximately 4-liters of distilled water. After which, the Field/Equipment blank will be collected into appropriate sample bottles. For the field blank for dissolved metals, the water will be pumped through the same type of filter(s)

that will be used to collect the dissolved metal samples. Separate field blank samples without the filter will be collected for the other parameters. Field/Equipment blanks are to be collected on the first day, prior to collecting any samples, and at least once per sampling event after cleaning.

Each bottle will be filled with a single sample collected from a single sample location. The bottle will then be packed with bubble wrap and placed in an insulated cooler with ice for shipment to the appropriate laboratory under proper chain of custody, as discussed later in this plan.

**Field parameters in water** – Handheld instruments will be used to measure pH, temperature, dissolved oxygen, turbidity, and conductivity of the water body in-situ after the water samples for mercury and the ancillary parameters are collected. To avoid disturbance of stream sediments, any turbid water will be allowed to move downstream prior to making the measurements. Instruments will be calibrated before, after field use, and at intermediate times during the sampling event, following the procedures in Section 2.5.

### **2.2.3 Sediment Sampling for Mercury**

SOPs for collection of trace-level mercury sediment samples and determining results on a dry weight basis are included in the appendix. Selected sediment and soil samples may be analyzed to determine the form of the mercury using the Selective Sequential Extraction procedure as described in the SOP in the appendix.

**Total Mercury** – Sediment samples will be collected for analysis of total mercury using a new, pre-cleaned, disposable polyethylene scoop and placed into a 125 mL Teflon bottle with air-tight-fitting Teflon-lined cap. Where the sediment is hard, the polyethylene scoop can be used to dig the sediment and place it in the bottle for chemical analyses. A new scoop is used for each mercury sampling location.

**Moisture content** – The moisture content will be determined on the total mercury samples so that they can be expressed on a dry and wet weight basis.

**Methylmercury** – The sediment sample for methylmercury will be collected using a new, pre-cleaned, disposable polyethylene scoop and placed in a 20-mL glass vial. The 20 mL vial will be filled to the half-way mark and frozen immediately in the field using dry ice kept in a separate, small cooler and maintained frozen until delivery to the laboratory.

### **2.2.4 Sediment Sampling for Ancillary Parameters**

Sediment samples will be collected for analysis of ancillary parameters using a new, pre-cleaned, disposable polyethylene scoop and placed into 250 mL HDPE jars for chemical analyses of the parameters listed in Table 1. The grain size distribution may be determined in selected sediment samples. If so, a separate 250 mL HDPE jar of sediment will be collected.



### **2.2.5 Fish Sampling for Mercury**

Fish will be collected by electrofishing, gillnetting, seining, or hook and line, whichever is appropriate to the waterbody being sampled. The guidance on selecting appropriate methods in Table 6-4 of the US EPA guidance document "Guide for Assessing Chemical Concentrations of Contaminant Data for Use in Fish Advisories" (2002) will be followed. Selection of specific target species such as smallmouth bass and the size classes to be sampled will be described in the specific Sampling Plans where fish sampling is to be conducted. For this project, individual fish will be sampled from the target species and pre-defined size classes. The total length and weight of each fish will be measured and noted in the field log, along with the species name and any comments on its condition. A sample of the skin-off muscle tissue is cut out of the fish and placed in a clean sample bottle. The sample label is taped to the outside of the bottle, which is then placed in a waterproof, plastic bag, sealed, and then put into coolers with dry ice and blue ice. The coolers will be shipped to the laboratory within 24 hours. The fish will be frozen in a freezer at  $<-20^{\circ}\text{C}$  at the laboratory upon receipt.

### **2.3 SAMPLE HANDLING, DOCUMENTATION, AND CUSTODY REQUIREMENTS**

All samples collected will be labeled in a clear and precise way for proper identification in the field and for tracking in the laboratory. The samples will have pre-assigned, identifiable, and unique codes. Each sample will be assigned a unique identification code. Individual sample identification codes will consist of the matrix type designated as "W" for water, "S" for sediment, or "F" for fish, waterbody name, and a unique number designating the sample itself. Sample containers will be labeled at the time of collection. Labels will include the sample identification code, depth collected, date and time of collection, the field sampler's initials, analytical parameter(s), and any method of sample preservation.

The following packaging procedures will be followed for all other water and sediment samples, except methylmercury in sediment. All samples will be placed in sturdy, insulated coolers with ice or ice-equivalent. When ice is used, the drain plug of the cooler will be secured with fiberglass tape to prevent melting ice from leaking out of the cooler. Ice used to cool samples will be double-sealed in two Ziploc plastic bags and placed on top and around the samples to chill them to at least  $4^{\circ}\text{C}$ . The bottom of the cooler will be covered with bubble wrap to prevent breakage during shipment. The screw caps will be checked for tightness and, if not full, a mark will be made noting the sample volume level of liquid samples on the outside of their sample bottles with indelible ink. The bottle/container tops and sample labels will be secured with clear tape. All sample containers will be placed in heavy-duty plastic bags and wrapped in bubble wrap to prevent breakage. All samples will be placed in coolers with the appropriate chain-of-custody form. All forms will be enclosed in a large plastic bag and affixed to the underside of the cooler lid. Empty space in the cooler will be filled with bubble wrap, newspaper, or Styrofoam peanuts to prevent movement and breakage during shipment. Each ice chest will be securely shut. The laboratories will be notified of the sample

shipment schedule. The schedule will be arranged so that the samples will arrive by courier during the week, and not the weekend.

The methylmercury sediment samples will be kept frozen using dry ice in a separate, small cooler that will be shipped to Frontier Laboratory for delivery within 24 hours.

Field calibration logs will be used to document calibration procedures and times for each of the field parameters measured (pH, temperature, dissolved oxygen, specific conductivity, and turbidity). These logs will note the time of day, the person performing the calibrations, and the calibration results.

A Field Log will be completed during the collection of each sample. Field Log entries will include the following information:

- Sample
- Sampler's name(s)
- Date and time of sample collection
- Depth where water and sediment samples collected
- Distance from stream or reservoir bank
- Preliminary sample descriptions (e.g., sediment type, approximate grain-size, color, and any unusual conditions such as stains or odors)
- Field parameters (pH, conductivity, temperature, turbidity, and dissolved oxygen)
- Weather conditions at time of sampling
- Type of nearby vegetation, if present up and downstream of sampling location

As conditions in the field may vary, it may become necessary to implement minor modifications to the sampling plan. Any variances will be recorded in the bound field log book.

Chain-of-custody records are used to document sample collection, analyses required, sample custody, and transportation to the analytical laboratory for analysis. All samples will be accompanied by a chain-of-custody record. A separate form will be completed, signed, and transported with each cooler containing samples being sent to each laboratory. The chain-of-custody record identifies the contents of each sample cooler, the analyses to be performed, and maintains the custodial integrity of the samples. Chain-of-custody entries will include the project name, names of field samplers, sample codes, sample types, total number of containers, any comments, signatures of person relinquishing the samples, and the time of the transfer to a courier or a laboratory. Generally, a sample is considered to be in someone's custody if it is either in someone's physical possession, in someone's view, or locked and kept in a secured area that is restricted to authorized personnel. Until the samples are transported to the individual laboratory, the custody of the samples is the responsibility of the sampling team. A copy of all of the original chain-of-custody records will be included in the project report.

Field documentation will be completed using indelible ink, with any corrections made by drawing a single line through the error and entering the correct value. The correct information would then be entered above, below, or after the mistake.

#### **2.4 SAMPLES SENT TO SUBCONTRACTED LABORATORIES**

In some cases, a laboratory may need to ship samples to another laboratory. This practice is not expected for this project, but a procedure has been included in the QAPP in case it is necessary. Should a subcontracted laboratory be needed, a chain of custody document would be supplied to accompany the samples. This chain of custody document would list the parameters to be analyzed for each media, the methods to be used, the identification codes for the sample containers being delivered to the laboratory, and any preservative used in the samples. This document is signed and dated by staff from the original laboratory and by staff from the laboratory receiving the samples. The receiving laboratory staff will check to make sure that all of the described containers have been delivered in good condition and within required holding times for the requested parameters.

#### **2.5 INSTRUMENT/EQUIPMENT CALIBRATION**

A portion of the samples collected will be analyzed for field parameters, including dissolved oxygen, dissolved oxygen percent saturation, pH, turbidity, and specific conductivity. These parameters will be analyzed using hand-held instruments such as the YSI 6820 Meter. Field instruments will be calibrated according to manufacturer's instructions for every parameter that will be measured. All instruments will be calibrated before sampling commences and at least once following each day of instrument use, or when noticeable drift is occurring. Records of these calibrations and calibration checks will be recorded on the field parameter sheets and in the field log books.

Dissolved oxygen meters are field calibrated using the air-saturation method, which assumes that the oxygen concentration in the environment is at 100% saturation. All of the other parameters use pre-mixed standardized calibrator solutions (at least 2) that must bracket the low and high ends of the expected range that will be encountered in the stream. The range, accuracy, and precision of the YSI 6820 Meter for the parameters listed in Table 1 are provided in the SOP for Field Instruments. Temperature will be calibrated by comparison to a digital thermometer. Information obtained during calibration will also be recorded in the logbook kept with the instrument. Any maintenance needed during sampling will be described in the logbook.

#### **2.6 INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND CONTAINERS**

Sample containers will be specifically prepared by the analytical laboratories for this sampling event. This ensures that all containers are new or have been recently prepared. The analytical laboratories will prepare each container using the appropriate standard methods for the analytical technique to be used on its contents. The SOP for cleaning containers for total and methylmercury is provided in the appendix.

### **3.0 LABORATORY QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES AND DOCUMENTATION**

#### **3.1 QUALITY ASSURANCE DOCUMENTATION**

The following documents and information will be current, and they will be available to all laboratory personnel participating in the processing of the Guadalupe Project samples.

1. Laboratory QA Plan: Clearly defined policies and protocols specific to a particular laboratory, including personnel responsibilities, laboratory acceptance criteria and corrective actions to be applied to the affected analytical batches, qualification of data, and procedures for determining the acceptability results.
2. Laboratory Standard Operating Procedures (SOPs): Containing instructions for performing routine laboratory procedures.
3. Laboratory Analytical Methods Manual: 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 a particular laboratory for the project
4. Control Charts: Control charts are useful in evaluating internal laboratory procedures and are helpful in identifying and correcting systematic error sources. Laboratories develop and maintain control charts whenever they may serve in determining sources of analytical problems.

#### **3.2 LABORATORY PERFORMANCE AND ONSITE AUDITS**

The selected analytical laboratories have rigorous quality control programs, including analysis of reagent blanks, method blanks, certified standards, and matrix spikes. The QA/QC programs for the selected analytical laboratories will be provided upon request. The laboratory will maintain a full data package for detailed data validation, if requested.

Adequacy of personnel, facilities and equipment, application of methodology and quality control procedures, and acceptability of data handling and documentation are evaluated in an onsite audit visit. Onsite audits by the QA Officer will be conducted of all local laboratories used for the ancillary parameters in water and sediment for the Task 5 Data Collection Effort. An onsite audit of the out-of-state laboratory for the mercury analyses is not planned at this time, but a meeting with a representative of the laboratory may be held to review the sampling plan and QA/QC procedures for the Task 5 Data Collection Effort.

Performance audits determine the accuracy of the measurement system by proficiency testing with the analysis of “unknown” samples. For example, the laboratory receives samples from the United States Environmental Protection Agency as part of their laboratory accreditation process. Verification of previous laboratory certification by federal and state agencies will be obtained. Performance audits may be conducted for the Task 5 Data Collection Effort, but will not be conducted for the Synoptic Survey.

### **3.3 QA/QC SAMPLES**

#### **3.3.1 QA/QC Samples for Ancillary Parameters in Water and Sediment**

Two types of QA/QC samples will be collected in the field as described below.

##### ***Equipment Blanks***

Equipment rinseate samples will be prepared by pumping or pouring high-purity water through the water sampling equipment. Field blanks will be prepared at the rate of one sample of each type for twenty samples. The purpose of these samples is to determine if any cross-contamination occurred due to inadequate cleaning of equipment.

##### ***Field Duplicates***

Extra water and sediment samples will be collected to prepare field replicate samples at a rate of one sample of each type per ten samples. These samples are labeled as if they are a distinct location, so that the laboratory cannot tell that the samples are field duplicates. These samples provide information on the variability of successive samples taken at the same location.

##### ***Laboratory Quality Control Samples***

For each batch of samples, additional samples are prepared at the laboratory. These samples include: method blanks, low concentration or control check standards, laboratory check standards, matrix spike and matrix spike duplicate (MS/MSD) results. Blank or low concentration spike samples and duplicates are prepared to determine if any contamination has occurred in the laboratory and to determine the percent recovery at low concentrations. Preservative blanks are also prepared in the laboratory to determine if any contamination was introduced from the preservatives. The MS/MSD samples are used to determine percent recoveries of the reference standards and matrix spikes, and are used to detect matrix interferences. The laboratory duplicate samples are used to determine the relative percent differences, which can be used to detect laboratory equipment problems such as drift in calibration. The frequency of these QA/QC samples and actions that can be taken are shown in Table 5 for mercury and in Table 6 for the other chemical ancillary parameters. A quality assurance/quality control (QA/QC) summary form will be completed by the laboratory for water and sediment samples. The sample numbers for all QA/QC rinseate samples, reference samples, laboratory QC samples, and duplicates will be documented on this form so that the QA/QC samples can be associated with each batch of environmental samples.

**Table 5  
Quality Control Criteria for Analysis of Mercury**

<b>QA Sample</b>	<b>QA Measure</b>	<b>Minimum Frequency</b>	<b>Acceptance Limits</b>	<b>Corrective Action*</b>
<b>Total and Dissolved Iron</b>				
Method Blank Limit Study	Determine MDL	Run 20 Method Blanks per batch of samples	MDL is 3X standard deviation of mean of 20 blanks	NA
Method Blank Spiked at PQL	Determine PQL	Run 20 spiked samples per batch of samples	PQL is 4 X MDL or mean of spiked blanks	NA
Method Blanks Analyzed with Samples	Accuracy	3 per analytical batch, whichever contains fewer samples	Analyte >MDL	Check reagents, clean instrument, prepare fresh standards and reanalyze samples
Certified Reference Material (CRM)	Accuracy	Once per analytical batch	Analyte Specific 75%< CRM<125% THg; 70%< CRM <130% MeHg	Check reagents and clean instrument, and reanalyze samples.  Accepting the data and acknowledging the level of uncertainty with a written explanation
Replicate	Precision	Once every 10 samples or every analytical batch, whichever contains fewer samples	Analyte Specific 75%< %D <125% THg; 70%< %D <130% MeHg	Reanalysis of samples  Accepting the data and acknowledging the level of uncertainty with a written explanation
Matrix Spike and MS/DS Samples	Accuracy	Once every 10 samples or every analytical batch, whichever contains fewer samples	Analyte Specific 75%< %R <125% THg; 70%< %R <130% MeHg	Reanalysis of samples  Accepting the data and acknowledging the level of uncertainty with a written explanation

%R = percent recovery; %D = percent difference; THg is total mercury; MeHg is methylmercury

\*Detailed corrective actions are presented in the SOPs for mercury in appendix.

**Table 6  
Quality Control Criteria for Analysis of Ancillary Water Quality Parameters**

<b>QA Sample</b>	<b>QA Measure</b>	<b>Minimum Frequency</b>	<b>Acceptance Limits</b>	<b>Corrective Action</b>
<b>Ancillary Parameters (SSC)</b>				
Replicate	Precision	Once every 10 samples or every analytical batch, whichever contains less samples	± 25% of other 2 replicates	Accepting the data and acknowledging the level of uncertainty with a written explanation
<b>Ancillary Parameters (TDS, DOC/TOC, Inorganic Ions)</b>				
Method Blank	Accuracy	Once every 10 samples or every analytical batch, whichever contains less samples	< PQL	Reanalysis of samples Amending analytical procedures, or Accepting the data and acknowledging the level of uncertainty with a written explanation
Replicate	Precision	Once every 10 samples or every analytical batch, whichever contains less samples	±5% of other 2 replicates	Reanalysis of samples Accepting the data and acknowledging the level of uncertainty with a written explanation
<b>Ancillary Parameters (Nutrients)</b>				
Matrix Spike and MSD Samples	Precision and Matrix Interference	Once every 10 samples or every analytical batch, whichever contains less samples	85% ≤ %R ≤ 115% for nutrients	Amending analytical procedures, or Accepting the data and acknowledging the level of uncertainty with a written explanation

PQL = Practical Quantification Limit; varies by parameter –see Table 1.

### **3.3.2 QA/QC Samples for Mercury in Water, Sediment, and Fish**

QA/QC samples prepared to evaluate mercury analyses include method blanks, spiked method blanks at PQL concentration, matrix duplicates, matrix spike duplicates, QC check samples of known mercury concentrations, and certified reference materials including tissue. The frequency of these samples is one set per 20 samples. The preparation of these samples and the recommended corrective actions are discussed in the SOPs for total mercury and methylmercury analyses in the appendix of this QAPP.

## **3.4 LABORATORY QUALITY CONTROL PROCEDURES**

### ***Initial Calibration***

Calibration procedures determine how the laboratory instruments are performing. An initial calibration develops a calibration curve using reference standards for each parameter analyzed. Initial calibration is performed on a frequency required by the analytical method. Typically, the frequency of calibration is performed with each analytical batch of samples, at a maximum of once per batch. It may be performed more (or less) frequently depending on instrument stability.

### ***Continuing Calibration***

Continuing calibration is performed during the analytical process to verify that the initial calibration is still applicable. Generally, continuing calibration is performed using check standards, though a replication of the initial calibration may be required instead. Check standards are run after every 20 samples, or as required by the method. Calibration range criteria are applied to determine if the instrument is performing optimally and measuring acceptably. The criteria are often expressed as a range of percent recovery of the initial calibration value. The criteria are narrower than precision and accuracy requirements of the measurements themselves, typically no worse than 80 to 120 percent or as required by the standard method. The results of all calibration procedures, initial and continuing, are recorded in QA/QC notebooks and/or instrument logbooks.

### ***Inter-comparison Studies***

In general, one laboratory will be contracted to analyze all of the samples of a given media and chemical parameter for the entire project. It is expected that most of the mercury samples will be analyzed by one laboratory and the ancillary parameters by a different laboratory for the synoptic survey. However, for the Task 5 Data Collection Effort of this project, several principal investigators are expected to conduct field or laboratory studies where the same parameters may be analyzed by several parties. Split samples of water have less variability than sediment, and may be used to conduct an intercomparison study of the various laboratories. Inter-comparison studies are more likely to be conducted for total and methylmercury.



### **Data Quality Assessment**

This section presents the specific calculations that will be used to describe the following data quality indicators: precision, accuracy, representativeness, completeness, and detection limits. The desired acceptance limits are provided in Table 5 for mercury and in Table 6 for the ancillary parameters in water. Sediment limits are similar, except greater variability is experienced between matrix duplicates ( $\pm 25$  percent).

### **Method Detection Limits**

Method detection limit studies are necessary for ultra-clean mercury analyses. Multiple runs are conducted of laboratory and spiked samples to determine an appropriate method detection limit for the samples from this project. The results are included in the laboratory report with the mercury analyses. A description of the procedures used by Frontier Geosciences is included in the SOPs for total and methylmercury analyses in water, sediment, and tissue samples in the appendix.

For the ancillary water quality and sediment parameters, the desired detection limits are determined by the laboratories for each method. The laboratory methods have been selected to meet project objectives given the expected extent of interference from the matrix. In the case of matrix interference, multiple dilutions may be needed to allow the detection of the desired chemical parameters.

### **Accuracy Assessment**

Accuracy is assessed by comparing concentration values with the “true concentration values” on mathematical terms of the recovery. The comparison is quantified by the calculation of the percent recovery (%R) of the true value. %R is calculated by:

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

where

- SSR = spiked sample result
- SR = sample result (unspiked)
- SA = spiked added to sample

A known amount of compound (spike) is added to a sample of known concentration and the amount recovered by analysis is measured. Spiking solutions are prepared from a source different from calibration standards, producing spike concentrations at or below the regulatory action level of the analyte in question.

Accuracy is also monitored by analyzing certified reference samples on a monthly basis. For mercury analyses, reference samples for each media will be analyzed with the project samples at a rate of at least 10 percent of the total number of mercury samples for that media. The percent deviation of the experimental value from the certified value is calculated to evaluate accuracy. The acceptance limits for certified reference materials

are analyte specific and dependent upon the manufacturer's Performance Acceptance Limits.

### **Precision Assessment**

Precision is the measure of the reproducibility of the results. Precision will be estimated by analyzing duplicate matrix spike (MS) samples and the laboratory control samples, separately but in a similar manner. The relative percent difference (RPD) between the analyte levels measured in the MS sample and the matrix spike duplicate (MSD) sample will be calculated using the following equation:

$$\text{RPD} = \frac{\text{ABS}[\text{MS} - \text{MSD}] \times 100}{0.5(\text{MS} + \text{MSD})}$$

Where:

RPD	=	Relative Percent Difference
ABS	=	Absolute value
MS	=	Matrix spike
MSD	=	Matrix spike duplicate

### **Representativeness**

Representativeness is the degree to which the data precisely and accurately represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is a qualitative parameter that is maximized by ensuring that sampling locations are selected properly and that a sufficient number of samples are collected.

### **Completeness**

Completeness is the measure of the percentage of the data that can be used to evaluate project objectives. Completeness will be reported as the percentage of all measurements judged representative and useful. The following equation will be used to determine completeness:

$$\%C = (V/T) \times 100$$

Where:

%C	=	Percent completeness
V	=	Number of measurements judged valid
T	=	Total number of measurements

### **3.5 CORRECTIVE ACTION**

Corrective action procedures may be required as the result of audited or self-discovered nonconformance with predetermined QA/QC criteria. The corrective action system functions to identify, document, and prevent recurrence of out-of-control situations. These situations include, but are not limited to, quality assurance acceptance limits being exceeded, deviations from normally expected results, divergence from SOPs and abnormalities in sample handling. Each nonconformance is documented by recording the circumstances in a Corrective Action Report. Documentation of corrective action steps includes problem identification, investigation, action to eliminate the problem, and verification that the problem has been solved.

### **3.6 FIELD AND LABORATORY DATA AND QA/QC REPORTING**

In addition, laboratory personnel carefully review all data for calculation and transcription errors. Supervisors compare quality control data against established acceptance limits and verify computations. The laboratory supervisor, or his designate, is responsible for the final review of the data. Only data which have met the quality criteria are reported by the laboratory.

All data reported from the field and laboratory are reviewed by the QA Officer beginning from the field sampling log and chain of custody forms to the laboratory reporting package for each batch of field and QA/QC samples. The QA/QC data will be reviewed by the QA Officer for the Project to determine if percent recoveries of the standard and matrix spike samples are within acceptable ranges, and if the relative percent differences are within the prescribed tolerance limits. Field blanks will be checked to see if any compounds were detected. Standard US EPA procedures for qualifying the data if any compounds are detected in the blanks will be followed. The relative percent differences between field replicates will be determined to estimate the field variability. The field and laboratory replicates are used to determine if there are any systematic biases in the analyses. Any issues will be reported to the Project Manager and discussed with the laboratory. The review by the QA Officer will be conducted in a timely manner, so that corrective action can be taken such as running additional dilutions of samples. If necessary, a meeting will be held with the laboratory chemist and QA staff and the QA Officer to resolve any issues.

The QA/QC data will be entered into a project QA database. This will allow more detailed assessments to be made in a timely manner and facilitate review of the QA data by others. The laboratory data results, the QA/QC results with a summary of the implications of the QA/QC results, and copies of the chain-of-custody forms will be included in the project report. Field measurements such as water temperature will also be included in the project report.

### **3.7 LABORATORY DATA MANAGEMENT**

The analytical laboratories will provide the data from their analyses to Tetra Tech in an electronic format. This will reduce the likelihood of transcription errors and increase data reliability. Upon arrival of the electronic files from the laboratories, limited checks of the database against the laboratory data sheets will be conducted to ensure accuracy.

All data will be merged into a single electronic database. Data collected in the field will be manually entered into the database. Manually entered data will be double checked for accuracy from the field logbook.

## **4.0 ASSESSMENT/OVERSIGHT**

### **4.1 ASSESSMENT AND RESPONSE ACTIONS**

Project assessment will include regular observation of field sampling, sample handling, sample preparation, sample analysis, data evaluation and verification of quality control. The QA Officer, Gary Wortham, will be responsible for monitoring of field activities and assuring that all field personnel are adequately trained for the sampling method requirements. Deviations from sampling and analytical protocols will be addressed by Gary Wortham. A QA report will be prepared by Mr. Wortham following each sampling event summarizing the results of the QA/QC analyses by the laboratory. Any deviations in the field or laboratory will be reported to the Project Manager for corrective action, if necessary.

## **5.0 DATA VALIDATION AND USABILITY**

### **5.1 DATA REVIEW, VALIDATION, AND VERIFICATION REQUIREMENTS**

Data review, validation and verification requirements were discussed previously. Equipment blanks will be used to aid in the identification of problems due to field contamination. Field duplicates will be used to assess the precision of analytical methods. The selected analytical laboratories all have rigorous quality control programs, including analysis of reagent blanks, method blanks, certified standards, and matrix spikes. The QAPPs for the selected analytical laboratories will be provided upon request.

### **5.2 RECONCILIATION WITH DATA QUALITY OBJECTIVES**

The data generated from the above analyses will be used to develop the TMDL for mercury for the Guadalupe River Watershed. A comparison of the requested data and final field and laboratory results will be made to show that all desired information was obtained, unless specific problems occurred that were previously documented by the QA Officer following each sampling event.

## 6.0 REFERENCES

EPA Method 1669: Sampling Ambient Water for Trace Metals At EPA Water Quality Criteria Levels. July 1996.

EPA Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020

EPA Method 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. July 1996. US EPA Engineering and Analysis Division, WDC. EPA 821-R-96-011.

EPA, 2002. Guide for Assessing Chemical Concentrations of Contaminant Data for Use in Fish Advisories. EPA-823-B-007 and EPA-823-B-00-008.

Frontier Geosciences Standard Operating Procedures (SOP)

Standard Methods for the Examination of Water and Wastewater

Annual Book of ASTM (Section 11)

## APPENDIX A

# RESPONSES TO GUADALUPE MERCURY TMDL WORK GROUP COMMENTS ON TECHNICAL MEMORANDUM 7.4.1 DRAFT QUALITY ASSURANCE PLAN

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### GENERAL COMMENTS

1. There is concern regarding the use of TSS and instead of the use of SSC. The USGS (Gray and Glysson) has done an extensive comparison on the bias of the TSS methodology in determining sediment concentrations. There are several problems associated with TSS lab analysis. Refer to these two USGS-authored documents: (See attached file: TSSvsSSC\_use.htm) (See attached file: tss\_ssc\_comparison.pdf) (See attached file: WRIR00-4191.pdf)

There are many other publications pointing to the deficiencies of using TSS. The definition of suspended sediment is inclusive of all suspended solids transported in alluvial systems (organic and inorganic). Table 1 in the Draft recommends using TSS EPA method 160.2. I strongly urge that this TMDL study use SSC ASTM method: D3977-97(2002) Standard Test Methods for Determining Sediment Concentration in Water samples which can be found at:

[http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/REDLINE\\_PAGES/D3977.htm?L+mystore+zqhj3193+105158114](http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/REDLINE_PAGES/D3977.htm?L+mystore+zqhj3193+105158114)

**Response:** The recommended method for suspended solids concentration will be used when samples have high sediment concentrations, expected during the wet season. This method is appropriate when suspended solids concentrations are high (>10 mg/L). The SSC method prevents the loss of sand-sized material, but sand-sized material is not likely to be present when suspended solids are <10 mg/L under dry season conditions. A modification of the EPA method (160.2) using a 0.45 $\mu$  nucleopore filter has been used by Frontier to measure suspended solids at these low concentrations. They prefer to take an aliquot from the same bottle as used for the mercury measurements, but they can filter the entire sample volume using this filter, rather than an aliquot, as long as the suspended sediment is not high. There is an issue with respect to comparability of the data at high

loads, since past measurements have used the TSS method, and this method is not readily compared to SSC method (Gray et al, 2000 – USGS Report “Comparability of Suspended-Sediment Concentration and Total Suspended Solids Data” WRIR 00-4191).

2. Page 11: “Water Sampling” section: The first sentence mentions following “strict procedures to ensure the collection of representative uncontaminated water samples”. The list of 8 items that follows mentions nothing about collecting a representative sample. It only lists ways to keep from contaminating a sample. There needs to be a second list for collecting representative samples. That list should include the recommendation of collecting samples using the EWI or EDI method described in USGS publication entitled: Edwards, Thomas K. and Glysson, G. Douglas, 1999, Field methods for measurement of fluvial sediment: Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 3, Applications of Hydraulics, Chapter 2, 89 p. which can be found at <http://water.usgs.gov/osw/techniques/Edwards-TWRI.pdf>

**Response:** Collection of samples using the equal width or equal depth increment methods is more appropriate for high flow conditions in the lower part of the Guadalupe River. Most of the planned sampling for the synoptic survey involves sampling small creeks under low flow conditions, typically less than 1 foot deep. A representative sample in such creeks will be obtained by collecting a grab sample in the middle of the creek just below the water surface. In deeper locations, profiles of the water quality parameters will be obtained. In the reservoirs, samples will be obtained above and below the thermocline.

3. Section 2.1, second sentence, delete the word “has”.

**Response:** Correction was made to QAPP.

4. Section 2.2 - Water Sampling, the depth that the sample bottle will be submerged is not specified. It should be made clear in this document or the Synoptic Survey Plan where in the water column the sample is collected, (i.e. just under the surface, one foot below the surface, etc.). The total depth of the water at the sampling point and the distance from shore should also be noted. This would be most important for the samples taken in the river and sloughs.

**Response:** The QAPP was revised to explain that the water samples in shallow creeks will be collected by submerging the bottles just enough to fill them. In deeper locations, profiles of the water quality parameters will be obtained. In the reservoirs, samples will be obtained above and below the thermocline. At all sampling locations, the total depth of the water, the depth at which the sample was taken, and the distance from the bank will be noted on the sampling sheet.

Also in Section 2.2, please elaborate on what the filtering process will entail in analyzing for dissolved mercury. Specifically, include the maximum time allowed between sample collection and filtration and where the filtration process will occur (i.e., field vs. lab).

**Response:** The QAPP was revised to explain that the water samples for mercury will be collected and shipped by courier so that they arrive at Frontier Lab within 24 hours. Filtering will be done at Frontier using a 0.45 $\mu$  nitrocellulose membrane filter as described in the SOP for Ultra-clean Sample Filtration.

5. As described in the Problem Statement, numerous data on mercury in the Guadalupe River Watershed are currently available. These data should be examined and incorporated into the analysis, where appropriate, to conduct a statistical analysis of power, which will aid in determining the number of samples needed in various locations to adequately represent the concentrations of mercury in the watershed. This may be planned, but if not it should be included in the Synoptic Survey Plan.

**Response:** Most of the existing data are for bank soil and sediment concentrations, not water concentrations. An analysis of the available data and statistical power analyses will be conducted for Task 5 sampling.

6. Quality Assurance Plans should be prepared and reviewed by qualified individuals; the review and approval often are indicated by signature blocks. Typically, a Quality Assurance Plan is prepared after a Sampling Plan has been developed. We recognize that due to the tight schedule for the Guadalupe TMDL project, this draft QAP was prepared before the Synoptic Survey Plan had been completed. We appreciate your commitment to meet the project schedule. For clarity and to make this QAP applicable to all sampling programs for this TMDL project, we request that the activities specific to the Synoptic Survey be removed from this document. Examples of our suggested edits are included below for Section 1.3, but are applicable to the entire document.

**Response:** The specific description of the synoptic survey was deleted to make the QAPP more general.

7. The document should state what guidance it follows.

**Response:** The QAPP generally followed procedures outlined in the QAPP for the CALFED Mercury Project and the SOPs for mercury from Frontier Geosciences Laboratory.

8. Section 1.1 Project Task/Organization and Responsibilities – Page 1: This narrative would be easier to read if it consisted of several paragraphs. Describe Mr. Wortham's expertise that qualifies him to be the QA Officer.

**Response:** His qualifications were added to the QAPP. The narrative was sub-divided.



9. Section 1.2 Problem Definition and Background – Page 1: This section is too long and not entirely consistent with the draft Problem Statement. We suggest the following changes:
  - a. Delete the first paragraph [Note: although specific waterbodies are designated on the 303(d) list, this TMDL project is for the entire Guadalupe River Watershed]
  - b. Condense the second paragraph to cover the following points:
    1. New Almaden Mining District was the largest producing mercury mine in North America;
    2. forms of mercury and the media in which they are present
    3. natural methylation process and bioaccumulation
  - c. Retain only the first sentence of the third paragraph.

**Response:** Correction was made to QAPP.

10. 1.3 Project/Task Description – Pages 2 – 3:
  - a. Revise the first sentence to reflect that this TMDL project is for the entire Guadalupe River Watershed.
  - b. Revise this section to present in detail only the tasks which this QAP will support (Tasks 2 and 5), and to state that QA/QC information will be captured in the database (Task 3).
  - c. The purpose of the main paragraph on page 3 seems to be to tie this QAP to the forthcoming Synoptic Survey activities. However, this QAP will also support the Data Collection activities, and it may need to be modified to support both of these sampling activities. Therefore, we suggest the following revisions:

Field sampling plans will be prepared prior to conducting sampling activities. The sampling plans will include sampling objectives, data quality objectives, sampling locations, specific parameters, number and type of samples to be collected, QA/QC procedures, and data analysis procedures.

The planned sampling is expected to include the following types of activities:

- Water samples will be collected using ultra-clean techniques and analyzed for four forms of mercury (total and filtered mercury and unfiltered and filtered methylmercury) using ultra-clean techniques. [Note: no need to specify sample locations and we may sample above the reservoirs; Question: are ultra-clean techniques only applicable to mercury samples?].
- Water samples will be collected and analyzed for suspended solids, turbidity sulfate, sulfide, chloride, DOC, temperature, pH, dissolved and total iron, specific conductivity, and dissolved oxygen. [Note: discuss this in data analysis section of sampling plans.]
- Flows will be measured at the river/creek locations at the time of sampling for use in estimating mercury loads.
- Planned laboratory methods and number of samples are listed in Table 1.
- Table 2 shows where field and QA/QC procedures are located in this document.

**Deleted:** The synoptic survey of the Guadalupe Watershed is the first field sampling effort for this project, and therefore will be described in more detail. The survey will be designed to determine mercury concentrations in water, sediment, and fish tissue, to identify wetlands or other areas where methylation may occur, and areas where high rates of sediment erosion or accumulation may occur. The purpose of this synoptic survey is to provide a concise and up to date summary of mercury concentrations within the watershed, and to provide data that can be compared between locations to help identify sources of mercury and areas needing further sampling. A f

**Deleted:** that includes

**Deleted:** and

**Deleted:** in the reservoirs and downstream rivers and creeks

**Deleted:** S

**Deleted:** will also be measured in the water column to provide information on the likely fate of the mercury and whether conditions are conducive to methylation.

[Note: discuss this in data analysis section of sampling plans.]d. Describe how the QAP will be updated if the actual sampling plans include more than the above list of activities.

**Deleted:** Profiles of DO, pH, temperature, specific conductivity, and turbidity will be made in the deep waters near the dam and at several upstream locations in the four reservoirs in the Upper Guadalupe River Watershed.

**Deleted:** ¶

**Response:** Changes requested to broaden applicability of QAPP were made. A statement was added to note that the QAPP can be amended, if additional activities need to be covered.

11. Table 1 Pages 4 – 5:

- a. After participating in the Mercury Roundtable on April 22, Ms. Luisa Valiela of the EPA questioned whether the parameter list includes all parameters relevant to methylation. Please adjust as necessary.
- b. Sediment and fish tissue samples are listed on Table 1, and therefore should be added to the bullet list on Page 3.
- c. Double check that all parameters included in this QAP are listed both on Table 1 and in the bullets on Page 3.

**Formatted:** Bullets and Numbering

**Response:** Additional ancillary parameters were included for water and sediment samples. Tables were checked to include all parameters where appropriate.

12. Page 6:

- a. Move text on this page to the Synoptic Survey Plan.
- b. Sediment moisture content is listed in the first bullet, but not on Table 2.

**Response:** Text describing the Synoptic Survey was deleted from QAPP. Moisture content was added to Table 2.

13. Quality Objectives and Criteria for Measurement Data Page 7:

- a. Refine the data quality objectives for this project beyond “obtain valid data”.
- b. Third paragraph lists precision, accuracy, representativeness, comparability and completeness, but only accuracy is discussed in detail. Discuss the four remaining concepts in detail here, or reference where detailed discussion is provided in other sections of this QAP.

**Response:** DQOs were modified. Discussion of all the data quality indicators was added.

14. Documentation and Records – Page 7:

- a. This section should reference Sections 2.3 and 2.4.
- b. Only chain-of-custody records and sample labels are discussed in this section, which are not only laboratory protocols or requirements, but also field protocols. The protocols provided here appear to be field protocols, not laboratory protocols.
- c. Many forms of documents and records are missing from this section, including but not limited to field notebooks, field data entry forms, laboratory protocols and requirements including data reporting and submission format.

**Response:** Lab protocols and reporting were discussed in Section 3.6. Other field documentation was discussed in Section 2.3. These sections were referenced in Section 1.5 Documentation and Records.

15. 2.1 Sampling Program Design – Page 8:

- a. These two paragraphs do not provide helpful information except the last several sentences describing changes. The first paragraph is somewhat confusing, and note that sampling will also likely occur above the reservoirs. Perhaps the CALFED Mercury QAPP would be a helpful document to use as a model.
- b. The second paragraph is poorly worded. In particular, it is not merely “additional sampling” that is planned, but a comprehensive “Data Collection” sampling program. The last sentence is unnecessary, and fails to mention the role of the Guadalupe Mercury Work Group in reviewing documents.

**Response:** Section 2.1 in QAPP was revised.

16. 2.2 Sampling Methods Requirements – Page 8:

This section is poorly worded and appears to cover several subjects, consequently it should be presented in several paragraphs to aid the reader. Changing to the future tense in the latter sentences pertaining to containers would be helpful. The Surface Water Ambient Monitoring Program (SWAMP) QAPP provides an excellent narrative. It is now available at the Region 2 website at [www.swrcb.ca.gov/rwqcb2/basinplan.htm](http://www.swrcb.ca.gov/rwqcb2/basinplan.htm) or at the State Board website.

**Response:** Section 2.2 in QAPP was revised.

17. Table 3 – Page 9:

- a. “Testing” is otherwise consistently referred to as “parameters” in this document.
- b. “Additional acid rinses” for 250 mL and 2-L HDPE – is this true for all parameters, or only select parameters? Rinses in accordance with which SOP?

**Response:** Table 3 was revised to indicate when special cleaning is required.

18. 2.2 Water Sampling Page 11:

- a. Provide the complete title (and revision date/number/letter if applicable) the first time EPA Method 1669 is mentioned. Is it ultra-clean or trace-level (be consistent)?

**Response:** Full title and year added for Method 1669. Ultra-clean is correct and has been consistently used.

- b. Will all water sampling be conducted using ultra-clean procedures, or just mercury sampling? If only mercury, then revise the ancillary water quality parameters sections to describe how these samples will be collected.

**Response:** Collection methods for other parameters and media were added.

- c. It would be helpful to the reader to expand the section titles as follows: a) water sampling – mercury ultra-clean, b) water sampling – other parameters, c) water sampling – field/equipment blanks, d) water sampling – field parameters.

**Response:** Titles were added.

- d. Clearly describe the order in which samples will be collected (i.e. 1<sup>st</sup>: ultra-clean mercury samples, 2<sup>nd</sup> ancillary water quality parameters, 3<sup>rd</sup> field parameters).

**Response:** The order of collecting the samples was described.

- e. Portions of the Water Sampling - mercury ultra-clean section are very confusing, for example: 1. “non-tackled gloves”; and perhaps you meant that “both ‘clean hands’ and ‘dirty hands’ should each wear a pair of PVC gloves”.

**Response:** “Non-tackled” was intended to be “non-talc” or dust-free. The term has been changed to “clean-room” gloves, as described in SOP FGS-0008 and EPA Method 1669. The “clean hands” person wears 2 pairs of gloves, while the “dirty hands” person wears 1 pair. The wording was changed and reference to the SOP provided.

- f. How would Water Sampling - mercury ultra-clean be handled in high-flow situations where it is not safe to hold the bottle with hands, but a pole or other equipment is required to keep the samplers at a safe distance from the water body?

**Response:** This section was revised to include using pole-mounted bottles and pumping when appropriate.

- g. Water Sampling – Field Parameters: “measurements are collected downstream from the water sample collection location” is not only confusing, but it begs the question as to how representative these field parameter measurements will be. The instrument calibration information is cryptic, and perhaps it belongs in an SOP and on field data forms.

**Response:** Text was revised to make clear that collection of field data was not in disturbed location. The section on instrument calibration was expanded and a note was added stating that field parameters will be written on sampling forms.

19. Sediment Sampling – Page 13:

- a. Are there any ultra-clean sampling requirements for sediment? If not, state that.

**Response:** Yes as described on p 12.

- b. Last sentence - this appears to be the first mention of grain size distribution.

**Response:** Grain-size distribution may be measured in some sediment samples, so it was added to the tables.

20. Fish Sampling – Page 13:

Are there no QA/QC procedures associated with catching and preserving fish? If not, state that. State that Fish tissue sampling to be conducted for this TMDL will be consistent with the *Guide for Assessing Chemical Concentrations of Contaminant Data for Use in Fish Advisories, US EPA*, (Vol 1: EPA-823-B-00-007 and Vol 2: EPA-823-B-00-008), and consistent with recent Toxic Substances Monitoring Program and Regional Monitoring Program sampling programs, and coordinated with OEHHA.

**Response:** Fish sampling may be conducted for Task 5. The section on collecting, handling, and processing fish samples has been expanded, in accordance with US EPA November 2000 guidance “Guide for Assessing Chemical Concentrations of Contaminant Data for Use in Fish Advisories, EPA Report EPA-823-B-008 and 008.

21. Section 2.3 Sample Handling and Custody Requirements: Top of page 14 – “pond number”.

**Response:** Deleted

22. Section 2.4 Samples sent to Subcontracted Laboratories: Top of page 15 – is ELAP a California program?

**Response:** The reference to ELAP was deleted, since it does not pertain to this project.

23. 2.5 Instrument/Equipment Testing, Inspection and Maintenance Requirements: It appears that this section does not adequately describe calibration and related procedures. Why is it not titled calibration?

**Response:** This section was revised.

24. 2.6 Inspection/Acceptance Requirements for Supplies and Containers:  
Is this true for all containers? What about the “bulk pack containers – no special certification” noted on Table 3?

**Response:** This section was revised.

25. 3.1 Quality Assurance Documentation Pages 15 – 16:  
#3 – “Streamflow Augmentation Pilot Project”? What is this?

**Response:** This reference was removed from this QAPP.

26. 3.2 Laboratory Performance and Onsite Audits:  
Who performs the audits? Are the results certified? How are the results reported and to whom?

**Response:** The QAPP was revised to explain that lab results are certified by Lab Project Manager and the project QA/QC Officer. Results are reported to Project QA Officer for review prior to distribution to Project Manager and other project staff. QA Officer would perform a lab audit, if necessary for the Task 5 sampling efforts.

27. Table 5 – whichever contains ~~less~~ fewer samples (and Precision Assessment page 21); Is “inorganic” at top of table accurate (is methylmercury analysis a trace metals analysis)?

**Response:** Table 5 was changed to provide QA/QC criteria for mercury and methylmercury. Table 6 was changed to provide similar criteria for the other parameters in water and sediment.

28. Method Detection Limits – Page 20:  
Indicate fact, not intention by changing next to last sentence as follows: “~~Suitable~~ These methods have been selected...”

**Response:** Change was made.

29. Inter-comparison Studies:  
This is a very weak commitment to conduct inter-comparison studies. What is the need for this activity? Revise this document according to the need.

**Response:** Inter-comparison studies are useful when several laboratories are analyzing total and methylmercury. Such studies may be conducted as part of Task 5.