

MARCH 2006

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**Quality Assurance Project Plan (QAPP)**  
***Revision 1.2.0 –***

Sacramento River Watershed Program  
Monitoring for 2005-2007



*Prepared by*

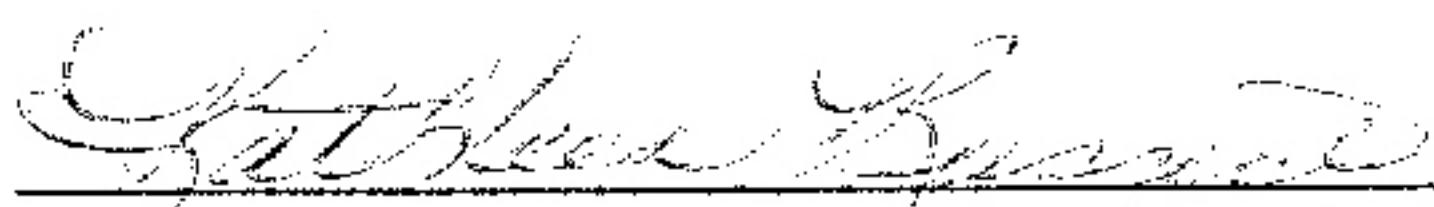
**Larry Walker Associates**

# 1 PROJECT MANAGEMENT

## 1.1 TITLE PAGE AND APPROVALS

### Quality Assurance Project Plan Sacramento River Watershed Program Monitoring for 2005-2007

SRWP  
Program  
Coordinator

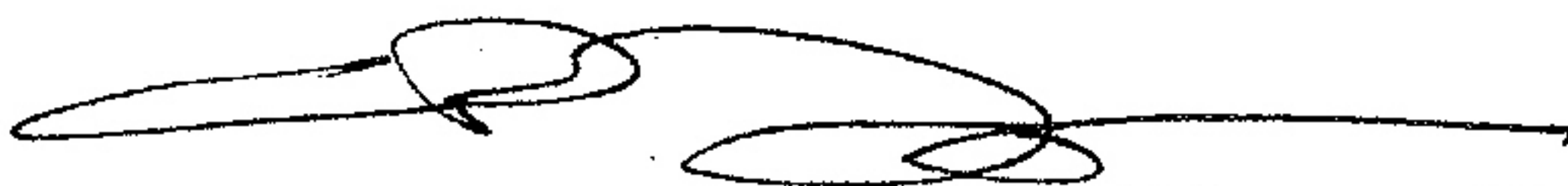


Kathy Russick, Sacramento River Watershed Program

3-30-06

Date

Monitoring  
Manager

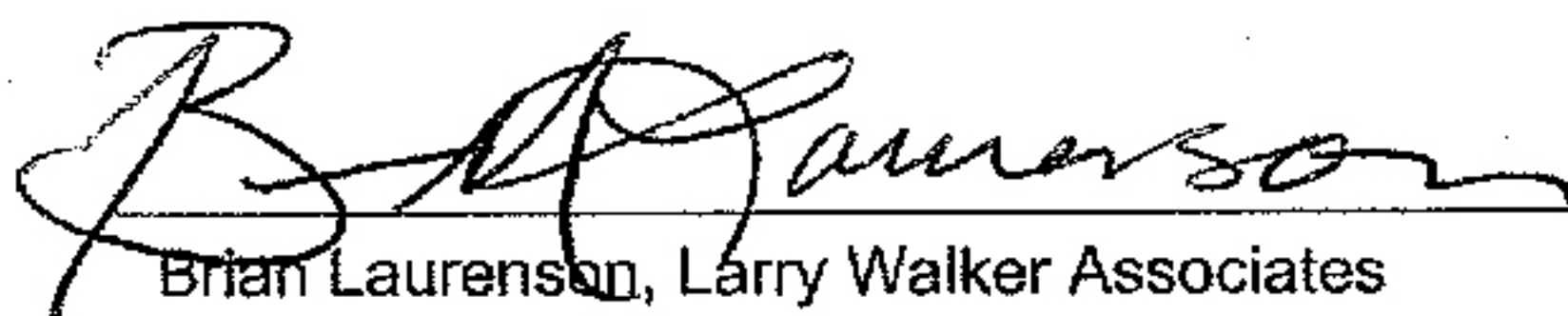


Claus Suverkropp, Larry Walker Associates

3.30.06

Date

QA  
Manager

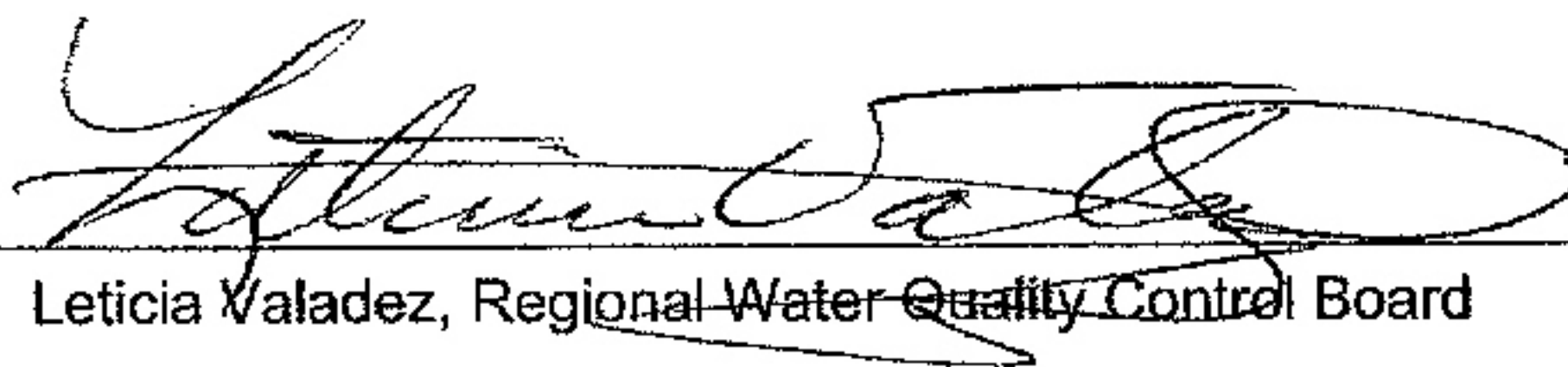


Brian Laurensen, Larry Walker Associates

3/30/06

Date

Regional  
Board QA  
Officer



Leticia Valadez, Regional Water Quality Control Board

3/24/2006

Date

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## 1.2 DISTRIBUTION LIST AND CONTACT INFORMATION

Name	Agency	Phone
Karen Larsen	Central Valley Regional Water Quality Control Board	(916) 464-4646
Leticia Valadez	Central Valley Regional Water Quality Control Board	(916) 464-4634
Kathy Russick	Sacramento River Watershed Program	(916) 201-2703
Steven Nebozuk	Sacramento Regional County Sanitation District	(916) 876-6118
David Guy	Northern California Water Association	(916) 442-8333
Stephen Clark	Pacific EcoRisk	(925) 313-8080
Todd Albertson	Caltest Laboratory	(707) 258-4000
Misty Mercier	CRG Marine Labs	(310) 533-5190
Cynthia Heeb	APPL, Inc.	(559) 275-2176
Gary Ichikawa	California Department of Fish and Game (Moss landing Marine Lab)	(831) 633-6032
David Crane	California Department of Fish and Game (Water Pollution Control Lab)	(916) 358-2859
Mark Stephenson	California Department of Fish and Game (Moss Landing Marine Lab)	(831) 771-4177

## 1.3 PROJECT ORGANIZATION AND RESPONSIBILITY

This Quality Assurance Project Plan (QAPP) describes the quality assurance requirements for the monitoring to be conducted in 2005-2007 for the Sacramento River Watershed Program (SRWP). The SRWP monitoring planned for 2005-2007 is supported by a Proposition 50 Grant awarded to SRWP in 2005, and administered by the Central Valley Regional Water Quality Control Board (RWQCB). The RWQCB Grant Manager for this grant is Karen Larsen. The SRWP project manager is Kathy Russick, the SRWP Coordinator. The SRWP monitoring program is managed by Larry Walker Associates (LWA). The monitoring program manager is Claus Suverkropp of LWA. Mr. Suverkropp also maintains the QAPP. The project quality assurance manager for the project is Brian Laurenson of LWA.

Sample collection and analyses will be performed by the agencies and subcontractors identified in Table 1. Additional contractors will be selected as required to successfully implement the monitoring program described in the Monitoring Plan (SRWP 2005) and this QAPP. The contractors selected to perform sampling and laboratory analyses provide the precision, accuracy, detection and reporting limits, and meet the quality control criteria necessary to satisfy the data quality objectives described in this document.

**Table 1. Sampling and Analytical Responsibilities and Contacts**

PROGRAM MANAGEMENT			
Agency or Company	Primary Contact (Phone #)	SRWP Monitoring Element	
SRWP Program Coordinator	Kathy Russick (916) 201-2703	Program Administration	
Larry Walker Associates	Claus Suverkropp (530) 753-6400	Monitoring Management	
WATER AND FISH TISSUE SAMPLING			
Agency or Company	Primary Contact (Phone #)	SRWP Monitoring Element	
Pacific EcoRisk (Aquatic Toxicity Laboratory)	Stephen Clark (925) 313-8080	<u>Water samples at all locations</u> • Water Chemistry • Pathogens • Aquatic Toxicity	
California Department of Fish and Game (Moss Landing Marine Lab)	Gary Ichikawa (831) 633-6032	• Fish Tissue at all sites	
CHEMICAL, MICROBIOLOGICAL, AND TOXICITY ANALYSES			
Laboratory	Address	Primary Contact (Phone #)	<u>Monitoring Element and Analytes</u>
APPL Labs	4203 West Swift Street Fresno, CA 93772	Cynthia Heeb (559) 275-2175	• <u>Water Chemistry</u> <i>carbamate and urea-substituted pesticides, selected herbicides</i>
Caltest Analytical Laboratory	1885 North Kelly Road Napa, CA 94558	Todd Albertson (707) 258-4000	• <u>Water Chemistry &amp; Pathogens</u> <i>conventional and physical parameters, nutrients, mercury and methylmercury, other trace metals, e.coli</i>
CRG Marine Lab	2020 Del Amo Blvd., Ste. 200 Torrance, CA 90501	Misty Mercier (310) 533-5190	• <u>Water Chemistry</u> <i>organophosphate, triazine, and pyrethroid pesticides</i>
Moss Landing Marine Lab	7711 Sandholdt Road Moss Landing, CA 95039	Mark Stephenson (831) 633-0253	• <u>Fish Tissue</u> <i>mercury</i>
Pacific EcoRisk	827 Arnold Dr., Ste. 100 Martinez, CA 94553	Stephen Clark (916) 921-9600	• <u>Water Chemistry</u> <i>hardness, alkalinity, ammonia</i> • <u>Aquatic Toxicity/TIEs</u> <i>Ceriodaphnia, Pimephales, Selenastrum</i>
CDFG Water Pollution Control Lab	2005 Nimbus Road, Rancho Cordova, CA 95670	David Crane (916) 358-2858	<u>Fish Tissue</u> <i>PCBs, chlorinated pesticides, PBDEs</i>

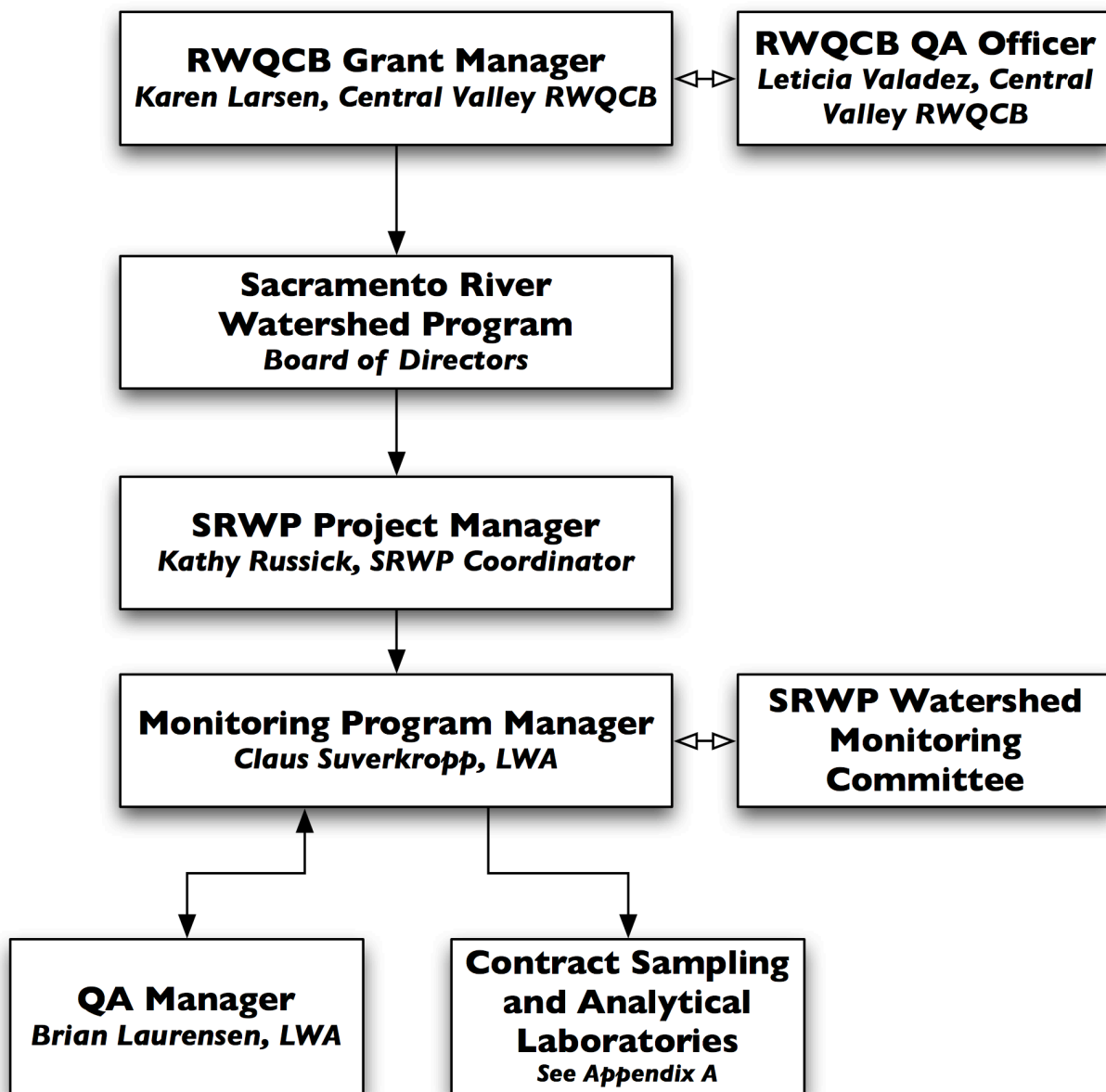


Figure 1. SRWP Monitoring Program Management Structure



## 1.5 PROJECT OBJECTIVES AND APPROACH

The goal statement developed by the participating stakeholders for the SRWP in 1996 is:

*“To ensure that current and potential uses of the watershed’s resources are sustained, restored and, where possible, enhanced while promoting the long-term social and economic vitality of the region.”*

The Monitoring Subcommittee has established the following long-term goal for the SRWP monitoring program:

***SRWP Monitoring Program Long-Term Goal:***

*“In coordination with other subcommittees and the larger stakeholder group, develop a cost-efficient and well-coordinated long term monitoring program within the watershed to identify the causes, effects and extent of constituents of concern that affect the beneficial uses of water and to measure progress as control strategies are implemented.”*

The SRWP monitoring program is envisioned by the subcommittee to be a long-term (e.g., 20 year) effort that will provide information to promote the understanding of conditions in the watershed and to assess the relative health of the watershed. The monitoring program will be a dynamic activity that will change over time as information is accumulated and new information needs are identified.

The Monitoring Subcommittee established the following goal for the first year of the monitoring program, and retained this goal for subsequent years of monitoring:

***SRWP Monitoring Program Short-Term Goal:***

*“To assess conditions in the main stem of the Sacramento River through the collection of baseline information, with an emphasis on examining the degree to which beneficial uses are attained.”*

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, Department of Pesticide Regulation, US Bureau of Reclamation, City of Sacramento, and City of Redding. The SRWP monitoring program includes chemical, physical, biological and toxicological monitoring elements.

Consistent with the objectives described, the SRWP monitoring program collects baseline monitoring data for several purposes. These data are used to examine the degree to which beneficial uses are attained or potentially impaired. The existing and potential beneficial uses for the Sacramento River watershed are outlined in the water quality control plan (Basin Plan) for the Central Valley Region. The following are existing beneficial uses in the Sacramento River watershed, as defined in the Central Valley Region Basin Plan (CVRWQCB 1995):

- municipal and domestic water supply
- industry (process, service supply, power)
- non-contact recreation
- agriculture (irrigation, stock watering)
- contact recreation
- freshwater habitat

- migration
- spawning
- wildlife habitat
- navigation

Another purpose of the SRWP monitoring program is the comparison of observed ambient concentrations with adopted water quality objectives and criteria<sup>1</sup>. Numeric and narrative objectives have also been adopted in the Basin Plan (CVRWQCB 1995) for surface waters of the Sacramento River watershed for selected toxic pollutants in California. (Basin Plan objectives are analogous to National water quality criteria.) Water quality criteria for toxic pollutants are also included in the California Toxics Rule (CTR) (USEPA 2000). The CTR criteria are largely the same as the current USEPA recommended national ambient water quality criteria (USEPA 1999).

These evaluations are in turn used to support management decisions by public agencies and stakeholders, and for public education efforts. No other more specific decisions or outcomes are dictated based on the monitoring data collected by SRWP.

### 1.5.1 Measurements

Parameters to be monitored for the SRWP are documented in the Monitoring Plan (SRWP 2006). The parameters to be monitored by the SRWP in 2005-2007 will include the following:

- Total Hg and MeHg (filtered and unfiltered)
- Hg and MeHg in suspended sediments (by calculation), photodegradation rate of MeHg, and sulfates
- TSS, TOC, DOC, UVA254, TDS, and Nitrogen and Phosphorus compounds
- DO, Temp, pH, EC, Turbidity
- Organophosphate, carbamate, triazine, and pyrethroid pesticides
- *E. coli* bacteria
- Aquatic toxicity testing with *Ceriodaphnia*, *Pimephales*, and *Selenastrum*, with Toxicity Identification Evaluations (TIEs) and other follow-up investigations
- Mercury in fish tissue
- PCBs, organochlorine pesticides, and PBDEs in fish tissue
- Support for bioassessment monitoring method comparison studies

These parameters are monitored as indicators of specific beneficial uses of the watershed and water bodies. Specific individual parameters to be measured for the SRWP monitoring effort are listed in Table 2, and relevant beneficial uses are summarized in Table 3.

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<sup>1</sup> The SRWP's review and evaluation of designated uses and the criteria developed to protect these uses is consistent with the Water Quality Standards program mandated by the Clean Water Act (33 U.S.C. §§ 1251 *et seq.*), wherein a Standard for a water body is defined by four elements: designated uses of the water body, water quality criteria to protect the designated uses, an antidegradation policy, and general policies addressing implementation issues.

**Table 2. Constituents to be Monitored for SRWP, 2005-2007**

	Quantitation Limit	Unit
<i>Physical Parameters in water</i>		
Flow	NA	CFS (Ft <sup>3</sup> /Sec)
pH	0.1 <sup>(1)</sup>	-log[H <sup>+</sup> ]
Conductivity	0.1 <sup>(1)</sup>	µmhos/cm
Dissolved Oxygen	0.1 <sup>(1)</sup>	mg/L
Temperature	0.1 <sup>(1)</sup>	°C
Turbidity	1.0	NTU
Alkalinity	10	mg/L
Hardness as CaCO <sub>3</sub>	5.0	mg/L
Total Dissolved Solids	3.0	mg/L
Total Suspended Solids	3.0	mg/L
Total Organic Carbon	0.5	mg/L
Dissolved Organic Carbon	0.5	mg/L
Ultraviolet Absorbance at 254 nm	0.01 <sup>(1)</sup>	cm <sup>-1</sup>
<i>Pathogen Indicators</i>		
<i>E. coli</i> bacteria	2	MPN/100 mL
<i>Water Column Toxicity</i>		
<i>Ceriodaphnia</i> , 7-d chronic	NA	% Mortality, Reproduction
<i>Pimephales</i> , 7-d chronic	NA	% Mortality, Reproduction
<i>Selenastrum</i> , 96-h short-term chronic	NA	Cell Growth
<i>Pesticides in Water</i>		
Organophosphorus	(2)	ug/L
Carbamate and urea-substituted	(2)	ug/L
Triazine	(2)	ug/L
Pyrethroid	(2)	ug/L
Selected Herbicides	(2)	ug/L
<i>Trace Elements in Water</i>		
Total Mercury (filtered, unfiltered, particulate)	0.2	ng/L
Methylmercury (filtered, unfiltered, particulate)	0.06	ng/L
Methylmercury photodegradation	TBD <sup>(3)</sup>	TBD <sup>(3)</sup>
<i>Nutrients in Water</i>		
Total Kjeldahl Nitrogen (TKN)	0.1	mg/L
Nitrate+nitrite, as N	0.1	mg/L
Soluble Reactive Phosphorus (SRP)	0.01	mg/L
Phosphorus, total, as P	0.1	mg/L
Sulfate, total, as S	0.5	mg/L
<i>Trace Elements and Organics in Fish Tissue</i>		
Total Mercury	10	ng/g
Organochlorine pesticides	Table 8 <sup>(4)</sup>	ng/g
Polychlorinated biphenyls (PCBs)	Table 8 <sup>(4)</sup>	ng/g
Polybrominated diphenyl ethers (PBDEs)	Table 8 <sup>(4)</sup>	ng/g

(1) Detection and reporting limits are not strictly defined. Value is required reporting precision.

(2) Limits are different for individual pesticides. Refer to Quantitation and Detection Limits in Table 7.

(3) Method and Quantitation Limit for methylmercury photodegradation to be determined.

(4) Limits are different for individual analytes. Refer to Quantitation and Detection Limits in Table 8.

**Table 3. Parameters Measured and Relevant Beneficial Uses**

Parameters Monitored	Beneficial Uses									
	Municipal and Domestic Water Supply	Industrial Water Supply	Agricultural Water Supply	Non-Contact Recreation (Aesthetic Value)	Contact Recreation	Sport and Subsistence Fishing	Freshwater Habitat and Aquatic Life	Spawning	Fish Migration	wildlife Habitat and Uses
<b>Physical and Chemical Parameters in Water</b>										
Alkalinity	X	X	X							
Conductivity	X	X	X							
Dissolved Oxygen							X	X	X	
Hardness	X	X	X							
Mercury, Filtered and Unfiltered						X				X
Methylmercury, Filtered and Unfiltered						X				X
Nutrients (N and P compounds)	X		X				X			
Organic Carbon, Total and Dissolved	X									
pH							X			
Sulfate	X	X	X			X				X
Temperature							X	X	X	
Total Dissolved Solids (TDS)	X	X	X							
Total Suspended Solids (TSS)							X	X		
Turbidity	X			X			X	X		
Ultraviolet Absorbance at 254 nm	X									
<b>Pesticides in Water</b>										
OP, triazine, pyrethroid, and carbamate pesticides							X			
Molinate and Thiobencarb	X						X			
<b>Microbiological Characteristics in Water</b>										
<i>Escherichia coli</i> Bacteria	X				X					
<b>Aquatic Toxicity</b>										
<i>Ceriodaphnia dubia</i> (Mortality and Reproduction)							X			
<i>Pimephales promelas</i> (Mortality and Growth)							X			
<i>Selenastrum capricornutum</i> (Cell Density)							X			
<b>Fish Tissue</b>										
Mercury and trace organics in fish						X				X

### 1.5.2 Project Schedule

The SRWP monitoring is anticipated to begin in October 2005.

The SRWP sampling strategy and schedule are based on significant hydrological events and periods of interest that are expected to constitute the major natural and anthropogenic sources of variability in water quality. This strategy has been employed by the SRWP for the last several monitoring years. Sample events are planned to coincide with a range of hydrological conditions and other events expected to significantly affect water quality (e.g., during seasonal pesticide

applications, expected periods of agricultural or urban runoff, and high and low flows), or conditions that match a previously observed pattern of toxicity or changes in concentrations of parameters. This strategy is designed to characterize the full range of water quality variation. It is recognized that this may result in some bias towards specific conditions or events. This potential bias is accepted as necessary to generate data for the conditions of interest, and is acknowledged as part of the data analysis process. Data produced by this strategy are considered to represent the results of a single grab sample per event per site, and the analytical results for different parameters are essentially for the same sample, within the limitations of parameter-specific sampling requirements. Fish tissue sampling will be conducted once annually (in the late summer and fall) for all sites monitored.

The decision to sample a specific event will be based on a number of factors, including seasonal and hydrological conditions, timing of pesticide applications and irrigation, and the potential for runoff to occur during an event. This decision will be made by the Monitoring Manager after consultation with local officials and representatives knowledgeable of local soil saturation conditions and potential for runoff. For wet weather events, sampling crews will make every attempt to sample each site near the peak of the hydrograph for a storm event. However, it is recognized that limited resources and logistical considerations (i.e., the large size of the watershed and distance between stations, and the unpredictable nature of precipitation) may prevent consistently achieving this goal for all sites and events.

A total of 9 water column events are budgeted annually. The types of events and approximate timing are as follows:

- Dry Weather low flows, late irrigation season (2 to 3 events, July – October)
- Early wet season storms and runoff (1 to 2 events, October – December)
- OP Application period, mid-wet season runoff (1 event, late January – early February)
- Late Wet season storms and runoff (1 or 2 events, February – March)
- Snow melt and late season runoff, early irrigation, (1 event, April – May)
- Rice field drainage, irrigation return flows (typically in mid to late June)

Monitoring is scheduled to begin in the dry season of 2005 (July through October), pending approval of monitoring plan and QAPP, and to continue through June 2007. Figure 2 illustrates the monitoring schedule for 2005-2006. The schedule for events will be similar in 2006-2007, although the events targeted may be modified based on monitoring results.

Annual monitoring reports are scheduled for completion on April 1, 2007 and March 3, 2008.

Monitoring to be conducted by SRWP in 2005 is summarized in Table 4.

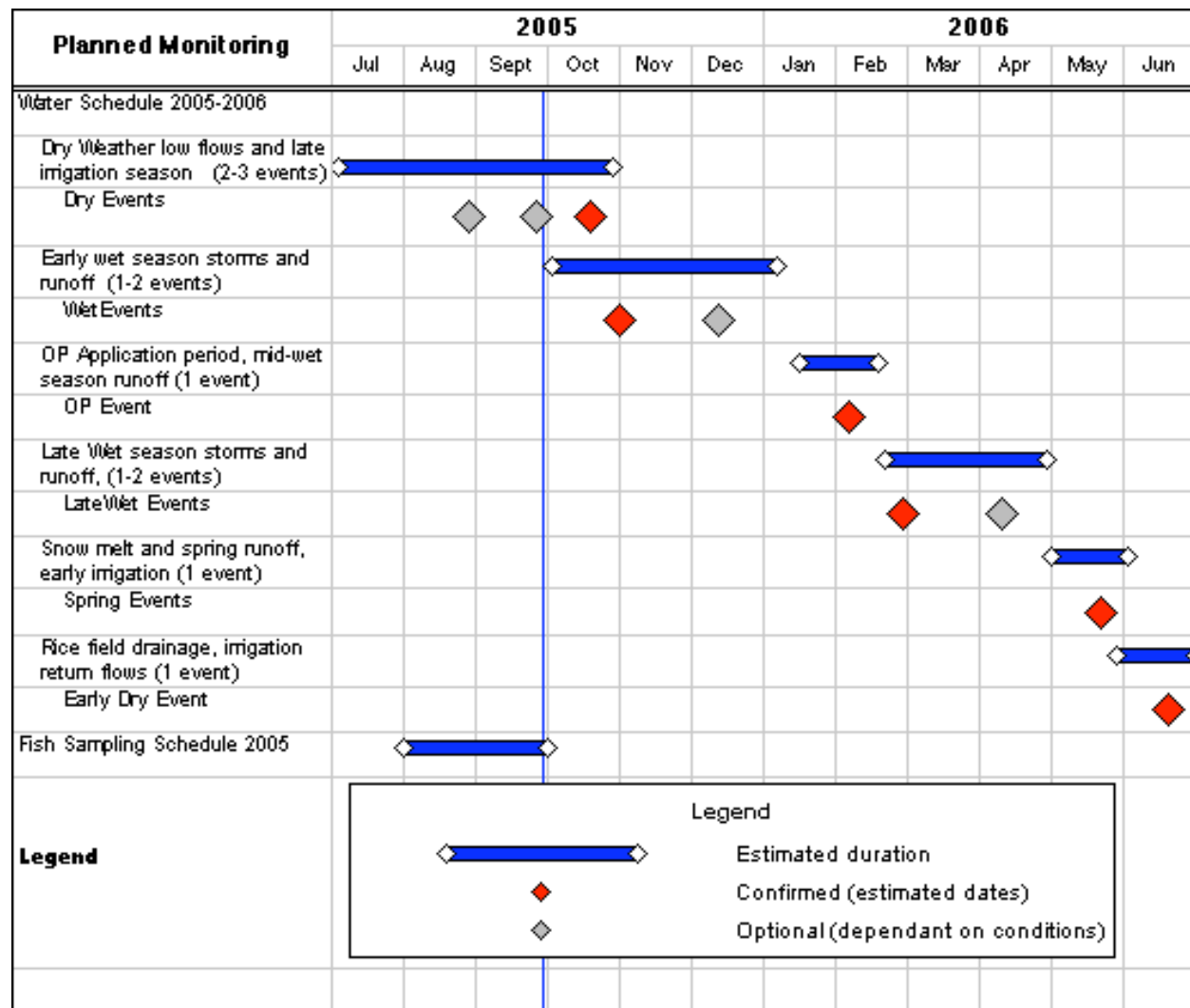


Figure 2. SRWP 2005 – 2006 Monitoring Schedule

**Table 4. SRWP Monitoring 2005-2007, Sites, Parameters and Annual Sample Frequency**

Site Type	Monitoring Locations	Chemical and Physical Characteristics					Pathogen Indicators	Aquatic Toxicity		Biota and Tissue <sup>(1)</sup>			
		Total Hg and MeHg (filtered and unfiltered)	Hg and MeHg in suspended sediments, photodegradation rates, sulfates	TSS, TOC, DOC, UVA254, TDS, N and P compounds	DO, Temp, pH, EC, Turbidity	Pesticides (OP, carbamates, triazines, pyrethroids) <sup>(2)</sup>		Ceriodaphnia, Fatheads, Selenastrum	WC Tox Followup (a)	Mercury in fish (individuals)	Mercury in algae, benthic invertebrates, and lower TL fish	PCBs & OC pest.	PBDEs in fish
Mainstem Sacramento River	Sac. R. below Keswick	COR		COR	COR	6	9	9	E				
	Sac. R. at Bend Br	9	9	9	9		9	9	E				
	Sac. R. near Hamilton City	9	9	9	9	6	9	9	E	CF, RB			
	Sac. R. @ Colusa	9	9	9	9	6	9	9	E	CF, RB			
	Sac. R. at Veterans Br.	6	9	MWQI, CMP	MWQI, CMP	6	CMP	9	E	10	14		2
	Sac. R. at Freeport	6	9	CMP	CMP		CMP	9	E				
	Sac. R. at RM44	6	9	MWQI, CMP	MWQI, CMP		CMP	SRCSD		CF, RB	14	10	2
Major Tributaries	Yuba R. at Marysville	9		9	9	6	9	9	E	CF, RB	14		
	Feather R. near Nicolaus	9		9	9	6	9	9	E	20	14		2
	American R. at Discovery	6		MWQI, CMP	MWQI, CMP		CMP	9	E	20	14	10	2
Agricultural Drains	Sac. Slough	9		9	9	6	9	9	E	CF, RB		2	
	Colusa Basin Dr	9		9	9	6	9	9	E	CF, RB		2	
Urban Creek	Churn Creek	9		9	9	6	9	9	E				

Notes: Tabled values are numbers of samples collected annually for each parameter. Text indicates coordinating programs: COR = City of Redding; MWQI = Municipal Water Quality Investigation program; CMP = Sacramento River Coordinated Monitoring Program; CF = CalFed; RB = Regional Board

- (1) Monitoring of organic compounds in fish tissue will be adjusted to take advantage of coordination with CalFed Bay-Delta Authority and Regional Board monitoring beginning in 2005.
- (2) The specific pesticides analyzed for any event will be adapted to seasonal pesticide use and application timing.

## 1.6 QUALITY OBJECTIVES AND CRITERIA FOR DATA MEASUREMENT

The objective of data collection for this monitoring program is to produce data that represents, as closely as possible, *in-situ* conditions of the selected water bodies in the Sacramento river watershed. This objective will be achieved by using standard accepted methods to collect and analyze surface water and sediment samples. Assessing the monitoring program's ability to meet this objective will be accomplished by evaluating the resulting laboratory measurements in terms of detection limits, precision, accuracy, representativeness, comparability, and completeness, as summarized below, and presented in detail in Section 5 and APPENDIX F. of this document.

### 1.6.1 Precision

The precision of data is a measure of the reproducibility of the measurement. Precision is assessed by evaluation of the results for duplicate samples and analyses, including field replicate samples and laboratory replicate analyses of environmental and QA samples.

Precision is expressed and assessed as the relative percent difference between two measured results. Generally, relative percent difference (RPD) is calculated as:

$$RPD = \frac{|R_1 - R_2| \times 100\%}{[R_1 + R_2] \div 2}$$

Where:  $RPD$  = the relative percent difference

$R_1$  = first replicate result,

$R_2$  = second replicate result.

### 1.6.2 Accuracy

The accuracy of an analysis is a measure of how close a measurement is to the true or accepted value. Accuracy is assessed by evaluation of field and method blanks, laboratory control spikes, matrix spikes. For trace organic analyses, recovery of surrogate analytes are also assessed. Analytical bias (i.e., a systematic lack of accuracy) is assessed and controlled through routine analytical calibration procedures.

Generally, accuracy is expressed and assessed as percent recovery of a known quantity of analyte. Generally, percent recovery (REC) is calculated as:

$$REC = \frac{V_m \times 100\%}{V_k}$$

where  $REC$  = percent recovery,

$V_m$  = the measured value, and

$V_k$  = the expected or "true" value.

In the specific case of matrix spikes, percent recovery (REC) is calculated as:

$$REC = \frac{[MS_m - M_m] \times 100\%}{V_k}$$

where  $MS_m$  = the measured value in the spiked matrix,

$M_m$  = the measured value in the matrix, and

$V_k$  = the expected or "true" concentration of the spike added to the matrix.



### **1.6.3 Comparability**

Comparability of the data can be defined as the similarity of data generated by different monitoring programs. For the purpose of the SRWP Monitoring Program, 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).

### **1.6.4 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 SRWP, 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 elements of the quality assurance program are addressed elsewhere in this document. Representativeness is also assured by avoiding the introduction of bias in sampling and analytical methods where possible, and by recognizing potential sources of bias inherent in the sampling design or methodology. For example, the sampling design for this program focuses on specific hydrological conditions expected to cause changes in water quality. Because these conditions are sampled more often than would occur during a random or regular sampling schedule, this will bias the data set produced toward the water quality that is represented by these types of events. This type of bias is accepted in order to build data sets for conditions of interest in a reasonable time frame, and is balanced by selecting types of conditions characterizing the reasonable expected range of factors affecting water quality. If necessary, this type of bias may also be moderated retroactively through specific statistical analysis methods that address seasonal or other factors responsible for potential bias.

### **1.6.5 Completeness**

Data completeness is a measure of the amount of successfully collected and validated data relative to the amount of data planned to be collected for the project, and is usually expressed 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 SRWP 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 an meaningful objective for data completeness. However, some reasonable objectives for data are desirable, if only to measure the effectiveness of the Monitoring Program. The 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. Completeness goals for the SRWP program are set at 90% for all water chemistry, toxicity, and microbiology results, and 85% for all fish tissue analyses.

Completeness is expressed and assessed as percent of validated data relative to data planned for the project. Percent completeness is calculated as:

$$\%C = \frac{N_{valid} \times 100\%}{N_{planned}}$$

where  $\%C$  = percent completeness,

$N_{valid}$  = the number of successfully collected and validated results, and

$N_{planned}$  = the number of planned results.

## 1.7 TRAINING AND CERTIFICATION

All staff performing field or laboratory procedures shall receive training to ensure that the work is conducted correctly and safely. At a minimum, all staff shall be familiar with the field guidelines and sample collection procedures and, the laboratory standard operating procedures (SOPs) included in this QAPP. All contractors and staff conducting fieldwork must receive field safety training. All work shall be performed under the supervision of experienced staff or a field coordinator. Specific responsibilities for providing and overseeing training is provided in the QA Manuals for each Contractor (provided in APPENDIX A). A copy of the staff training records must be maintained in the specific project file by each contractor performing work for this project.

## 1.8 DOCUMENTATION AND RECORDS

Copies of all field logs and Chain-of-Custody (COC) forms for each sample event will be provided to the Monitoring Manager within 48 hours of the completion of each sample event. Electronic versions of these documents (e.g., PDF files) are preferred for this purpose. An SRWP Chain-of-Custody form and an example SRWP Field Log sheet are provided in APPENDIX G. Sampling status reports will be provided to the Monitoring Manager within one week of the completion of each sampling event, and will consist of a brief (one to two page) narrative summary of samples successfully collected, a summary of any deviations from the Sample Plan or QAPP, and a discussion of any problems encountered during the sample event.

Analytical data reports will consist of a hardcopy report in each laboratory's standard format, and in a electronic format compatible with the Surface Water Ambient Monitoring Program database. This electronic format will be provided or approved by the Monitoring Manager. All final data reports will include the results of Quality Assurance analyses and a narrative summary of Quality Assurance data for the environmental results reported. Results of chemical analyses, toxicity testing, and any Toxicity Identification Evaluations (TIEs) performed will be provided to the Monitoring Manager in the laboratory's standard report format within 45 days of sample delivery and in the approved electronic data format.

Original field logs and COCs will be retained by the field sampling consultants for at least one year after the date of sample collection. Hard copies of field logs, COCs, and final analytical data reports will be retained by the Monitoring Manager for at least three years after the completion of monitoring described in this QAPP.

Monitoring data collected for this program will be stored in an electronic database system compatible with the California Environmental Data Exchange Network (CEDEN) database maintained by the California Department of Water Resources. CEDEN serves as the SWAMP Data Management System for the SRWCB. Final validated and reviewed data will be submitted

to the SWAMP Data Management System. All electronic data files and databases will be regularly backed up to a separate location.

An Annual Monitoring Report (AMR) will be completed after all testing and analysis is completed for each year of monitoring. At a minimum, annual monitoring reports will include the following elements:

- Executive Summary
- Description of monitoring objectives
- Sampling site descriptions and map of sampling locations
- Summary of sampling and analytical methods used
- Tabulated monitoring results (included as an appendix)
- Data interpretation. Includes summary of relevant sampling conditions for SRWP monitoring (including but not limited to weather, rainfall, and hydrological conditions), assessment of data quality objectives (completeness, representativeness, precision, and accuracy), summary statistics for water quality and toxicity data, and a summary and discussion of exceedances of relevant water quality objectives.
- Conclusions and recommendations.

Additional evaluations may be included in annual reports, subject to budget availability and approval by the SRWP Watershed Monitoring Committee, SRWP Board of Directors, and the SRWP Program Coordinator. These evaluations may include (but are not limited to) trend analysis, mass loading analysis, assessment of compliance with objectives, and comparative evaluation of water quality. The final scope of the monitoring reports will be determined through consultation with the SRWP Program Coordinator and the SRWP Watershed Monitoring Committee.

The final approved QAPP for this project (and any subsequent amendments) will be provided in a printable electronic format to all of the individuals identified in Section 1.3 of this QAPP.

### **1.8.1 Data to be Included in Annual Monitoring Reports**

As part of the AMR, SRWP shall provide the Waterboard's Grant Manager (or designated Waterboard Staff) with copies of the field data sheets (relevant pages of field logs) and copies of the COC forms for all samples submitted for analysis for each sampling event. At minimum, the following sample-specific information will be provided to the Waterboard staff as part of the Annual Monitoring Report:

- Sample Identification
- Monitoring location
- Sample type, e.g. grab or composite type (cross-sectional, flow-proportional, etc.)
- QA sample type
- Date and time(s) of sample collection
- Requested analyses (specific parameters or method references)
- Results of samples collected and all laboratory QC samples (calibrations, blanks, surrogates, laboratory spikes, matrix spikes, reference materials, etc.) and the identification of each analytical sample batch.

### 1.8.2 Reporting Formats

All results meeting data quality objectives and results having satisfactory explanations for deviations from objectives shall be reported in Final Laboratory Reports. The final laboratory reports shall include the results of all environmental and laboratory quality control samples. The Contractors may provide a summary of the data with the final laboratory data sheet. All results will also be provided in an electronic format agreed to by the Monitoring Program Manager and Analytical Contractor.

## 2 DATA ACQUISITION

### 2.1 SAMPLING DESIGN

For 2005-2007, monitoring will be conducted at a total of 13 sites considered to be the “backbone” of the monitoring program. Seven of the sites are located on the mainstem of the Sacramento River, from the Sacramento River below Keswick Reservoir to the Sacramento River at River Mile 44. Three sites are located on major tributaries to the Sacramento River, two sites are located on major agricultural drains, and one site is located in the rapidly developing urbanized drainage. The monitoring locations were selected to allow a consistent suite of parameters to continue to be monitored at these sites. With the exception of Churn Creek in the Redding area, all of these locations are continued from previous years of monitoring. All water quality monitoring samples will be collected as “event-based” grab samples. Churn Creek was selected as a representative indicator site for creeks in rapidly developing urban areas. Churn Creek replaces Arcade Creek (in the Sacramento area) which has benefited from extensive monitoring by multiple agencies. The numbers of water and fish tissue samples planned for collection and analysis were summarized in Table 4, and relevant beneficial uses are summarized in Table 3.

### 2.2 RATIONALE FOR SAMPLING DESIGN

#### 2.2.1 Site Selection Procedures

Early in the development of the SRWP monitoring program, the Monitoring Subcommittee established a set of criteria to evaluate and select the monitoring locations for the SWRP monitoring program. Criteria used for the selection of sites included the following:

- existing sampling station
- flow gauging station
- magnitude of streamflow
- critical habitat area
- predominant land use (e.g., agriculture, municipal, industrial, mining, etc.)
- site access constraints
- sampling access constraints
- available water quality data
- in existing watershed program
- potential water quality impairment, including 303(d) listed waterbodies

After an initial screening using the criteria listed above, the selection was narrowed to include sites along the mainstem of the Sacramento River and at the mouths of major tributaries. Major tributaries were identified based on existing streamflow data. Mainstem sites were selected to facilitate coordination with existing programs and to provide information below major reservoirs.

Major tributaries were selected based on the magnitude of flow into the mainstem. The final list of monitoring sites for 2005-2007 is provided in Table 5.

**Table 5. SRWP 2005 – 2007 Monitoring Sites and Land Use Characteristics**

Category	Location	Lat	Long	Percent Contributing Land Use				
				Rangeland	Forest	Agriculture	Urban, Residential	Other <sup>(1)</sup>
Mainstem River	Sacramento River below Keswick	40.6011	-122.4433	20	70	4.5	0.3	4.9
	Sacramento River at Bend Br	40.2886	-122.1856	20	71	4.5	0.7	3.9
	Sacramento River near Hamilton City	39.7520	-121.9940	21	69	6.6	0.7	3.4
	Sacramento River at Colusa	39.2142	-121.9992	22	67	7.5	0.8	3.2
	Sacramento River at Veterans Br.	38.6747	-121.6275	18	62	16	1.1	3.0
	Sacramento River at Freeport	38.4582	-121.5026	18	62	15	1.8	3.4
	Sacramento River at Mile 44	38.4347	-121.5192	18	62	15	1.9	3.4
Major Tributaries	Yuba River at Marysville	39.1444	-121.5764	9.9	85	1.0	0.8	3.5
	Feather River near Nicolaus	38.9030	-121.5862	11	77	7.0	1.3	3.4
	American River at Discovery Park	38.6020	-121.5011	12	76	3.1	3.8	5.6
Agricultural Drains	Sacramento Slough	38.7833	-121.6338	18	17	64	1.4	0.2
	Colusa Basin Drain near Knight's Landing	38.8121	-121.7741	12	18	63	2.8	3.3
Urban Creek	Churn Creek (Redding area) <sup>(2)</sup>	40.4803	-122.3065	—	—	—	—	—

(1) Includes water, wetlands, snowfields, shrub and brush tundra, and transitional areas.

(2) Sampling location coordinates for Churn Creek are map estimates. Land use percentages have not yet been established for the Churn Creek drainage.

## 2.2.2 Classification of Measurements

All measurements resulting from the monitoring described in this QAPP are classified as *Critical*, i.e., they are required to achieve project objectives or have a limit on the number of errors in order to be acceptable. Critical measurements undergo additional scrutiny during the data gathering and review process. The expected number of samples, specific analytical methods and procedures, and defined acceptance criteria for QC samples (as described in Section 5) will be included as part of the assessment of critical measurements.

## 2.2.3 Validation of Non-Standard Methods

For non-standard sampling and analysis methods, sample matrices, or other unusual situations, appropriate method validation study information shall be documented to confirm the performance of the method for the particular need. The purpose of this validation is to assess the potential impact on the representativeness of the data generated. Such validation studies may

include round-robin studies performed by USEPA or other organizations. If previous validation studies are not available, some level of validation study will be performed during the project and included as part of the project's final report.

### **3 FIELD PROCEDURES**

Surface water and fish tissue samples will be collected for analysis of the constituents listed in Table 2. Surface water samples will be collected for chemical analyses and toxicity testing. Sampling for additional constituents may be required in the future, dependent on the results of Toxicity Identification Evaluations (TIEs). In this case, the QAPP will be amended to provide adequate sampling and analytical guidance, as necessary.

#### **3.1 SAMPLE COLLECTION METHODS**

All samples will be collected in a manner appropriate for the specific analytical methods to be used. Water samples will typically be collected as mid-depth mid-channel grab samples. Abbreviated sampling methods (i.e., weighted-bottle or dip sample) may also be used for collecting a representative water samples. Standard operating procedures (SOPs) for collection of surface water and fish tissue samples are provided in APPENDIX B of this QAPP.

##### **3.1.1 Water Column Samples**

Water quality samples will be collected using clean techniques that minimize sample contamination. Sampling methods will generally conform to USEPA "clean" sampling methodology described in *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (USEPA 1996). Although these "clean hands/dirty hands" methods were specifically developed for trace metals, the techniques are appropriate for collection of other water quality samples. Samples shall be mid-stream, mid-depth grab samples. Samples will be taken at approximately mid-stream and mid-depth at the location of greatest flow (where feasible). Grab samples will be collected by wading or boating to mid-stream and filling bottles by direct submersion of the sample bottle to approximately mid-depth. Clean powder-free nitrile gloves will be worn for collection of grab samples. Samples will be collected using a peristaltic pump and acid-cleaned Teflon™ tubing. Grab samples will be collected by boat or from shore using the same equipment. Composite and grab water quality samples will be collected into glass, polyethylene, or Teflon™ sample containers appropriate for the analyses to be performed. Samples to be analyzed for dissolved metals (if required) may be filtered to 0.45 µm in the field using Gelman in-line filters, or may be transported to the laboratory for filtration within 24 hours of sample collection.

##### **3.1.2 Sample Storage, Preservation and Holding Times**

Sample containers must be pre-cleaned and certified free of contamination according to the United States Environmental Protection Agency (U.S. EPA) specification for the appropriate methods. Sample container, storage and preservation, and holding time requirements are provided in Table 6.

**Table 6. Summary of Sample Container, Volume, Initial Preservation, and Holding Time Recommendations for Water Samples**

Parameter	Sample Container	Sample Volume <sup>(1)</sup>	Immediate Processing and Storage	Holding Time <sup>(2)</sup>
<b>Mercury</b>				
Total Mercury, filtered and unfiltered	500 mL Glass w/ PTFE-lined cap	500 mL	Store at 4°C; Filter <sup>(3)</sup> and preserve in lab with HCl or BrCl within 48 h	90 days
Methylmercury, filtered and unfiltered	500 mL Glass w/ PTFE-lined cap	500 mL	Store at 4°C; Filter <sup>(3)</sup> and preserve in lab with HCl within 48 h	6 months
Methylmercury photodegradation	To Be Determined	TBD	TBD	TBD
<b>General Chemical and Physical Constituents, Nitrogen and Phosphorus Compounds</b>				
Turbidity	2 L polyethylene	150 mL	Store at 4°C	48 hours
Total Suspended Solids		500 mL	Store at 4°C	7 days
Total Dissolved Solids		500 mL	Store at 4°C; Filtered in lab;	7 days
UVA <sub>254</sub>		125 mL	Store at 4°C;	48 hours
Orthophosphate, dissolved		250 mL	Store at 4°C; Filter in lab to 0.45 µm;	48 hours
Sulfate	0.5 L polyethylene	250 mL	Store at 4°C	28 days
Total Kjeldahl Nitrogen		250 mL	Preserve to pH<2 with H <sub>2</sub> SO <sub>4</sub> ; Store at 4°C	28 days
Nitrate + Nitrite		125 mL		
Total Phosphorus		125 mL		
Total Organic Carbon	3x40 mL VOA Glass, PTFE-lined cap	120 mL	Preserve with H <sub>2</sub> SO <sub>4</sub> w/in 48 h; Store at 4°C;	28 days
Dissolved Organic Carbon	125 mL amber Glass, PTFE-lined cap	125 mL	Filter and preserve in lab with H <sub>2</sub> SO <sub>4</sub> w/in 48 h; Store at 4°C;	28 days
<b>Pathogen Indicator Organisms</b>				
<i>E. coli</i>	Polyethylene	125 mL	Store at 4°C	24 hours <sup>(4)</sup>
<b>Pesticides</b>				
Organophosphates Organochlorines Carbamates Pyrethroids Herbicides	1-L I-Chem 200-series certified trace clean amber glass bottle, with PTFE-lined cap	1-2 Liters for each category	Store at 4°C; Extract as soon as possible within 7-d maximum.	40 days after extraction
<b>Trace Metals</b>				
As, Cd, Cu, Pb, Ni, Zn, total recoverable or dissolved	500 mL polyethylene	500 mL	Cool to 4°C. For dissolved fraction, filter using 0.45 micron filter within 24 h of collection. Acidify to pH<2 in lab with ultra-pure HNO <sub>3</sub> w/in 48h.	6 months at room T°C after acidification
<b>Toxicity</b>				
Aquatic toxicity & TIEs	Fluorocarbon-lined polyethylene	15 L	Store at 4°C	36 hours <sup>(5)</sup>

1. Additional volumes may be required for QC analyses;

2. Holding time after initial preservation or extraction.

3. Samples to be analyzed for filtered mercury or methylmercury will be filtered and preserved in the laboratory within 48 hours. Both filtered and unfiltered mercury and methylmercury are collected.

4. Samples for bacteria analyses shall be set up as soon as possible. The lab shall be notified well in advance of sample receipt.

5. Toxicity tests should be initiated by 36 hours after collection. The hold time does not apply to subsequent analyses for TIEs. For interpretation of toxicity results, samples may be split from toxicity samples in the laboratory and analyzed for additional chemical parameters. All other sampling requirements (sample containers, filtration, preservation, holding times) for these samples are as specified in this document for the specific analytical method. Results of these analyses are qualified for any other use (e.g. characterization of ambient conditions) because of potential holding time exceedances and variance from sampling requirements.

### 3.1.3 Fish Tissue Samples

Tissue monitoring will include sampling of fish for analysis of mercury and trace organic concentrations in tissue. Fish tissue samples will be collected by the California Department of Fish and Game Moss Landing Marine Lab, using protocols detailed in *Sampling And Processing Trace Metal And Synthetic Organic Samples Of Marine Mussels, Freshwater Clams, Marine Crabs, Marine And Freshwater Fish And Sediments*: DFG METHOD 102 (CDFG 2001). Details of the protocols are documented in APPENDIX B and summarized below.

Collection of fish for analysis of mercury, PCBs, and chlorinated pesticides in tissue may be accomplished by a variety of methods, including hook and line, seines, gill nets, and electroshocking. Species collected are generally non-migratory species that are most representative of a given location. Efforts will be made to collect individual fish in a range of sizes to allow development of a species-specific size-concentration relationships at each location. Fish will be wrapped in trace metal- and organic-free Teflon™ sheets and frozen for transportation to the laboratory. The tissue samples are prepared in the laboratory using non-contaminating techniques in a clean room environment. Individual fish will analyzed for mercury in a range of legal catchable sizes. Composite samples analyzed for trace organics or mercury will consist of equal-weight tissue samples from up to five fish of a similar size and combined into a single 200 g composite sample.

Largemouth bass and Sacramento pikeminnow are the primary target species for mercury analyses. These selections will be made by consensus of the SRWP Fish Focus Group. Other species may be targeted at sites where these species are less abundant or unavailable. Representative non-target species (“by-catch”) will kept and archived to allow analysis of trace organics in composite samples or individual fish. Species to be analyzed for trace organics will be selected from the available target species and by-catch. Total length (longest length from tip of tail fin to tip of nose/mouth) and fork length shall be measured in the field for all fish sampled.

Collection, handling and storage of tissue samples will be performed in a manner so as to assure the collection of representative, uncontaminated tissue chemistry samples. Briefly, the key aspects of quality control associated with chemistry sample collection are as follows:

- Field personnel will be thoroughly trained in the proper use of sample collection gear and will be able to distinguish acceptable versus unacceptable samples in accordance with pre-established criteria.
- Field personnel will be thoroughly trained to recognize and avoid potential sources of sample contamination (e.g., engine exhaust, winch wires, deck surfaces, ice used for cooling).
- Samplers and utensils which come in direct contact with the sample will be made of non-contaminating materials (e.g., glass, high-quality stainless steel and/or Teflon™) and will be thoroughly cleaned between sampling stations.
- Sample containers will be pre-cleaned and of the recommended type.

In general, sampling protocols are consistent with national guidance developed by USEPA (2000). If, after expending a reasonable amount of effort, the field crew is unable to catch the targeted number of fish of an appropriate size range at a location, the sampling contractor will contact the SRWP Monitoring Manager to discuss whether sampling should continue at that location. When composites are to be analyzed, the recommendations of the USEPA guidance document should be followed. The target number of fish used to construct each composite is at least five (5) fish for all species, but may be higher for some smaller species. In any single



composite, the total length of the smallest fish should be no less than 75% of the total length of the largest fish.

If the performance requirements documented in the sampling protocols and the QAPP are not met, the sample(s) will be re-collected. Sample collection will be conducted between September 1 and October 31. Samples will be distributed to the analytical laboratories within 30 days (i.e., by November 30) after the completion of sampling.

#### **3.1.4 Sample Identification Scheme**

All samples must be identified with a unique identification code to ensure that results are properly reported and interpreted. Samples will be identified such that the site, sampling location, matrix, sampling equipment and sample type (i.e., normal field sample or QC sample) can be distinguished by a data reviewer or user. Sample identification codes will consist of a site identification code, a matrix code, and a unique sample ID number assigned by the monitoring manager. Sampling date and time information will be recorded on the sample labels and in the field logs by the sampling contractors at the time of sample collection.

#### **3.1.5 Field Measurements**

For all water bodies sampled, water quality parameters including pH, specific conductance, dissolved oxygen, and temperature must be measured prior to collecting samples for laboratory analyses. Field parameters will be measured using a YSI Model 57 Oxygen Meter for dissolved oxygen, VWR Scientific Traceable Digital Thermometer (Cat. #61220416) for temperature, Orion Model 230A pH meter, and an Orion Model 130 conductivity meter, or comparable instrument(s).

#### **3.1.6 QC Sample Collection**

Field blanks and field duplicates are collected at a frequency of about 1 per 20 normal environmental samples. Additional sample volumes will be collected for matrix spike analyses at a frequency of about 1 per 20 normal samples. Matrix spike samples will be collected using the same methods as normal environmental samples and will be spiked in the laboratory prior to sample preparation. Field blanks will be collected before collecting any other samples at a site. Field duplicates and additional volumes for matrix spikes will be collected immediately following the corresponding samples collected for the specific analysis.

#### **3.1.7 Field Instrument Calibration**

Routine field instrument calibration must be performed at least once per day prior to instrument use to ensure instruments are operating properly and producing accurate and reliable data. Calibration shall be performed at least as frequently as recommended by the manufacturer.

#### **3.1.8 Decontamination Procedures**

All field and sampling equipment that may contact samples must be decontaminated after each use in a designated area if it will be used for subsequent sampling. A detailed description of cleaning procedures for water sampling equipment is included in APPENDIX E of this QAPP.

### 3.1.9 Field Documentation

All field activities must be adequately and consistently documented to ensure defensibility of any data used for decision-making and to support data interpretation. Pertinent field information, including (as applicable) the width, depth, flow rate of the stream, the surface water condition, and location of the tributaries must be recorded on the field sheets.

Field crews shall be required to keep a field log for each sampling event. The following items will be recorded in the field log for each sampling event:

- Name(s) of field personnel
- Sampling location identification, including decimal latitude and longitude coordinates using the NAD 1983 State Plane California datum.
- Whether field measurement calibration was performed
- Results of all required field measurements (depth, width, velocity, temperature, D.O., pH, conductivity) and the time that measurements were made
- Date and time of sample collection
- Sample ID numbers, including unique IDs for replicate and blank samples
- Observations of weather or other conditions that may influence sample results (e.g., wind, rain)
- Problems or unusual occurrences associated with the sampling event, particularly those that may affect sample or data quality.

Relevant pages from the field log will be scanned and transmitted to the Monitoring Program Manager at the conclusion of each sampling event.

## 3.2 SAMPLE CUSTODY AND DOCUMENTATION

Sample custody procedures provide a mechanism for documenting information related to sample collection and handling. Sample custody must be traceable from the time of sample collection until results are reported. 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).

### 3.2.1 Documentation Procedures

A field activity coordinator must be responsible for ensuring that each field sampling team adheres to proper custody and documentation procedures. A master sample logbook of field datasheets shall be maintained for all samples collected during each sampling event.

### 3.2.2 Chain-of-Custody Form

A chain-of-custody (COC) form must be completed after sample collection and prior to sample shipment or release. The COC form, sample labels, and field documentation will be cross-checked to verify sample identification, type of analyses, number of containers, sample volume, preservatives, and type of containers.

### 3.2.3 Sample Shipments and Handling

The field crews shall have custody of samples during field sampling. Chain of custody forms will accompany all samples during shipment to contract laboratories. All water quality samples will be transported to the analytical laboratory by the field crew or by overnight courier.

All sample shipments are accompanied by the COC form, which identifies the contents. The original COC form accompanies the shipment and a copy is retained in the project file.

All shipping containers must be secured with COC seals for transportation to the laboratory. The samples must be placed with ice to maintain the temperature between 2-4 degrees C. The ice packed with samples must be sealed in re-sealable bags, be approximately 2 inches deep at the top and bottom of the cooler, and must contact each sample to maintain temperature. Samples must be shipped to the contract laboratories according to Department of Transportation standards. The method(s) of shipments, courier name, and other pertinent information is entered in the "Received By" or "Remark" section of the chain of custody form.

The following procedures are used to prevent bottle breakage and cross-contamination:

- Prior to packaging, outsides of the bottles need to be rinsed off with DI water.
- Bubble wrap or foam pouches are used to keep glass bottles from contacting one another to prevent breakage.
- All samples are transported inside hard plastic coolers or other contamination-free shipping containers.
- The coolers are taped shut and sealed with chain-of-custody seals to prevent accidental opening.
- If pre-arrangements are not made, prior to shipment of the samples field staff must notify laboratory sample control.

### 3.2.4 Laboratory Custody Procedures

The following sample control activities must be conducted at the laboratory:

- Initial sample login and verification of samples received with the COC form;
- Document any discrepancies noted during login on the COC;
- Initiate internal laboratory custody procedure;
- Verify sample preservation (e.g., temperature);
- Notify the project monitoring manager if any problems or discrepancies are identified; and
- Maintain proper sample storage, including daily refrigerator temperature monitoring and sample security.

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. Procedures for proper disposal are documented in Laboratory QA Manuals (APPENDIX A).

## 4 ANALYTICAL REQUIREMENTS

Laboratory standard operating procedures (SOPs) for all analyses performed for this program are listed and provided in Appendices D and E. These SOPs document any options or modifications

from standard method procedures and identify all equipment or instrumentation necessary for the analyses. Corrective measures, responsibilities, and documentation requirements are detailed in the QA Manuals for individual laboratories. Corrective measures to address specific QA problems are also summarized in APPENDIX F.

Unless specifically requested by the Monitoring Manager, all “turnaround times” required for laboratory analyses are the standard turnaround times for each individual laboratory. Typical acceptable turnaround times are approximately 30 days for chemical analyses water of water, and 90 days for analyses of fish tissue.

#### 4.1 CHEMICAL ANALYSES

Water quality samples may be analyzed for filtered (dissolved) or unfiltered/ whole (total) fractions of the samples. Pesticide analyses will be conducted on unfiltered (whole) fractions of the samples. Prior to the analysis of any environmental samples, the laboratory must have demonstrated the ability to meet the minimum performance requirements for each analytical method. Initial demonstration of laboratory capabilities includes the ability to meet the project-specified quantitation limits (QL), the ability to generate acceptable precision and recoveries, and other analytical and quality control objectives documented in this QAPP. Analytical methods used for chemical analyses follow accepted standard methods and the procedures for analyses are documented in standard operating procedures (SOPs), available for review and approval at each laboratory.

#### 4.2 TOXICITY TESTING AND TOXICITY IDENTIFICATION EVALUATIONS

Water quality samples will be analyzed for chronic toxicity to *Ceriodaphnia dubia*, *Pimephales pimephales*, and *Selenastrum capricornutum*. Determination of chronic toxicity shall be performed generally as described in *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4<sup>th</sup> Edition* (USEPA 2002). Toxicity tests with *Ceriodaphnia* and *Pimephales* are conducted as static renewal tests, with daily test solution renewal. Toxicity tests with *Selenastrum* are conducted as a 96-hour static non-renewal test.

Because it has been found to be necessary to control pathogen-related mortality for tests with *Pimephales*, test procedures will be modified as described in Geis et al. (2003). These modifications consist of using smaller test containers (30 mL), including only two fish per container, and increasing the number of replicates to ten. This modification differs from the pathogen control procedures in the 4<sup>th</sup> edition test in that it uses 10 replicates, instead of 20. This modification was previously approved for the SRWP for several reasons: (1) The minor increase in statistical power gained by additional replicates did not warrant nearly doubling the test cost; (2) In the history of SRWP monitoring, toxicity to fathead minnows has been observed to be rare, but in the form of substantial mortality when observed; (3) Because the SRWP is a non-profit and non-regulatory program focused on baseline and trend assessment, it was considered that the minor deviation in this protocol and slight decrease in test sensitivity was acceptable to control costs. In order to evaluate the performance of the Geis modification under “real world” testing conditions, field replicate samples will be analyzed using the EPA 4<sup>th</sup> Edition procedure with 20 replicates per test.

Test procedures for *Selenastrum* shall be performed as described in *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4<sup>th</sup> Edition* (USEPA 2002). *Selenastrum* tests will omit the addition of EDTA to the lab controls and samples being tested. This modification to the *Selenastrum* test is allowed by the 4<sup>th</sup> Edition procedures and is preferred when metals may cause or contribute to toxicity, due to the chelation of metals by EDTA.

If initial testing indicates significant toxicity, Toxicity Identification Evaluation (TIE) procedures may be initiated. Initiation of TIEs will be governed by the following general strategy:

- TIEs will be conducted on samples in which *Ceriodaphnia* or *Pimephales* survival is less than 50% of the control at any time during the test, or when *Selenastrum* growth is less than 50% of the control growth at the end of the test. TIEs may be conducted as acute or chronic tests, depending on the level of toxic response.
- TIEs will be conducted using all species tested that meet the above criterion for a specific sample.
- TIEs will be initiated within 24 hours of observing the threshold response (>50% effect compared to control).
- If the 50% effect threshold is observed within 48 hours of initiating the toxicity tests, additional samples will be collected from the same location and retested using all toxicity species exhibiting a >50% effect compared to control in the initial sample. These follow-up samples may include samples collected at additional sites if these may assist in the determination of causes or sources of toxicity.
- If 100% mortality to a test species is observed at any time during the initial screening toxicity test, then a multiple dilution test using a minimum of five sample dilutions will be conducted with the same water sample to determine the magnitude of toxicity.

These procedures and triggers may be modified based on site- and event-specific considerations or budgetary constraints by the Toxicity Testing Focus Group (comprised of members of the Watershed Monitoring Committee of the Sacramento River Watershed Program). When considering whether to modify TIE triggers and procedures for a specific site and sample event, the Focus Group will consider a number of different factors including the history of toxicity at the site, the level of toxicity, the species and endpoints exhibiting toxic effects, and the follow-up budget that remains for the program. The rationale for initiating or modifying TIE procedures for a specific sample will be clearly documented in subsequent data reports. TIE methods will generally adhere to EPA procedures documented in conducting TIEs (USEPA 1991, 1992, 1993a-b). For samples exhibiting toxic effects consistent with carbofuran, diazinon, or chlorpyrifos, TIE procedures will follow those documented in Bailey *et al.* (1996). Laboratory Standard Operating Procedures for conducting TIEs are documented in APPENDIX D. Any project-specific modifications to these methods will be documented in future amendments to this QAPP.

For toxicity samples for the Sacramento Slough and Colusa Basin Drain sites coordinated with the Sacramento Valley Water Quality Coalition (SVWQC), if 100% mortality to a test species is observed within 96 hours of the start of the initial screening toxicity test, a multiple dilution acute test using a minimum of five sample dilutions will be conducted with the same water sample to determine the magnitude of toxicity. Pesticide-focused acute TIEs will also be initiated if 96-hour survival of *Pimephales* or *Ceriodaphnia*, or *Selenastrum* cell growth is less than 50% of control. In addition to dilution series tests and TIEs, sites exhibiting a statistically significant mortality in the initial tests may be resampled (as soon as is practical) to estimate the duration of the toxicant in the waterbody. Additional samples may also be collected upstream of the original site to determine the potential sources(s) of the toxicity in the subwatershed drainage. Selection of these additional sites will be based on analysis of crop types and pesticide use within the contributing subwatershed drainage, and consideration of other site-specific and event-specific

factors. The basis for selection of these additional sites will be clearly documented in any subsequent data reports. Decisions to initiate TIE procedures or re-sampling for these sites will also include consultation with the SVWQC program manager.

### 4.3 DETECTION AND QUANTITATION LIMITS

Method detection limits (MDL) and quantitation limits (QLs) must be distinguished for proper understanding and data use. The MDL is the minimum analyte concentration that can be measured and reported with a 99% confidence that the concentration is greater than zero. The QL represents the concentration of an analyte that can be routinely measured in the sampled matrix within stated limits and confidence in both identification and quantitation. For this program, QLs must be verifiable by having the lowest non-zero calibration standard or calibration check sample concentration at or less than the QL.

For this program, QLs have been established based on the verifiable levels and general measurement capabilities demonstrated for each method. These QLs should be considered as maximum allowable limits to be used for laboratory data reporting. Note that samples diluted for analysis or corrected for percent moisture for sediment samples may have sample-specific QLs that exceed these QLs. This will be unavoidable in some cases.

#### Method Detection Limit Studies

Each laboratory performing analyses under this program must routinely conduct method detection limit (MDL) studies to document that the MDLs are less than the project-specified QLs. If any analytes have MDLs that do not meet the project QLs, the following steps must be taken:

1. Perform a new MDL study using concentrations sufficient to prove analyte quantitation at concentrations less than the project-specified QLs per the procedure for the Determination of the Method Detection Limit presented in Revision 1.1," 40 Code of Federal Regulations (CFR) 136, 1984.
2. No samples may be analyzed until the issue has been resolved. MDL study results must be available for review during audits, data review, or as requested. Current MDL study results must be reported at the beginning of every project for review and inclusion in project files.

An MDL is developed from seven aliquots of a standard containing all analytes of interest spiked at five times the expected MDL. These aliquots are taken through the analytical method sample processing steps. The data are then evaluated and used to calculate the MDL. If the calculated MDL is less than 0.33 times the spiked concentration, another MDL study shall be performed using lower spiked concentrations.

#### Project Quantitation Limits

Laboratories generally establish QLs that are reported with the analytical results—these may be called *reporting limits*, *detection limits*, *reporting detection limits*, or several other terms by the reporting laboratory. These laboratory-defined limits must be less than or equal to the project QLs listed in Table 7 and Table 8. Wherever possible, project QLs are lower than the relevant proposed or existing numeric water quality objectives, toxicity thresholds, or tissue screening

values. Laboratories performing analyses for this project must have documentation to support quantitation at the required levels. Note that Table 7 and Table 8 include some pesticide parameters that are part of standard analytical scans and may not necessarily be constituents of specific concern.

Laboratories must report all analytical results between the MDL and QL. These results must be reported as numerical values and qualified as estimates (“J-values”). Reporting as “*trace*”, “*ND*”, or “*<QL*” is not acceptable. Sample results less than the MDL will be reported for GC/MS analyses only if the mass spectral fingerprint provides positive identification; these results must be qualified as estimated values by the laboratory.

**Table 7. Method Detection Limit and Quantitation Limit (QL) Requirements for Analyses of Water**

Method	Analyte	Fraction	Units	MDL	QL
<i>Mercury</i>					
EPA 1631	Total Mercury	Total & Dissolved	ng/L	0.2	0.5
EPA 1630	Methylmercury	Total & Dissolved	ng/L	0.02	0.05
<b>TBD<sup>(1)</sup></b>	<b>Methylmercury photodegradation</b>	<b>Total</b>	<b>TBD</b>	<b>TBD</b>	<b>TBD</b>
<i>Physical and conventional Parameters</i>					
EPA 130.2	Hardness	Total as CaCO <sub>3</sub>	mg/L	3	5
EPA 180.1	Turbidity	NA	NTU	0.02	0.1
EPA 160.1	Solids (TDS)	Total Dissolved	mg/L	6	10
EPA 160.2	Solids (TSS)	Total Suspended	mg/L	2	3
EPA 415.1/SM 5130	Organic Carbon	Total & Dissolved	mg/L	0.3	1
EPA 300	Sulfate	Filtered	mg/L	0.02	0.5
SM5910B	Ultraviolet Absorbance at 254 nm	Filtered	cm <sup>-1</sup>	NA	0.01
<i>N and P Compounds</i>					
EPA 351.3	Total Kjeldahl Nitrogen	Total	mg/L	0.07	0.1
EPA 365.2	Phosphorus	Total	mg/L	0.01	0.1
EPA 353.2	Nitrate + nitrite as N	Total	mg/L	0.02	0.1
EPA 365.2	Reactive Phosphorus, as P	Dissolved	mg/L	0.01	0.05
<i>Pathogen Indicators</i>					
SM 9223B	<i>E. Coli</i> bacteria	NA	MPN/100 mL	2	2
<i>Organophosphorus Pesticides<sup>(1)</sup></i>					
EPA 625(m)	Azinphos-methyl	Total	µg/L	0.01	0.02
EPA 625(m)	Chlorpyrifos	Total	µg/L	0.005	0.01
EPA 625(m)	Diazinon	Total	µg/L	0.005	0.01
EPA 625(m)	Dimethoate	Total	µg/L	0.005	0.01
EPA 625(m)	Disulfoton	Total	µg/L	0.01	0.02
EPA 625(m)	Malathion	Total	µg/L	0.005	0.01
EPA 625(m)	Methamidophos	Total	µg/L	0.01	0.02
EPA 625(m)	Methidathion	Total	µg/L	0.01	0.02
EPA 625(m)	Parathion, Methyl	Total	µg/L	0.01	0.02
EPA 625(m)	Parathion, Ethyl	Total	µg/L	0.01	0.02
EPA 625(m)	Phorate	Total	µg/L	0.01	0.02
EPA 625(m)	Phosmet	Total	µg/L	0.01	0.02
<i>Carbamate and Urea-substituted Pesticides<sup>(1)</sup></i>					
EPA 8321	Aldicarb	Total	µg/L	0.05	0.4
EPA 8321	Carbaryl	Total	µg/L	0.04	0.07
EPA 8321	Carbofuran	Total	µg/L	0.25	0.4
EPA 8321	Diuron	Total	µg/L	0.05	0.4
EPA 8321	Linuron	Total	µg/L	0.1	0.4
EPA 8321	Methiocarb	Total	µg/L	0.1	0.4
EPA 8321	Methomyl	Total	µg/L	0.1	0.4
<i>Pyrethroid Pesticides<sup>(1)</sup></i>					
EPA 625(m)	Bifenthrin	Total	µg/L	0.005	0.025
EPA 625(m)	Cyfluthrin	Total	µg/L	0.005	0.025
EPA 625(m)	Cypermethrin	Total	µg/L	0.005	0.025
EPA 625(m)	Esfenvalerate	Total	µg/L	0.005	0.025
EPA 625(m)	Deltamethrin	Total	µg/L	0.005	0.025
EPA 625(m)	Permethrin	Total	µg/L	0.005	0.025



Method	Analyte	Fraction	Units	MDL	QL
<i>Herbicides</i>					
		<i>Total</i>	$\mu\text{g/L}$		
EPA 625(m)	Atrazine	Total	$\mu\text{g/L}$	0.005	0.01
EPA 625(m)	Simazine	Total	$\mu\text{g/L}$	0.005	0.01
EPA 8141	Molinate	Total	$\mu\text{g/L}$	NE <sup>(2)</sup>	0.04
EPA 8081	Oxyfluorfen	Total	$\mu\text{g/L}$	0.01	0.03
EPA 8141	Thiobencarb	Total	$\mu\text{g/L}$	NE <sup>(2)</sup>	0.04
<i>Trace Elements</i>					
EPA 200.8	Arsenic		$\mu\text{g/L}$	0.14	0.5
EPA 200.8	Cadmium		$\mu\text{g/L}$	0.03	0.1
EPA 200.8	Copper	Total Recoverable	$\mu\text{g/L}$	0.3	0.5
EPA 200.8	Lead	& Dissolved	$\mu\text{g/L}$	0.04	0.25
EPA 200.8	Nickel		$\mu\text{g/L}$	0.2	0.5
EPA 200.8	Zinc		$\mu\text{g/L}$	0.3	1.0

(1) Standard methods have not been established for this parameter. Specific methods will be amended to this QAPP if laboratories capable of providing the required data quality and reporting are selected.

(2) The MDLs for molinate and thiobencarb are being established by the analyzing laboratory.

**Table 8. Method Detection Limit (MDL) and Quantitation Limit (QL) Requirements for Analyses of Tissue**

Analyte	MDL, ng/g	QL, ng/g
Total Mercury by MLML SOP 103	25	100

*Organochlorine pesticides (all units are ng/g)*

Analyte	MDL, ng/g	QL, ng/g	Analyte	MDL, ng/g	QL, ng/g
<i>Chlorinated Pesticides</i>					
Aldrin	0.26	1.0	Endosulfan II	TBD	10
Chlordane, cis	0.68	1.0	Endosulfan sulfate	TBD	10
Chlordane, trans	0.40	1.0	Endrin	0.71	2.0
Chlordene, alpha	0.26	0.5	HCH, alpha	0.36	0.5
Chlordene, gamma	0.25	0.5	HCH, beta	0.56	1.0
Chlorpyrifos	0.81	1.0	HCH, gamma	0.27	0.5
Dacthal	0.58	1.0	Heptachlor	0.51	1.0
DDD, o,p'	0.71	1.0	Heptachlor epoxide	0.37	0.5
DDD, p,p'	0.84	1.0	Hexachlorobenzene	0.10	0.3
DDE, o,p'	0.53	2.0	Methoxychlor	1.3	3.0
DDE, p,p'	0.56	2.0	Mirex	0.93	1.5
DDMU, p,p'	1.1	3.0	Nonachlor, cis	0.96	1.0
DDT, o,p'	1.0	3.0	Nonachlor, trans	0.35	1.0
DDT, p,p'	2.0	5.0	Oxadiazon	0.88	1.0
Diazinon	6.4	20	Oxychlordane	0.29	1.0
Dichlorobenzophenone, p,p'	TBD	10	Parathion, ethyl	0.64	2.0
Dieldrin	0.40	0.5	Parathion, methyl	1.2	4.0
Endosulfan I	0.74	2.0	Tetradifon (Tedion)	0.54	2.0

*PCB Congeners and Aroclor Mixtures*

All PCB congeners	NA	0.2
Aroclor 1254	NA	10
Aroclor 1260	NA	10
Aroclor 5460 (polychlorinated terphenyl)	NA	100

*Polybrominated Diphenyl Ethers (PBDEs)*

PBDE 17	NA	0.6
PBDE 28	NA	0.6
PBDE 47	NA	0.8
PBDE 66	NA	0.6
PBDE 100	NA	0.6
PBDE 99	NA	0.8
PBDE 85	NA	0.8
PBDE 154	NA	0.6
PBDE 153	NA	0.8
PBDE 183	NA	0.8
PBDE 183	NA	1.2
PBDE 190	NA	4.0

#### **4.4 LABORATORY STANDARDS AND REAGENTS**

All stock standards and reagents used for extraction and standard solutions must be tracked through the laboratory. The preparation and use of all working standards must be recorded in bound laboratory notebooks that document standard tractability to U.S. EPA, A2LA or National Institute for Standards and Technology (NIST) criteria. Records must have sufficient detail to allow determination of the identity, concentration, and viability of the standards including any dilutions performed to obtain the working standard. Date of preparation, analyte or mixture, concentration, name of preparer, lot or cylinder number, and expiration date, if applicable, must be recorded on each working standard.

#### **4.5 SAMPLE PREPARATION METHODS**

Surface water samples will be prepared in solvent or via other extraction techniques prior to sample analyses. All procedures must follow the methods or SOPs referenced in this QAPP.

Preparations of water and sediment samples for analysis for this monitoring program are as follows:

- Water samples to be analyzed for trace elements will be prepared using the extraction procedures described in EPA 200.8, as specified in Table 7.
- Water samples to be analyzed for pesticides will be prepared using Separatory Funnel Liquid-Liquid Extraction (EPA 3510) or Continuous Liquid-Liquid Extraction (EPA 3520).

### **5 QUALITY CONTROL REQUIREMENTS**

The types of quality control assessments required in the monitoring program are discussed below. Detailed procedures for preparation and analysis of quality control samples are documented in the analytical method documents or Standard Operating Procedures (SOP) provided by the analytical laboratories.

#### **5.1 CORRECTIVE ACTIONS**

During the course of sample collection and analysis for this study, field supervisors and team members, and laboratory supervisors and analysts, will strive to ensure that all measurements and procedures are followed as specified in this QAPP and that measurements meet the prescribed acceptance criteria. If a problems or deviations from specified procedures are observed, prompt action will be taken to correct the immediate problem and to identify its cause(s). Any related systematic problems must also be identified. Problems regarding field data quality that may require corrective action will be documented in the field data sheets. Corrective actions for specific analyses are documented in APPENDIX F. Problems regarding analytical data quality that require corrective action are also documented in the laboratories' QA Manuals (APPENDIX A). Responsibility and documentation requirements for corrective actions taken are specified in the QA Manuals for the individual laboratories and sampling contractors. Evaluation of the effectiveness of corrective actions is determined through continued QA assessments.

## **5.2 QUALITY ASSURANCE OBJECTIVES (QAOS)**

Quality assurance objectives are the detailed QC specifications for precision, accuracy, representativeness, comparability, and completeness. These QAOS are used as comparison criteria during data quality review to determine if the minimum requirements have been met and the data may be used as planned.

## **5.3 DEVELOPMENT OF PRECISION AND ACCURACY OBJECTIVES**

Laboratory control spikes (LCSs) are used to measure achievement of the precision and accuracy objectives. The laboratory fortifies the LCSs with target compounds to monitor the laboratory precision and accuracy. Field duplicates measure sampling precision and variability for comparison of project data. Acceptable relative percent difference (RPD) is less than 25% for field duplicate analyses. If field duplicate sample results for a specific parameter vary beyond these objectives, the results for that parameter are qualified.

## **5.4 INTERNAL QUALITY CONTROL (QC)**

Internal quality control (QC) is achieved by collecting and/or analyzing a series of duplicate, blank, spike, and spike duplicate samples to ensure that analytical results are within the specified QA objectives. The QC sample results are used to quantify precision and accuracy and identify any problem or limitation in the associated sample results. The internal QC components of a sampling and analyses program will ensure that the data of known quality are produced and documented. The internal QC samples, frequency, acceptance criteria, and corrective action must meet the minimum requirements presented in the following sections.

## **5.5 FIELD QUALITY CONTROL**

Field QC samples are used to assess the influence of sampling procedures and equipment used in sampling. They are also used to characterize matrix heterogeneity. For basic water quality analyses, quality control samples to be prepared in the field will consist of equipment and field blanks, and field duplicates. The number of field duplicates and field blanks are set to achieve an overall rate of at least 5% of all analyses for a particular parameter. The external QA samples are rotated among sites and events to achieve the overall rate of 5% field duplicate samples and 5% blanks (as appropriate for specific analyses).

### **5.5.1 Equipment Blanks**

Equipment blanks will be collected and analyzed for all analytes of interest along with the associated environmental samples. Equipment blanks will consist of laboratory-prepared blank water (certified contaminant-free) processed through the sampling equipment using the same procedures used for environmental samples.

### **5.5.2 Field Duplicates**

Field duplicates will be collected at the rate of one per sampling event, and analyzed along with the associated environmental samples. Field duplicates will be collected at the same time as environmental samples or will consist 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 shall be reanalyzed if possible to verify the results.

## **5.6 LABORATORY QUALITY CONTROL**

For basic water quality analyses, quality control samples prepared in the contract laboratory will typically consist of method blanks, laboratory control samples, laboratory duplicates, matrix spikes and duplicates, and surrogate compounds added to each sample (for organic analysis). Note that while laboratories strive to achieve recoveries between 70-130 for pesticide analyses, it is not possible to achieve those limits for all analytes in a specific scan. Laboratory acceptance criteria for all analyte recoveries are equal to or better than the control limits specified by the Surface Water Ambient Monitoring Program (SWAMP) and defined as *mean recovery*  $\pm 3$  *standard deviations*.

### **5.6.1 Method Blanks**

Method blanks will be prepared and analyzed by the contract laboratory with each batch of samples. If any analyte is detected in the blank, the blank must be re-analyzed and the associated samples re-extracted and re-analyzed, if possible.

### **5.6.2 Laboratory Control Samples and Surrogates**

Laboratory control samples (LCS) will be analyzed at the rate of one per sample batch. Surrogate compounds may be added to samples for organic analyses. Laboratory acceptance criteria and corrective actions for specific analyses are documented in APPENDIX F.

### **5.6.3 Matrix Spikes and Matrix Spike Duplicates**

Matrix spikes and matrix spike duplicates will be analyzed at the rate of one pair per sample event. Matrix spike samples are collected at the same time as the environmental samples and are spiked at the laboratory. Laboratory acceptance criteria and corrective actions for specific analyses are documented in APPENDIX F.

## **6 INSTRUMENTATION AND EQUIPMENT PREVENTIVE MAINTENANCE**

### **6.1 SAMPLE EQUIPMENT CLEANING PROCEDURES**

Equipment used for sample collection must be cleaned according to the specific procedures documented in each sampling SOP.

### **6.2 ANALYTICAL INSTRUMENT AND EQUIPMENT TESTING PROCEDURES AND CORRECTIVE ACTIONS**

Testing, inspection, maintenance requirements, and corrective actions for assessments of analytical equipment used by the contract laboratories are documented in the quality assurance manuals for each analyzing laboratory. Laboratory quality assurance manuals for all contract laboratories performing analyses are provided in APPENDIX A. Generally, as a minimum requirement, laboratory equipment will be tested and maintained according to the manufacturer-recommended schedules of maintenance. Due to the cost of some laboratory equipment, back up

capability may not be possible. Commonly replaced parts will have spares available for rapid maintenance of failed equipment. Such parts include but are not limited to batteries, tubes, light bulbs, tubing, specific ion electrodes, electrical conduits, glassware, and pumps.

All field equipment will receive preventive maintenance and testing according to the manufacturer-recommended schedules of maintenance. Other equipment used only occasionally will be inspected for availability of spare parts, cleanliness, and battery strength prior to being taken into the field. Common spare parts which should be available in the contractor's facilities (laboratory or office) include, but are not limited to: batteries, tubes, light bulbs, tubing, replacement probes, glassware. After use in the field, equipment will be re-checked for needed maintenance.

Separate log books documenting all preventive and corrective maintenance will be maintained for each type of field or laboratory equipment. Maintenance logs will be available for inspection during systems audits. Individuals responsible for maintenance shall be identified in the QA Manual for each laboratory and sampling contractors.

### **6.3 INSTRUMENT CALIBRATIONS AND FREQUENCY**

#### **6.3.1 Analytical Procedures and Calibration**

This section briefly describes analytical methods and calibration procedures for samples that will be collected under this monitoring program.

Analytical methods selected for use in this program follow the general guidance of the following methods:

- *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater* (EPA-600/4- 85/054)
- *U.S. EPA Methods for Chemical Analysis of Water and Wastes* (EPA-600/4-79-020, third edition, 1983)
- *Methods for Determination of Organic Compounds in Drinking Water* (EPA-600/4- 88/039)
- USEPA. 2002. *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, Fourth Edition*. Office of Water, Washington, D.C. EPA-821-R-02-013.

For this program, only linear calibration, with either an average response factor or a linear regression, is acceptable for organic analyses. Non-linear calibration is not allowed because this calibration option creates a potential for poor quantitation or biased concentrations of compounds at low or high concentrations (near the high and low ends of the calibration range. Laboratories shall prepare an initial 5-point calibration curve, where the low level standard concentration is less than or equal to the analyte quantitation limit. For inorganic analysis, laboratories shall follow the analytical method requirements and, at a minimum, perform a 3 point calibration curve. Calibrations must be performed prior to each analytical batch. The individual analyst performing the analysis is responsible for conducting and assessing calibrations prior to analysis.

All field measuring equipment shall be inspected and calibrated within 24 hours prior to use for a specific sample event. Laboratory measuring equipment shall be inspected and calibrated at least daily prior to use. Equipment to be calibrated includes thermometers, DO meters, pH meters, conductivity meters, flow meters, and multiparameter field meters (if used). Calibrations will be

performed and evaluated according to the SOP specific to each piece of equipment. Calibration log books will be issued to and maintained by each field crew conducting field data measurements using field equipment. Field equipment logbooks are to be kept in a safe place and otherwise taken only to the field when instruments are to be used over a period of days requiring calibration in the field. Calibration log books for laboratory equipment will be maintained for each piece of laboratory measuring equipment and must be kept in a safe location in the laboratory.

#### **6.4 INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND CONSUMABLES**

The procurement of supplies, equipment, and services must be controlled to ensure that specifications are met for the high quality and reliability required for each field and laboratory function. Inspection protocols and acceptance criteria for laboratory analytical reagents and other consumables are documented in the Quality Assurance Manuals for individual laboratories. Equipment and materials are purchased independently by laboratories and sampling contractors. It is the responsibility of each staff person doing the ordering to inspect the equipment and materials for quality.

Gloves, sample containers, and any other consumable equipment used for sampling will be inspected by the sampling crew on receipt and will be rejected or returned if any obvious signs of contamination (*e.g.*, torn packages, etc.) are observed. Calibration supplies must be ordered on a timely basis to ensure that they are available when needed, and have not exceeded the manufacturer's expiration date.

Upon receipt of materials or equipment, designated staff receives and signs for the materials. The items are reviewed to ensure the shipment is complete and they are then delivered to the proper storage location. All chemicals are dated upon receipt. All supplies are stored appropriately and are discarded upon expiration date.

### **7 DATA MANAGEMENT**

Copies of field logs, a copy of COC forms, original preliminary and final lab reports, and electronic media reports will be kept by the Monitoring Manager for review by the SRWP Coordinator, the SRWP Watershed Monitoring Committee, and the Regional Board's grant manager for this project. Original field logs and COCs will be retained by the field crew manager or designee. Contract laboratories shall retain original COC forms. The contract laboratories will retain copies of the preliminary and final data reports. These records will be kept for a minimum of three years after the completion of monitoring described in this document. An SRWP Chain-of-Custody form and an example SRWP Field Log sheet are provided in APPENDIX G.

Concentrations of chemicals and toxicity endpoints, and all numerical biological parameters shall be calculated as described in the referenced method document for each analyte or parameter, or laboratory SOP. Field data will be entered by staff designated by the sampling contractor's field crew leader into a standard electronic format (supplied or approved by the Monitoring Manager). Laboratory analyses data will be entered or converted by the designated laboratory staff into a standard SWAMP-compatible electronic format approved by the Monitoring Manager. Computer hardware and software to accomplish these tasks are selected by laboratory and sampling contractors. Acceptability of hardware and software is determined by the ability to provide data in the approved format.

The data generated will be converted to a standard database format maintained on personal computers in the Monitoring Manager's office by designated staff and made available for the Regional Board staff review. 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 will be added to the final database.

Monitoring data will be submitted electronically to the Regional Board with the annual report in either Microsoft Access or Excel format. The data will also be made available via the California Environmental Data Exchange Network (CEDEN) database, as well as tabular hard-copy data required for the annual report.

## **7.1 DATA ASSESSMENT PROCEDURES**

Data will be evaluated and documented after each sample event to determine whether project quality assurance objectives (QAOs) have been met, to quantitatively assess data quality, and to identify potential limitations on data use. The following assessments of compliance with quality control procedures will be performed during the data collection phase of the project:

- Performance assessment of the sampling procedures will be performed by the field sampling crews. Corrective actions shall be carried out by the field sampling crew, documented in field logs, and reported to the quality assurance manager.
- The laboratory is responsible for following the procedures and operating the analytical systems within the statistical control limits. These procedures include proper instrument maintenance, calibration of the instruments, and the laboratory QC sample analyses at the required frequency (e.g., method blanks, laboratory control samples, etc.). Associated QC sample results are reported with all sample results so that project staff can evaluate the analytical process performance.

All project data must be reviewed as part of the data assessment. Review is conducted on a preparation batch basis by assessing QC samples and all associated field sample results.

Project data review established for this project includes the following steps:

- Initial review of analytical and field data for complete and accurate documentation, chain of custody procedures, analytical holding times compliance, and required frequency of field and laboratory QC samples;
- Evaluation of analytical and field blank results to identify random and systematic contamination;
- Comparison of all spike and duplicate results with project objectives for precision and accuracy;
- Assigning data qualifier flags to the data as necessary to reflect data use limitations identified by the assessment process; and
- Calculating completeness by matrix and analyte.

The monitoring management contractor is responsible for conducting the data assessment and for ensuring that data qualifier flags are assigned, as needed, based on the established QC criteria.



## **8 ASSESSMENT AND OVERSIGHT**

### **8.1 ASSESSMENTS AND RESPONSE ACTIONS**

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

- Performance assessments of sampling procedures will be performed by the field sampling crews. Corrective actions shall be carried out by the field sampling crew and reported to the Quality Assurance Manager in QA Reports.
- 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. Corrective actions will be in
- Assessment of field QC results and oversight of implementation of corrective actions shall be the responsibility of the Quality Assurance Manager and shall be included in QA reports to project management.

Routine procedures to assess precision and accuracy, criteria for success, and corrective actions have been discussed previously (section 1.6 and Section 5) and are also presented in APPENDIX F. These assessments will be performed for every event.

The following additional assessments may be performed for this project, but are not currently scheduled for 2006-2007 monitoring.

#### **8.1.1 Performance Evaluation Audits**

Performance evaluation (PE) audits quantitatively assess the data produced by a measurement system. Performing an evaluation audit involves submitting certified samples for each analytical method. The matrix standards are selected to reflect the concentration range expected for the sampling program. Any problem associated with PE samples must be evaluated to determine the influence on field samples analyzed during the same time period. The laboratory must provide a written response to any PE sample result deficiencies. No Performance Evaluation Audits are planned because the SRWP relies on the State laboratory certification process to assure adequate overall laboratory performance.

#### **8.1.2 Field Technical Audits**

Sampling contractors should routinely observe field operations to ensure consistency and compliance with sampling specifications presented in this QAPP. Field observations and activities should be documented using an audit checklist. No audits of field operations are planned for the SRWP, however, the Monitoring Program manager may perform audits of field operations, if it is determined to be necessary.

#### **8.1.3 Laboratory System Audit**

Regional Board staff may conduct laboratory system audits during conduction of sample analysis for this program. A laboratory system audit is a quantitative review of a sampling or analytical system. Laboratory system audit results are used to review operations and ensure that the technical and documentation procedures provide valid and defensible data. System audits are

performed by qualified technical staff members who have authority to act independently of the laboratory, field and project management.

Critical items for a laboratory system audit include:

- Sample storage procedures;
- Availability of and compliance with calibration procedures and documentation requirements;
- Standard operating procedures;
- Source and handling of standards;
- Completeness of data forms, notebooks and other records of analysis and QC activities;
- Data review and verification procedures;
- Data storage, filing and record keeping procedures;
- Sample custody procedures;
- Establishments and use of quality control procedures, control limits and corrective actions that comply with specification in this QAPP;
- Operating conditions of the facilities and the equipment;
- Documentation of the instruments maintenance activities; and
- Laboratory staff training and documentation.

## **8.2 QUALITY ASSURANCE REPORTS TO MANAGEMENT**

Quarterly status reports will be produced by the Monitoring Program Manager to document project status, results of performance evaluations, data quality assessments, and any significant QA problems and recommended solutions. Quarterly project status reports will be distributed to the SRWP Coordinator and the Regional Board Grant Manager.

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 SRWP. 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 quality assurance report will include results of any performance evaluation audits or field technical audits performed. The annual report will be distributed to the SRWP Coordinator and the Regional Board Grant Manager, as well as to all other program participants and interested parties.

## **9 DATA VALIDATION AND USABILITY**

The quality assurance objectives and procedures used by the SRWP and documented in this QAPP are SWAMP-compatible. These procedures generally adhere to the guidance provided in *Guidance on Environmental Data Verification and Data Validation (EPA QA/G-8)*, (USEPA 2001). Relevant details of this process have been discussed previously in sections 1.6, 5, and 7 of this document. No additional SRWP-specific SOPs or checklists for this process have been created. A summary of this process is provided below.

## 9.1 LABORATORY DATA REVIEW, VERIFICATION, AND REPORTING

The quality assurance manual for each participating laboratory must be used to accept, reject, or qualify the data generated by the laboratory. The laboratory management will be responsible for validating all data generated by the laboratory.

The laboratory's personnel must verify that the measurement process was "in control" (i.e., that all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with analysis of a subsequent batch. In addition, each laboratory will implement a system for detecting and reducing transcription and/or calculation errors prior to reporting data. Specific laboratory procedures for identifying unacceptable analytical bias, outliers, or missing data are documented in the QA Manuals provided in APPENDIX A. Criteria used to accept or reject data are provided in APPENDIX F.

Only data that have met data quality objectives, or data that have acceptable deviations explained will be submitted by the laboratory. When QA objectives 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.

## 9.2 DATA VALIDATION

Data validation is a data quality audit conducted to verify that an analytical method has been performed according to the method and project specifications, and that results have been correctly calculated and reported. The Monitoring Manager is responsible for data validation prior to submitting any data to Regional Board. The QA Manager will provide independent oversight and resolution of any specific QA issues. Specific items that will be reviewed during data validation are:

- Chain of custody records
- Documentation of the laboratory procedures (e.g., standard preparation records, run logs, data reduction and verification)
- Accuracy of data reduction, transcription, and reporting
- Adherence to method-specific calibration procedures and quality control parameters
- Precision and accuracy of recorded results

## 9.3 RECONCILIATION WITH USER REQUIREMENTS

Procedures to assess uncertainty of validated data have been discussed previously in QAPP Sections 1.6 and 5. This data may be used in the context of the "SWAMP umbrella" and SWAMP database. This is addressed by submitting data to the Regional Board, as described in Section 7.

# 10 AMENDMENTS TO THE QAPP

*This section is reserved for documentation of future additions and modifications to QAPP.*

## 11 REFERENCES

- Bailey H, C DiGiorgio, K Kroll, J Miller, D Hinton, and G Starrett. 1996. Development of procedures for identifying pesticide toxicity in ambient waters: Carbofuran, diazinon, and chlorpyrifos. *Environmental Toxicology and Chemistry* 15: 837-845.
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- USEPA. 1996a. *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. U.S. Environmental Protection Agency (USEPA), Office of Water. (EPA 821-R-96-011). July 1996.
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- USEPA 2001. *Laboratory Documentation Requirements for Data Evaluation* (R9QA/004.1)

USEPA 2001. *Guidance on Environmental Data Verification and Data Validation (EPA QA/G-8)*.

USEPA. 2002. *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, Fourth Edition*. U.S. Environmental Protection Agency (USEPA), Office of Water, Washington, D.C. EPA-821-R-02-01

## **APPENDIX A: LABORATORY QA MANUALS**

*The following documents are provided on the accompanying CD-ROM disc.*

- Pacific EcoRisk Quality Assurance/Quality Control Manual, September 2005 Revision
- Marine Pollution Studies Lab, Moss Landing Marine Lab QAM
- CDFG Water Pollution Control Lab QAM
- CalTest QA Manual, January 2004 Revision
- CRG Marine Labs Quality Assurance Program Document Revision E (2004)
- APPL Quality Assurance Program Plan, September 2004

These documents are provided by the contract laboratories. Additional manuals will be added to the QAPP as needed for new laboratories.

## **APPENDIX B: STANDARD OPERATING PROCEDURES FOR FIELD SAMPLING**

*The following documents are provided on the accompanying CD-ROM disc.*

- Ambient Water Sampling (Pacific EcoRisk 2001)
- Field Sampling Methyl and Total Mercury in Water Based Upon Frontier Geoscience's SOP 008 and Modified EPA Method 1669, DFG SOP—100 (CDFG 2000)
- Sampling And Processing Trace Metal And Synthetic Organic Samples Of Marine Mussels, Freshwater Clams, Marine Crabs, Marine And Freshwater Fish And Sediments: DFG METHOD 102 (CDFG 2001)

## APPENDIX C: STANDARD OPERATING PROCEDURES FOR CHEMICAL AND MICROBIOLOGICAL ANALYSES

*The following Standard Operating Procedures are provided on the accompanying CD-ROM disc.*

- Laboratory Preparation - Mussels and Clams (CDFG Marine Pollution Laboratory, Moss Landing, undated)
- Analysis of Mercury in Sediments and Tissue by Flow Injection Mercury System (FIMS) DFG-103. (CDFG Marine Pollution Laboratory, Moss Landing, 2000)
- Method 3052: Microwave Assisted Acid Digestion Of Siliceous And Organically Based Matrices (CDFG Marine Pollution Laboratory, Moss Landing, 1996)
- Modification of EPA Method 3052 (CDFG Marine Pollution Laboratory, Moss Landing, undated)
- Digestion Of Tissues For Total Mercury Using Nitric And Sulfuric Acids (70:30) (DRAFT, CDFG Marine Pollution Laboratory, Moss Landing, 2005)
- Analysis Of Extractable Synthetic Organic Compounds In Tissue And Sediment (CDFG Water Pollution Control Laboratory, Rancho Cordova, 2005)
- Total Alkalinity (Pacific EcoRisk, 2005)
- Ammonia (Pacific EcoRisk, 2005)
- Total Hardness by EPA 130.1 (Pacific EcoRisk, 2005)
- TDS by EPA 160.1 (Caltest 2003)
- TSS by EPA 160.2 (Caltest 2004)
- TOC/DOC EPA 415.1 (Caltest 2003)
- Turbidity by EPA 180.1 (Caltest 2004)
- UVA<sub>254 nm</sub> by SM5910B (Caltest 2004)
- Ortho- and Total Phosphorus by EPA 365.2/3 (Caltest 2004)
- TKN by EPA 351.3 (Caltest 2004)
- Nitrate plus Nitrite by EPA 353.2 (Caltest 2005)
- Inorganic Anions By Ion Chromatography by EPA 300 (Caltest 2005)
- Analysis of Mercury by EPA 1631 (Caltest 2005)
- Analysis of Methyl Mercury by EPA 1630 (Caltest 2005)
- E. coli by SM 9223B (Caltest 2004)
- Pesticides in water by EPA 625(m) (CRG 2004)
- Trace metals in water by EPA 200.8 (Caltest 2002)

*The following proprietary SOPs are on file with the Regional Water Quality Control Board and are not available for public review.*

- Organophosphorus Compounds by Gas chromatography: Capillary Column Technique by Gas Chromatography by EPA Method 8141A (APPL 2004)
- Carbamate and urea-substituted pesticides by High Performance Liquid Chromatography: Capillary Column Technique by Gas Chromatography by EPA Method 8321, (APPL 2005)
- Organochlorine Compounds by Gas chromatography by EPA Method 8081A, (APPL 2004)



*The following SOP will be added when a laboratory capable of performing this analysis has been selected. Selection is determined based on criteria outlined in the SRWP Monitoring Plan for 2005-2007 (SRWP 2006)*

- MeHg Photodegradation (*method to be determined*)

## **APPENDIX D: STANDARD OPERATING PROCEDURES FOR TOXICITY TESTING AND TOXICITY IDENTIFICATION EVALUATIONS**

*The following Standard Operating Procedures are provided on the accompanying CD-ROM disc.*

- *Ceriodaphnia dubia* Chronic Bioassay Standard Operating Procedures, SOP# C005-4 (Pacific EcoRisk, 2005)
- *Pimephales promelas* (Fathead Minnow) Chronic Bioassay Standard Operating Procedures, SOP# C001-4 (Pacific EcoRisk, 2005)
- *Selenastrum capricornutum* Algal Growth Bioassay Standard Operating Procedures, SOP# C0020-4 (Pacific EcoRisk, 2005)
- Flow Charts of TIE Procedures
- The Use of Ion Exchange Resins to Determine the Biototoxicity and Concentration of Dissolved Trace Metals in Natural Waters (Connor 1991)

## **APPENDIX E: STANDARD OPERATING PROCEDURES FOR SAMPLE EQUIPMENT CLEANING**

*The following Standard Operating Procedure is provided on the accompanying CD-ROM disc.*

- Sample Equipment Cleaning SOP  
(Central Valley Regional Water Quality Control Board, 2001)

## **APPENDIX F: QUALITY CONTROL ACCEPTANCE CRITERIA AND CORRECTIVE MEASURES FOR ANALYSES OF WATER AND TISSUE**

*The tables of Acceptance Criteria and Corrective Actions are provided on the accompanying CD-ROM disc.*

## **APPENDIX G: FORMS**

*The following forms are provided on the accompanying CD-ROM disc.*

- SRWP Chain of Custody
- Field Log (Example)
-