# QUALITY ASSURANCE PROJECT PLAN (QAPP) for CDPR Studies 243 and 244

# Study #243: Surface Water Quality Monitoring – Orestimba and Del Puerto Creek Watersheds

# Study #244: Resident Vegetation Buffers as a Management Practice to Reduce Pesticide Runoff in Dormant Almonds

(Revision 2.4)

# **Prepared By**

Michael Ensminger California Department of Pesticide Regulation Environmental Monitoring Branch 1001 I Street, Sacramento, CA 95812

# **Prepared For**

Coalition for Urban/Rural Environment Stewardship (CURES) 531-D North Alta Ave. Dinuba, CA 93618

December 12, 2007

# **GROUP A: PROJECT MANAGEMENT**

# 1. APPROVAL SIGNATURES

Coalition for Urban Rural Environmental Stewardship (CURES)						
<u>Title:</u>	Name:	Signature:	Date:			
Program Manager	Parry Klassen					
Project Coordinator	Jim Markle					
California	Department of Pesticide Regulation, En	vironmental Monitoring Branch				
<u>Title:</u>	Name:	Signature:	Date:			
Environmental Program Manager	Kean S. Goh, Ph.D.					
Staff Environmental Scientist	Sheryl Gill					
Staff Environmental Scientist	Carissa Ganapathy					
California Depart	ment of Fish and Game, Fish and Wildl	ife Water Pollution Control Labo	ratory			
<u>Title:</u>	Name:	Signature:	Date:			
Laboratory Supervisor	Dave Crane					
	Central Valley Regional Water Qual	ity Control Board				
<u>Title:</u>	Name:	Signature:	Date:			
QA Officer	Leticia Valadez					
Grant Manager	Diane Beaulaurier					
	University of California, Davis, Aquat	c Toxicology Lab				
<u>Title:</u>	Name:	Signature:	Date:			
Laboratory Director	Inge Werner, Ph.D.					

# **2.** TABLE OF CONTENTS

	Page:
Group A: Project Management	
1. Approval Signatures	2
2. Table of Contents	3
3. Distribution List	
4. Project/Task Organization	6
4.1 Involved Parties and Roles	6
4.2 Quality Assurance Officers role	7
4.3 Persons Responsible for QAPP Update and Maintenance	8
4.4 Organizational Chart and Responsibilities	
5. Problem Definition/Background	
5.1 Problem Statement	
5.2 Decisions or Outcomes	
5.3 Water Quality or Regulatory Criteria	
6. Project/Task Description	
6.1 Work Statement and Produced Products	10
6.2 Constituents to be Monitored and Measurement Techniques	
6.3 Project Schedule	
6.4 Geographical Setting	
6.5 Constraints	
7. Quality Objectives and Criteria for Measurement Data	
7. Quarty objectives and effective for Measurement Data	
7.2 Accuracy	
7.3 Representativeness	
7.3 Kepresentativeness	
7.4 Completeness	
7.5 Comparability	
8. Special Training Needs/Certification	
8.1 Specialized training or certifications	
8.2 Training and certification documentation	
8.3 Training personnel	
9. Documents And Records	
Group B: Data Generation and Acquisition	
10. Sampling Process Design	
11. Sampling Methods	
12. Sample Handling and Custody	
13. Analytical Methods and Field Measurements	
14. Quality Control	
14.1 Data Quality Objectives and Quality Assurance Objectives	
14.2 Field Quality Control (QAOs)	
14.3 Laboratory Quality Control (QAOs)	
15. Instrument/Equipment Testing, Inspection, and Maintenance	
15.1 Field Instrument/Equipment	
15.2 Laboratory (C. dubia and H. azteca) Toxicity Testing	
15.3 Laboratory Instrument/Equipment	
16. Instrument/Equipment Calibration and Frequency	
17. Inspection/Acceptance of Supplies and Consumables	
18. Non-Direct Measurements (Existing Data)	35
19. Data Management	35
GROUP C: Assessment and Oversight	36
20. Assessments & Response Actions	36

21. Reports to Management
Group D: Data Validation and Usability
22. Data Review, Verification, and Validation
23. Verification And Validation Methods
24. Reconciliation with User Requirements
25. Literature cited

# LIST OF TABLES

Table 1.	Personnel responsibilities (Element 4).	7
Table 2.	Study 243 (surface water monitoring) schedule timeline (Element 6).	. 11
Table 3.	Study 244 (BMPs, dormant sprays) schedule timeline (Element 6).	. 12
Table 4.	Data quality objectives for field measurements (Element 7).	. 16
Table 5.	Data quality objectives for laboratory toxicity (C. dubia and H. azteca) tests (Element 7)	. 16
	Data quality objectives for sediment size, TOC, and TSS (Element 7)	
	Data quality objectives for analytical laboratory measurements (Element 7).	
Table 8.	Document and record retention, archival, and disposition (Element 9).	. 19
	Sampling locations and methods (Element 11).	
Table 10.	Field analytical methods (Element 13).	. 25
Table 11.	Laboratory analytical methods (Element 13).	. 26
Table 12.	Field QC samples (Element 14)	. 30
Table 13.	Laboratory toxicity (C. dubia and H. azteca) testing QC samples (Element 14)	. 30
Table 14.	Laboratory QC samples (Element 14).	. 31
Table 15.	Grain size, TSS, and TOC QC samples (Element 14)	. 31
	Testing, inspection, and maintenance of sampling equipment and analytical instruments (Element 15)	
	Calibration of sampling equipment and analytical instruments (Element 16)	
	(Element 21) QA management reports.	
Table 19.	Definitions of data qualifier (Element 22).	. 40

# LIST OF FIGURES

Figure 1.	Organization Chart1	)
Figure 2.	Location Map, Study #2431	4

# LIST OF APPENDIXES

Appendix A. Study #243 Monitoring Plan	43
Appendix B. Study #244 Monitoring Plan	
Appendix C. DPR Standard Operating Procedures	44
Appendix D. Sample Tracking and Transport Standard Operating Procedures	44
Appendix E. Example Field Forms	45
Appendix F. Laboratory Quality Control Procedures	48
Appendix G. Analytical Methods-Water	48
Appendix H. Analytical Methods-Sediment	48
Appendix I. Mass Deposition Analysis SOP	48
Appendix J. TOC Determination and Sediment Size Analysis SOP	48
Appendix K. Laboratory Methods and QA/QC for C. dubia and H. azteca Toxicity Tests	49
Appendix L. CDFG Laboratory Quality Assurance Program Plan	49

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 5 of 49

# 3. DISTRIBUTION LIST

Parry Klassen\* Coalition for Urban Rural Environmental Stewardship (CURES) 1801 I Street, Suite 200 Sacramento, CA 95814 Phone: 559-297-5182 Fax: 559-297-9341 parryk@comcast.net

Kean Goh Department of Pesticide Regulation Environmental Monitoring Branch 1001 I Street Sacramento, CA 95812 kgoh@cdpr.ca.gov

Carissa Ganapathy Department of Pesticide Regulation Environmental Monitoring Branch 1001 I Street Sacramento, CA 95812 cgana@cdpr.ca.gov

Leticia Valadez\* California State Water Resources Control Board 11020 Sun Center Drive Suite 200 Rancho Cordova, CA 95670 Phone: 916-464-4634 <u>lvaladez@waterboards.ca.gov</u>

Inge Werner UC Davis ATL University of California – Davis Davis, CA 95616 Phone: 530-752-0585 iwerner@ucdavis.edu

\* Advisors to the Project

Jim Markle\* CURES 2750 Kingfisher Lane Lincoln, CA 95648 Phone: 916-25-3670 jmarkle@starstream.net

Sheryl Gill Department of Pesticide Regulation Environmental Monitoring Branch 1001 I Street Sacramento, CA 95812 Phone: 916-324-5144 sgill@cdpr.ca.gov

Diane Beaulaurier\* California State Water Resources Control Board 11020 Sun Center Drive Suite 200 Rancho Cordova, CA 95670 Phone: 916-464-4637 dbeaulaurier@waterboards.ca.gov

Dave Crane Department of Fish and Game Fish and Wildlife Water Pollution Control Laboratory 2005 Nimbus Road Rancho Cordova, CA 95670 Phone: 916-358-2859 dcrane@ospr.dfg.ca.gov

# 4. PROJECT/TASK ORGANIZATION

# 4.1 Involved Parties and Roles

Parry Klassen is the Executive Director of the Coalition for Urban Rural Environmental Stewardship (CURES). He will serve as the Contract Manager and will manage the grants and project on behalf of the Authority. He is responsible for obtaining all services and deliverables for the two studies. Jim Markle (CURES) will coordinate the activities between CURES and DPR (Department of Pesticide Regulation).

Kean S. Goh, Ph.D., is the DPR Environmental Program Manager and will assist the project leader by hiring, training and supervising all DPR staff and contributing to the study reports.

Sheryl Gill, Staff Environmental Scientist for the California Department of Pesticide Regulation (DPR), Environmental Monitoring Branch, Surface Water Protection Program will be the Project Leader for this project. She will be responsible for all field aspects of the project including developing the study protocols, organizing the field staff, scheduling of collection timings, and directing staff in sampling techniques, sampling frequency, and sampling duration. Sheryl will be responsible for delivering the samples to the California Department of Fish and Game (DFG) laboratory and to University of California at Davis Aquatic Toxicity Laboratory (UCD ATL) and for maintaining contact with the Authority, CURES, UCD ATL, and the DFG laboratory. She will also be responsible for reviewing and evaluating the data, and reporting study results.

Dave Crane is the DFG Fish and Wildlife Water Pollution Control Laboratory supervisor. He will maintain all records associated with the receipt and analysis of samples and will verify that the measurement process was "in control" (i.e., all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with analysis of a subsequent batch.

Inge Werner, Ph.D., is the laboratory director for the UCD ATL and she will oversee the invertebrate toxicity studies.

The DFG will be the contract laboratory for all chemical analyses. DFG will analyze submitted samples in accordance with the method and quality assurance requirements found in this Quality Assurance Project Plan (QAPP). The QAPP was prepared by DPR for the Coalition for Urban/Rural Environment Stewardship (CURES). DFG will act as technical resource to DPR staff and management.

Name	Organizational Affiliation	Title	Contact Information
Parry Klassen	en Coalition for Urban Rural Environmental Stewardship (CURES) Contract Manager		Phone: 559-297-5182 Fax: 559-297-9341 parryk@comcast.net
Jim Markle	Coalition for Urban Rural Environmental Stewardship (CURES)	Project Coordinator	Phone: 916-253-3670 jmarkel@starstream.net
Diane Beaulaurier	Central Valley Regional Water Quality Control Board (CVRWQCB)	Grant Manager	Phone: 916-464-4637 <u>dbeaulaurier@waterboards.ca.gov</u>
Leticia Valadez	Central Valley Regional Water Quality Control Board (CVRWQCB)	QA Officer	Phone: 916-464-4634 <u>lvaladez@waterboards.ca.gov</u>
Kean S. Goh, Ph.D.	Department of Pesticide Regulation (DPR), Environmental Monitoring Branch, Surface Water Protection Program	Environmental Program Manager	Phone: 916-324-4072 Fax: 916-324-4088 kgoh@cdpr.ca.gov
Sheryl Gill	Department of Pesticide Regulation (DPR), Environmental Monitoring Branch, Surface Water Protection Program	Staff Environmental Scientist (Project Leader)	Phone: 916-324-5144 sgill@cdpr.ca.gov
Carissa Ganapathy	Department of Pesticide Regulation (DPR), Environmental Monitoring Branch	Staff Environmental Scientist (Project QA Officer)	Phone: 916-322-3082 cgana@cdpr.ca.gov
Dave Crane	California Department of Fish and Game	Laboratory Supervisor	Phone: 916-358-2859 Fax: 916-985-4301 dcrane@ospr.dfg.ca.gov
Loc Nguyen	DFG Lab	Contract Laboratory QA Officer	Phone: 916-358-0314 Inguyen@ospr.dfg.ca.gov
Inge Werner	UCD ATL	Laboratory Director	Phone: 530-752-0585 iwerner@ucdavis.edu

Table 1. Personnel responsibilities (Element 4).

# 4.2 Quality Assurance Officers role

Carissa Ganapathy, Staff Environmental Scientist, is the Quality Assurance/Quality Control (QA/QC) Officer. She is responsible for reviewing the project QA program as it relates to the collection and completeness of data from field and laboratory operations, including training personnel to follow established protocols and procedures. She is responsible for reviewing quality control data from the lab.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 8 of 49

Leticia Valadez is the CVRWQCB Project Quality Assurance Officer. She will be responsible for verifying that the quality assurance and quality control procedures found in this QAPP meet the standards developed for Surface Water Ambient Monitoring Program (SWAMP) QAMP (Puckett, 2002) as set forth in the Electronic Template for SWAMP-Compatible Quality Assurance Project Plans (Nichol and Reyes, 2004). Diane Beaulaurier, CVRWQCB, is the Grant Manager for the project.

# 4.3 Persons Responsible for QAPP Update and Maintenance

CVRWQCB's Project QA Officer may request changes and updates to this QAPP after a review of the QAPP. Michael Ensminger, Associate Environmental Research Scientists for DPR, will be responsible for making the changes, submitting drafts for review, preparing a final copy, and submitting the final copy for signatures.

# 4.4 Organizational Chart and Responsibilities

The organizational chart for the study teams is shown in Figure 1. This chart may be periodically updated to reflect changes in personnel or roles.

Individuals that will advise on the project, but not participate in the execution of this program and delivery of the final report are listed with an asterisk in the <u>distribution list</u>.

# 5. PROBLEM DEFINITION/BACKGROUND

# 5.1 Problem Statement

The San Joaquin River (SJR) watershed is an important agricultural production area in the Central Valley of California. The SJR drains about 32,000 square miles through the San Joaquin Valley. Beneficial uses of the receiving waters have been threatened by elevated concentrations of pesticides in these waters resulting in the SJR listing in the Clean Water Act (CWA) § 303(d) list for pesticide impairment (CA EPA, 2002). Organophosphorous insecticides (OPs) are common pollutants (CA EPA, 2005). In addition, pyrethroid insecticides have been detected in the water column and sediment of subwatersheds of the SJR. Many pyrethroid insecticides are replacing OP use in various crops and in certain regions they are becoming a threat to water quality.

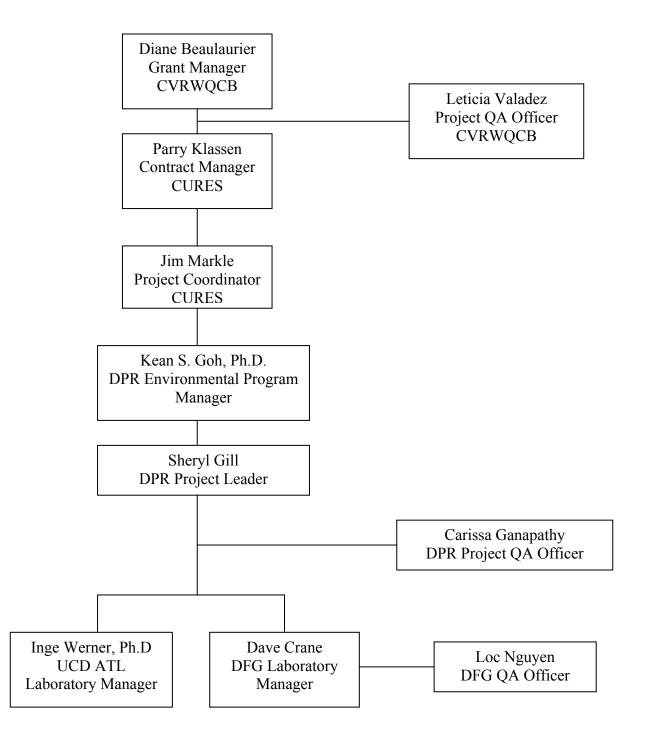
# 5.2 Decisions or Outcomes

From this work, we will be able to provide information about the effectiveness of a specific BMP – the use of resident vegetation - to reduce OP and pyrethroid runoff from dormant orchard fields into nearby bodies of water. This work will be developed for the Orestimba Creek and Del Puerto Creek subwatersheds within the SJR watershed. These subwatersheds are representative of the larger SJR watershed that is dominated by agricultural lands. Because the identified pesticides are commonly used in almond orchards to control several insect pests, this project focuses on BMP implementation in almond orchards although the results will be applicable for other crops and BMPs. Also from this work we will be providing UC Davis researchers water quality and pesticide loading data for environmental assessment models.

# 5.3 Water Quality or Regulatory Criteria

Orestimba Creek and Del Puerto Creek are on the 2002 CWA § 303(d) list. Chloropyrifos and diazinon were added to the Water Quality Objective for the Lower San Joaquin River (LSJR) from Mendota to Vernalis (<u>http://www.swrcb.ca.gov/tmdl/docs/sjr\_pest\_agenda\_resltn.pdf</u>). Orestimba and Del Puerto Creeks flow into the LSJR between Mendota and Vernalis.

# Figure 1. Organization Chart Studies #243 and #244 Department of Pesticide Regulation, Environmental Monitoring Branch



# 6. PROJECT/TASK DESCRIPTION

#### 6.1 Work Statement and Produced Products

### 6.1.1 Study #243 (Surface Water Monitoring)

The primary objective of this study is collect water quality and pesticide loading data. UCD researchers will specifically use this data to support and calibrate a geographic information system (GIS) integrated model that calculates long-term water quality impacts of various agricultural management practices for the Orestimba and Del Puerto Creek basins of the San Joaquin River watershed. Sampling sites and frequencies were chosen to fill gaps in available water quality monitoring data.

# 6.1.2 Study #244 (BMPs)

The objective of this study is to determine if resident vegetation in an almond orchard will reduce pesticide runoff into surface waters after a dormant insecticide spray. The study site has been selected, a 35 acre almond field in the San Joaquin Valley. The study will have two treatments: 1) resident vegetation in the row middles that has been allowed to grow in the fall and winter, after almond harvest, and 2) bare ground, where weeds have been controlled with weed control practices common to the area. A dormant spray containing a tank-mix of an OP and pyrethroid insecticide will be applied to the entire orchard. We will select products that are most commonly applied in the dormant season in this area, likely esfenvalerate and diazinon. Rainfall will be simulated with sprinklers that are permanently installed at this site.

### 6.2 Constituents to be Monitored and Measurement Techniques

Constituents that will be monitored and measured are briefly discussed below and more specifically in Element 10 and 11 (field aspects), in element 12 (transport procedures), and in Element 13 (analytical methods).

#### 6.2.1 Study #243

DPR scientists will collect water and sediment samples from stream monitoring. These samples will be transported to the DFG, where scientists will measure the total OP and pyrethroid concentrations in these water and sediment samples. In addition, DPR scientists will also analyze total suspended solids (TSS) from collected water samples. Additional water and sediment samples will also be transported to UCD ATL. Scientists at this location will conduct acute invertebrate toxicity tests with *Ceriodaphnia dubia* (water samples) and they will conduct invertebrate toxicity tests with *Hyalella azteca* (sediment samples). From sediment samples, DPR will we will also determine total organic carbon (TOC) and DFG will determine grain size.

In addition, DPR scientists will also measure numerous water quality parameters in the field: electrical conductivity (EC), pH, dissolved oxygen (DO), and temperature. Flow rate data for Orestimba Creek and for Del Puerto Creek (USGS gauge stations 11274538 and 11274630, respectively) will be will be accessed from the USGS website (http://waterdata.usgs.gov/ca/nwis/current/?type=flow).

# 6.2.2 Study #244

In this study we will collect and measure total OP and pyrethroid concentrations in runoff waters and in sediments to determine if resident vegetation will significantly reduce runoff of these two insecticides into surface waters. In addition to water and sediment samples, we will determine application rate by analyzing the concentration of the insecticides in the tank-mix, and collect deposition sheets to determine amount of insecticide applied in the field.

# 6.2.3 Analytical Methods

In both studies, concentrations of OPs and pyrethroids will be determined with gas chromatography. DFG scientists detect OPs using a modified method 8141A from the US EPA. They detect OPs using liquid-liquid extraction and high resolution gas chromatography with Flame Photometric Detector and Thermionic Bead Specific Detector. For confirmation, if needed, they will use gas chromatography with a mass spectrophometer and ion trap detector (GC/MS-ITD). DFG scientists detect pyrethroids using liquid-liquid extraction and high resolution gas chromatography with electron capture detector (GC/ECD). For confirmation, the use gas chromatography with mass spectrophotometer and ion trap detector (GC/MS-ITD).

DFG scientists will determine sediment grain size by using an EPA modified method provided by Allied Marine Science (AMS, Livermore, CA). For this method, sediments are separated into large and fine particles by filtering through a wire mesh screen. Fine particles are further separated by mixing with a dispersant solution and removing aliquots at specific depths and time.

DPR scientists will determine TSS using EPA method 160.2 for non-filterable sediments and TOC by using a Dohrmann DC-85A TOC analyzer.

### 6.3 Project Schedule

The project schedules for each study are shown in Table 2 (study 243) and Table 3 (study 244). The schedule may be periodically updated to reflect changes in schedules or tasks.

Activity	Date (MM/DD/YY)		Deliverable	Deliverable Due Date	
	Anticipated Date of Initiation	Anticipated Date of Completion			
Start Project	12/01/2007	NA	None	NA	
<i>In situ</i> water quality measurements	12/01/2007	06/30/2008	None	NA	
Collect water samples	12/01/2007	06/30/2008	Water samples to lab	OPs within 7 days after sampling; PYs within 4 days of sampling or need chemical preservation	
Collect sediment sample	12/01/2007	06/30/2008	Sediment samples to lab	Within 40 days after sampling	
Chemical analysis	01/01/2008	07/31/2008	Laboratory reports	Monthly	
C. dubia testing	01/01/2008	07/31/2008	Laboratory reports	Monthly	
<i>H. azteca</i> testing	01/01/2008	07/31/2008	Laboratory reports	Monthly	
Summarize Data	03/31/2008	08/15/2008	Complete data set	08/15/2008	
Draft Final Report	05/01/2008	08/31/2008	Draft report	08/31/2008	
Final Report	08/01/2008	09/30/2008	Written final report	09/30/2008	

Table 2. Study 243 (surface water monitoring) schedule timeline (Element 6).

Activity	Date (MM/DD/YY)		Deliverable	Deliverable Due Date
	Anticipated Date of Initiation	Anticipated Date of Completion		
Start Project	12/01/2007	NA	None	NA
Insecticide application	12/01/2007	02/29/2008	None	NA
Collect spray tank samples	Immediately prior to application	12/31/2007	Samples to lab	Within 7 days after collection
Collect spray deposition samples	During insecticide application	Within 4 hours of insecticide application	Deposition sheets to lab	Within 7 days after collection
Collect water samples from plots	Within 48 hours of insecticide application	Within 7 days of insecticide application	Samples to lab	OPs within 7 days after sampling; PYs within 4 days of sampling or need chemical preservation
Collect sediment samples from plots	Within 48 hours of insecticide application	Within 7 days of insecticide application	Samples to lab	Within 40 days after sampling
Chemical analysis	12/01/2007	02/29/2008	Laboratory reports	Monthly
Summarize Data	03/31/2008	05/31/2008	Complete data set	05/31/2008
Draft Final Report	06/01/2008	07/31/2008	Draft report	07/31/2008
Final Report	08/01/2008	09/30/2008	Written report	09/30/2008

Table 3. Study 244 (BMPs, dormant sprays) schedule timeline (Element 6).

# 6.4 Geographical Setting

# 6.4.1 Study #243

The sample site will be Orestimba Creek at River Road near the town of Crow's Landing and at Del Puerto at Vineyard Road near the town of Patterson (Figure 2), both in the San Joaquin River watershed. GPS coordinates (NAD27) are as follows:

- Orestimba Creek, N37°24'49" W121°00'54"
- Del Puerto Creek, N37°31'15" W121°08'55"

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 13 of 49

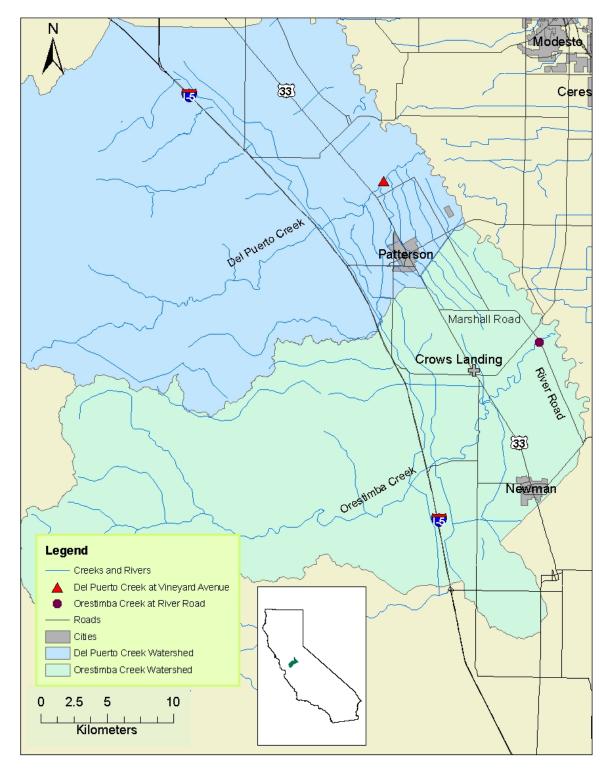


Figure 2. Location of the sampling sites for Study 243 (Orestimba and Del Puerto Creeks) and for Study 244 (near Crow's Landing, California).

# 6.4.2 Study #244

The sample site will be near the town of Crow's Landing in the San Joaquin Valley (Figure 2).

# 6.5 Constraints

<u>Pesticide application</u>. We will apply esfenvalerate and diazinon according to the label for use in dormant almonds. Application may be delayed if high winds occur, pest problems in adjacent fields require the rescheduling of application equipment, rain, or if other unforeseen obstacles arise. Any postponed application is expected to be a temporary occurrence. In addition, we may apply a different OP or pyrethroid if advised by the grower's PCA. If we change to a different OP or pyrethroid insecticide, it will be a commonly used insecticide for the area, orchard, and pest problem.

<u>Sample collection</u>. DPR staff consists of trained personnel to collect samples. SOPs are available for all aspects of sample collection. No delay in sample collection is anticipated.

### 7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Data quality objectives (DQOs) are quantitative and qualitative statements that specify the tolerable levels of potential errors in the data and ensure that the data generated meet the standards for published data in the peer-reviewed literature. As defined in this plan, DQOs specify the quantity and quality of data required to support the study objectives. Analytical performance requirements for this project are expressed in terms of precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS).

Data quality objectives for this project will consist of the following:

- Field measurements: accuracy, precision, and completeness
- Toxicity (*C. dubia* and *H. azteca*) testing: accuracy, precision, completeness, and specific acceptance criteria
- TOC measurements accuracy, precision, and completeness
- Chemical analyses: accuracy, precision, recovery, and completeness
- TSS and grain size precision, completeness
- USGS stream flow data completeness, accuracy (data verification by USGS procedures [Carter and Davidson, 1968; Wahl et.al., 1995])

Numerical DQOs for the field and laboratory analytical performance requirements are summarized in Tables 4 - 7. The following subsections present a summary of each PARCCS parameter and calculation equations as appropriate.

# 7.1 Precision

Precision is a measurement of the degree of agreement between replicate data, which is quantitatively assessed based on the relative percent difference or standard deviation. Precision measurements will be determined on both field and laboratory samples. To determine the precision of laboratory analyses, we will calculate the RPD (relative percent difference) for each pair of duplicate samples and field duplicate sets using the following equation:

$$\% RPD = \frac{S_1 - S_2}{x \, 100}$$

where:

 $S_1$  = first sample result (original value)

 $S_2$  = second sample result (duplicate value)

 $S_{av}$  = average of sample and duplicate =  $(S_1 + S_2)/2$ 

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 15 of 49

# 7.2 Accuracy

Accuracy is the degree of agreement between a measurement or observation and an accepted value. Accuracy measures close a measurement is to the true or expected value. Laboratories can assess laboratory accuracy with the use various blanks and spiked samples. The percent recovery (% R) is calculated with the following equation:

$$\% R = \frac{A - B}{C} \times 100$$

where:

- A = The analyte concentration determined experimentally from the spiked sample.
- B = The background level determined by a separate analysis of the unspiked sample.

C = The amount of the spike added.

# 7.3 Representativeness

Representativeness is a qualitative measure of the degree to which sample data accurately and precisely represent a characteristic environmental condition. Representativeness is a subjective parameter and is used to evaluate the efficacy of the sampling plan design. Representativeness is demonstrated by providing full descriptions of the sampling techniques and the rationale used for selecting sampling locations in the project planning documents. The measure of representativeness is answered during the preparation of the sampling and analysis approach and rationale, and then reassessed during the data usability process. There are no numerical goals that can be used to evaluate this subjective measure.

### 7.4 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount of data one planned to obtain under normal conditions. Percent completeness is calculated with the following equation:

% Completeness =  $\frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} x 100$ 

From experience on similar projects where both field and laboratory procedures were used, 90% completeness is a reasonable goal. If sufficient valid data are not obtained, the DPR Project Leader will initiate corrective action.

#### 7.5 Comparability

Comparability expresses the confidence that one data set can be accurately compared to another data set obtained during parallel or previous investigations. Comparability can be related to precision and accuracy, as these parameters are measures of data reliability. Contract laboratories use standardized methods, usually EPA-approved analytical methods or versions thereof.

Chemical samples from the same media are generally considered comparable if the same procedures for collecting and analyzing the samples are used, if the samples comply with the same QA/QC procedures, and if the units of measurement are the same. To ensure comparable data, all data generated for this project will be subject to the QA/QC procedures specified in this QAPP.

#### 7.6 Sensitivity

Sensitivity is the measure of the concentration at which an analytical method can positively identify and report analytical results. The sensitivity of a given method is commonly referred to as the detection limit. Although there is no single definition of this term, the following terms and definition of detection limits will be used:

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 16 of 49

- Instrument detection limit (IDL) is the minimum concentration that can be measured from instrument background noise under ideal conditions.
- Method detection limit (MDL) is a statistically determined concentration. It is the minimum concentration of an analyte that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero as determined in the same or a similar matrix. Because of the lack of analytical precision at this range, sample results greater than the MDL but less than the reporting limit (RL) would be qualified as "estimated".
- Reporting limit (RL) is the concentration of the target analyte that the laboratory has demonstrated the ability to measure within specified limits of precision and accuracy during routine laboratory operating conditions. This value is variable and highly matrix dependent. It is the minimum concentration that will be reported as unqualified by the laboratory.

Method sensitivity is dealt with by the inclusion of the required SWAMP Target Reporting Limits (<u>Table 7</u>) No Target Reporting Limits were set for the field analyses (specific conductance, pH, DO, and temperature).

Parameter	Accuracy	Precision	Recovery	Completeness
рН	<u>+</u> 0.5 pH units	$\pm 0.5$ pH units	NA	90%
Electrical Conductivity	<u>+</u> 5%	<u>+</u> 10%	NA	90%
Dissolved Oxygen (DO)	<u>+</u> 5%	<u>+</u> 10%	NA	90%
Temperature	$\pm 0.5^{\circ}C$	<u>+</u> 0.5°C	NA	90%

Table 4. Data quality objectives for field measurements (Element 7).

where NA = not applicable

Table 5.	Data quality	objectives t	for laborator	y toxicity (	C. dubia and H.	azteca) tests (	(Element 7).	
----------	--------------	--------------	---------------	--------------	-----------------	-----------------	--------------	--

Test Organism	Accuracy	Precision	Recovery	Completeness	Acceptance Criteria
C. dubia	Meet all performance	Meet all performance	NA	90%	a. Survival in the controls of $\geq$ 90%
	criteria in method relative	criteria in method relative			b. All performance criteria outlined in SOP are met
H. azteca	to reference to sample toxicant. replication.		NA	90%	a. Survival in the controls of $\geq$ 80%
					b. Measurable growth in the controls
					c. All performance criteria outlined in SOP are met

where NA = not applicable

Parameter	Accuracy	Precision	Recovery	Target RL	Completeness
Sediment size	NA	Field Duplicates < 25% RPD	NA	NA	90%
ТОС	Laboratory Reference Material within 95% CI of certified value	Field Duplicates < 25% RPD	NA	NA	90%
TSS	NA	Field Duplicates < 25% RPD	NA	NA	90%

Table 6. Data quality objectives for sediment size, TOC, and TSS (Element 7).

where NA = not applicable

# 8. SPECIAL TRAINING NEEDS/CERTIFICATION

# 8.1 Specialized training or certifications

The DPR Project Supervisor is responsible for assembling a project team with the necessary experience and technical skills. Since DPR currently has a highly trained field staff that has conducted similar programs in the past, it is not anticipated that any special training or certifications will be necessary to successfully execute this project. At a minimum, all staff will be familiar with the field guidelines and procedures included in this QAPP. All work will be performed under the supervision of experienced staff.

# 8.2 Training and certification documentation

No special training is required.

# 8.3 Training personnel

No special training personnel are required. Trained field staff and scientists will conduct this trial. If additional training is required, the Project QA officer will ensure that the training is complete.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 18 of 49

Table 7. Data quality objectives for analytical laboratory measurements (Element 7).

Group	Parameter	Accuracy	Precision	Recovery	Target RL* Water	Target RL* Soil/Sediment	Completeness
Organophosphorous	Azinphos methyl	Standard reference	5% of all MS should	Matrix spike recovery	0.050		90%
pesticides in water	Chlorpyrifos	materials within 95%	include a MSD. The	must be within control	0.020		90%
	Diazinon	confidence interval (CI) stated by provider of	RPD must be <25%.	limits set at $\pm 3$ standard deviations based on	0.020		90%
	Dimethoate	material. If not	The Laboratory	actual lab data.	0.050		90%
	Disulfoton	available, then with a standard reference	duplicate samples		0.050		90%
	Malathion	material of another	must be < 25% RPD		0.050		90%
	Methidathion	percentage, but must be certified.			0.050		90%
	Methyl parathion				0.050		90%
	Phosmet				0.050		90%
	Triphenyl Phosphate (surrogate)			na		90%	
Pyrethroids in water	Bifenthrin	Standard reference	within 95% MS/MSD RPD	Matrix spike recovery must be within control limits set at <u>+</u> 3 standard deviations based on actual lab data.	0.002	2.00	90%
and sediment	Cyfluthrin	materials within 95% confidence interval (CI)			0.004	5.00	90%
	Lambda-Cyhalothrin	stated by provider of	minimum.		0.002	5.00	90%
	Cypermethrin	material. If not	vailable, then with a tandard reference naterial of another ercentage, but must be $\frac{1116 \text{ Labolatory}}{\text{duplicate samples}}$		0.004	5.00	90%
	Deltamethrin	standard reference			0.004	na	90%
	Esfenyalerate/Fenyalerate material of another				0.002	5.00	90%
	Fenpropathrin	in percentage, but must be certified.			0.004	na	90%
	Permethrin				0.005	2.00	
	Dibromooctafluorobiphen yl (surrogate)				na	na	90%

\* Target Reporting Limits are in parts per billion (ppb); µg/L for water and ng/g (dry weight basis) for soil/sediment. "na" indicates data not available.

# 9. DOCUMENTS AND RECORDS

The critical records required for this project include field and laboratory records and technical reports. The DPR Project Leader will collect records for sample collection, field analysis, toxicity testing data, and laboratory analysis. Samples sent to the DFG Laboratory and to UCD ATL will include a Chain of Custody form. DPR will generate records for sample receipt and storage, analyses, and reporting. All records generated by this project will be stored at DPR's main office. Table 8 summarizes the document and record retention, archival and disposition minimum requirements for these studies.

Table 8. Document and record retention, archival, and disposition (Element 9).
--

	Identify Type Needed	Retention	Archival	Disposition
Sample Collection Records	Chain of Custody	Until completion and approval of final reports	5 years	Archivist may continue storage or dispose of at the end of 5 years
Field Records	Field Data Sheets	Same as above	5 years	Same as above
Analytical Records	Sample Reports	Same as above	5 years	Same as above
Toxicity Testing Records	Data Summary Report	Same as above	5 years	Same as above
Data Records	Excel Database	Same as above	Indefinitely	N/A
Assessment Records	Final Data Reports	Same as above	5 years	Archivist may continue storage or dispose of at the end of 5 years

Copies of this QAPP will be distributed to the parties involved with the project (<u>Section 3, Distribution List</u>). Any future amended QAPPs will be held and distributed in the same fashion. All originals, and subsequent amended QAPPs, will be retained by CURES. Copies of versions, other than the most current, will be discarded so as not to create confusion.

The contract laboratories will report all analytical results in the laboratory's approved format. In addition to the reported data, the laboratory data report will, at a minimum, include a narrative that will discuss any problems or discrepancies, with sufficient calibration and QC information to ensure that DPR Scientists can verify the data according to EPA guidelines for contract laboratories (EPA 1999). QC information will generally include the following:

- Chain of Custody (COC) documentation;
- Condition and temperature of samples upon receipt;
- Sample collection receipt, extraction, and analysis dates for holding time verification;
- Laboratory sample ID, field sample ID, matrix, and dilution factors;
- Final analyte concentration including reporting limit, laboratory qualifiers, and re-analyses;

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 20 of 49

- Percent recovery of surrogate samples and surrogate recovery control limits;
- Percent recovery of each compound in the MS sample and MS recovery control limits;
- RPD for all MS/MSD samples;
- Laboratory control sample (LCS) results when analyzed;
- Results for method blanks, field blanks, and spiked samples;
- Method blank and matrix spike summary indicating associated samples.

In addition to the hard-copy report requirements, the laboratory will provide electronic data deliverables (EDD) conforming to an ASCII comma-delimited or Microsoft Excel format as specified for all data reported. All electronically stored raw data is routinely backed up daily to tape. In addition, hard copies of COCs and raw data are kept for a minimum of five years.

Final data reports will be prepared containing the data collected for each study and summarizing the activities conducted to generate that data – including sample collection, storage and analysis. The reports will also include the results of the analysis of QC samples and an assessment of the overall quality of the data generated in comparison to the goals described in this QAPP.

The following persons are responsible for maintaining records of this project:

- Sheryl Gill, Project Leader, is responsible for maintaining field data sheets and field records;
- Carissa Ganapathy, DPR QA officer, is responsible for maintaining chain of custody forms and QA/QC data reported by the DFG laboratory to DPR;
- Loc Nguyen, DFG QA officer, is responsible for records associated with the receipt and analyses of samples analyzed for analytes;
- Inge Werner, director of the UCD ATL, is responsible for records associated with the toxicity testing;
- DPR computer group is responsible for maintaining tape backups of data on DPR computer drives.

# **GROUP B: DATA GENERATION AND ACQUISITION**

# **10. SAMPLING PROCESS DESIGN**

The sampling program for each study is described in their respective monitoring plans included in Appendixes A and B. Monitoring plans were written according to DPR SOP ADMN003.01 (Dias, 2007a). The water quality measurements (DO, EC, and pH) are informational; all other data collected are critical for the study.

The sites for these studies have already been determined. If they become inaccessible or unsafe another site will be may be difficult to obtain because: 1) the normal grower practice does not allow vegetation (weeds) to flourish, and 2) we have designed these studies to be conducted in the predetermined sites. Sampling personnel will notify the Project Leader of the issue and any conditions that may influence the quality of a sample collected at the site. The Project Leader will then seek permission from the CURES Project Coordinator and Regional Board Grant Manager to collect the samples at a later date.

The concentration of target pesticides will fluctuate on a temporal basis depending upon the rate at which pesticide runoff occurs, the amount of pesticide entering the subject water body, distance the pesticide has traveled from its source, the speed at which it travels and the volume of water passing by that point. Localized weather patterns may affect the rate of pesticide runoff with heavy rainfall generating faster runoff than light rain.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 21 of 49

Factors that could bias contaminant levels found in the samples include poor sampling techniques and improper cleaning of equipment as well as limited access to parts of the field. These sources of bias will be avoided through strict adherence to the methods described in Element 11 and Appendixes A and B.

# **11. SAMPLING METHODS**

The proposed sampling methods are summarized in Table 9. The relevant DPR Standard Operating Procedures (SOPs) are included in Appendix C. Field crew will be required to keep field data sheets. Field data sheets will include the following:

- Date and time of sample collection
- Sample location
- Sample identification numbers
- Results of field measurements, study 243 (water temperature, DO, EC, water pH, salinity)
- Field crew members
- Weather conditions
- Qualitative description of water conditions (study 243)

An example of the field data sheets can be found in Appendix E. Any problems that occur during the sampling process will be documented on the field data sheets. The project leader will be notified to determine the impact, if any, on the quality of the data.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 22 of 49

Table 9. Sampling locations and methods (Element 11).

Sampling Location	Matrix	Analytical Parameter	# Samples (include field duplicates)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ Analysis
Study #243 (i	in stream monito	ring)	T					
	Water (for C. dubia toxicity)	Organophosphorous	21	DPR FSWA002.00	2 liters	2, 1-L glass amber bottle	Sample stored at	7 days/48 hours after sample receipt at UCD ATL
	Water (for OP Screen)		23		1 liter	1, 1-L glass amber bottle	4 <sup>0</sup> C/ dark	7*/40 days
	Water (for PY Screen)		23	DPR FSWA002.00	1 liter	1, 1-L glass amber bottle		/ /+0 uays
Orestimba Creek	Sediment (for PY Screen)	Pyrethroids	23	מתכו	250 ml	1, 1-pint glass mason jar	- Sample stored	28 days
and Del Puerto Creek	Sediment (for <i>H. azteca</i> toxicity)		DPR   FSWA016.00   21   2 liters		2 liters	2, 1-L polyethylene container	frozen/dark	7 days/14 days after sample receipt at UCD ATL
	Water	TSS	23	DPR FSWA002.00	1 liter	1, 1-L glass amber bottle	Sample stored at 4 <sup>o</sup> C/ dark	10/40 days
Sedime	Sediment	Sediment grain size		DPR	105 1	1, 1-pint	Sample stored at 4 <sup>o</sup> C/ dark	8 months
	Scument	тос	23	FSWA016.00	125 ml	glass mason jar	Sample stored frozen/dark	6 months

\*for PYs, holding time of greater than 4 days, up to 7 days, will require chemical preservation.

# QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 23 of 49

Table 9 continued. Sampling locations and methods (Element 11).

Sampling Location	Matrix	Analytical Parameter	# Samples (include field duplicates)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation	Maximum Holding Time: Preparation/ Analysis**
Study #244 (BMP)								
	Soil Samples		24	DPR SOP FSSO002.00	250 ml	1, 1 pint mason jar	Sample stored frozen/dark	7/40 days
	Spray Tank Samples	Diazinon (OP) and Esfenvalerate (PY)	2	DPR SOP FSOT007.00	1 liter	2, 1 L poly- propylene brown bottles	Sample stored at 4 <sup>o</sup> C/ dark	7/40 days
In field monitoring	Deposition sheets		60	DPR SOP FSOT005.00	929 cm <sup>2</sup> deposition sheet	1, 40.6 x 22.9 cm deposition sheet	Sample stored on dry ice or in a freezer at < 0°C/ dark	7/40 days
	Water		264	DPR SOP FSWA008.00	1 liter	1, 1-L glass amber bottle	Sample stored at 4 <sup>o</sup> C/ dark	
	Sediment		100	DPR SOP FSWA016.00	250 ml	1, 1 pint mason jar	Sample stored frozen/dark	7/40 days
	Water	TSS	120	DPR SOP FSWA008.00	500 ml	1, 500 ml glass amber bottle	Sample stored at 4 <sup>o</sup> C/ dark	

\*\*If other OPs or PYs are chosen, the holding times may have to decrease or the sample may need to be chemically preserved.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 24 of 49

# **12. SAMPLE HANDLING AND CUSTODY**

Proper sample handling and shipment of samples are critical to ensure quality data. Components of sample custody procedures include the use of field data sheets, container/sample labels, COC forms, and check in/check out forms. DPR will collect all samples into pre-labeled containers and store them on ice for transport. Each sample will be documented on a COC form at the time of collection. The COC form will be used as a shipping record from the field, to the Environmental Monitoring Branch warehouse, and to the final destination, either DFG or UCD ATL.

The field crew will transport the samples from the field to the Environmental Monitoring Branch warehouse according to DPR SOP QAQC004.01 (see Appendix D). Briefly, the following methods will be used:

- Sample labels will at minimum contain: project number, unique sample number, and sample type. Labels will be affixed horizontally to the sample container using clear tape;
- All sample related information will be recorded in the field data sheets;
- Samples will be transported on wet ice at 4°C in ice chests;
- The field sampler will retain custody of samples until they are properly transferred;
- When samples are delivered to the lab, the sampler will relinquish custody by signing the appropriate space on the COC form. The lab attendant will accept custody by also signing the appropriate space on the chain of custody form;
- Check-in and check-out forms will also be completed for every sample (see DPR SOP QAQC003.02, Appendix D). These forms will include the following information: sample number, date sample collected, sample type, analysis type, date checked in/checked out.

The Project Leader will notify the Project QA Officer of upcoming field sampling activities and the subsequent transfer of samples to the laboratory. The Project Leader will also inform UCD ATL of upcoming field sampling activities and timeframe of sample transfer. This notification will include information concerning the number and type of samples to be shipped, analyses requested, and the expected date of arrival. The Project QA Officer will notify appropriate laboratory personnel about the expected shipment including the sample custodian.

Upon arrival at the laboratory, the samples will be received and logged in by a trained sample custodian in accordance with the laboratory's sample handling and internal sample custody program. Upon sample receipt, the sample custodian is responsible for performing the following activities, where appropriate, during sample receipt:

- Examining all sample containers for damage;
- Comparing samples received against those listed on the COC record;
- Verifying sample holding times have not been exceeded;
- Immediately signing and dating COC record after shipment is accepted;
- Noting any sample receipt problems on the COC record, initiating a Condition Upon Receipt report (CUR), and notifying the Laboratory Project Manager;
- The Laboratory Project Manager or Supervisor must notify the Project QA Officer of any problems upon receipt of the samples;
- Attaching laboratory sample container labels with laboratory identification number and test;
- Placing the samples in proper laboratory storage;
- Notifying the Laboratory Supervisor of samples received;
- Store all documentation in the project file.

The Project QA Officer is responsible for contacting the Project Leader as soon as possible if any problems are identified during sample receipt. All identified sample receiving problems will be resolved prior to sample preparation and analysis.

# 13. ANALYTICAL METHODS AND FIELD MEASUREMENTS

DPR personnel will collect field data according to SOPs (see Table 10). DPR staff will also conduct total organic carbon (TOC) analysis following the SOPs listed in Table 11, and DPR will conduct total suspended solid (TSS) measurements by vacuum infiltration of the samples and subsequent oven drying of the filtrate collected on tared, rinsed, and oven-dried filters following the method prescribed by the US EPA (1971).

Two contract labs will help in the analyses in this study. UCD ATL will conduct aquatic (*C. dubia*) and sediment (*H. azteca*) toxicity tests (SOPs in Appendix K). The California Department of Fish and Game, Fish and Wildlife Water Pollution Control Laboratory (DFG), will conduct chemical analysis of all water and sediment samples. DFG will also conduct sediment grain size and conduct analysis of the mass deposition sheets based on a SOP from the California Department of Food and Agriculture (CDFA) for detecting OPs. DFG is reviewing this method and will make modifications for detecting PYs, especially esfenvalerate and permethrin . DFG will validate the method for the analytes examined in this study and any differences or modifications will be corresponded to DPR. Analytical method SOPs indicated in Table 11 and can be found in the Appendixes. The SOPs do not indicate sample disposal; unused portions of samples are poured down the laboratory drains which are discharged to an evaporation pond. Sediment samples and any highly contaminated samples are picked up by a hazardous waste contractor. Holding and turnaround time of samples are found in <u>Table 9</u>.

There may be instances of failure, either in the laboratory or in the field; the SOPs listed in Tables 10 and 11 document the corrective action plan for field and analytical instruments. In most cases, the immediate field or laboratory personnel can correct them, and these corrections will be documented in their field or laboratory notes. However, if the problem cannot be resolved, then the immediate supervisor or project leader has the primary responsibility for responding to the failed systems and to determine if the failure compromised the sample results.

		<b>Project Action</b>	Project	Analytical Method		
Analyte	Laboratory / Organization	Limit (units, wet or dry weight)	Quantitation Limit (units, wet or dry weight)	Analytical Method/SOP	Modified for Method?	
рН	DPR Staff <i>in situ</i> field monitoring using YSI 60 pH meter	None	0.5 pH units	Appendix C (EQWA002.00)	No	
Electrical Conductivity	DPR Staff <i>in situ</i> field Monitoring using YSI 85 meter	None	0.01 mS/cm	Appendix C (EQWA004.00)	No	
Dissolved oxygen	DPR Staff <i>in situ</i> field Monitoring using YSI 85 meter	None	0.5 mg/L	Appendix C (EQWA003.00)	No	
Temperature	DPR Staff <i>in situ</i> field Monitoring using YSI 85 meter and YSI 60 meter	None	0.5°C	Appendix C (EQWA004.00)	No	

Table 10. Field analytical methods (Element 13).

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 26 of 49

Table 11. Laboratory analytical methods (Element 13).

	Laboratory /	Project Action	Project Reporting	Analytical	Method	Achievable Laboratory Limits	
Analyte	Organization	Limit (units, wet or dry weight)	Limit (units, wet or dry weight)	Analytical Method/SOP	Modified for Method?	MDLs	Method
Organophosphorous pesticides (water samples)	DFG	NA	20 – 50 ng/L	Appendix G (DFG: OP- WATER)	No	5 – 30 ng/L	GC/FPD
Pyrethroid pesticides (water samples)	DFG	NA	2 – 5 ng/L	Appendix G (DFG: PY- WATER)	No	1 – 3 ng/L	GC/ECD
Pyrethroid pesticides (sediment samples)	DFG	NA	2 - 5 ng/g	Appendix H (DFG: PY-SED)	No	1- 3 ng/g	GC/ECD
Mass Deposition Samples	DFG	NA	Target <1.0 μg/MDS	Appendix I (CDFA Method 19.4)	No	Target <1.0 μg/MDS	GC/FPD
Total Organic Carbon (TOC)	DPR	NA	5 mg/kg	DPR METH005.00 (Appendix J)	No	NA	NA
Total suspended sediments (TSS)	DPR	NA	4.0 mg/L	US EPA 160.2, 1971	No	NA	NA
Sediment grain size	DFG	NA	2 μm, smallest particle	AMS SOP 2101 (Appendix J)	No	NA	NA

Abbreviations: NA = not applicable; MDL, minimum detection limit

# 14. QUALITY CONTROL

To determine internal quality assurance and quality control (QA/QC), the scientists involved in this study will collect and analyze various QA/QC samples. To ensure field QA/QC, we will collect field duplicate samples and field blanks. To ensure laboratory QA/QC, we will analyze a series of blanks, spikes, duplicate, and spike duplicate samples.

We will use field samples to evaluate potential contamination and sampling error prior to sample delivery to the analytical laboratory. Laboratory samples evaluate the analytical process for contamination, accuracy, and reproducibility. Field quality control and laboratory control processes are listed in 14.2 and 14.3, respectively.

# 14.1 Data Quality Objectives and Quality Assurance Objectives

Data Quality Objectives (DQOs) and Quality Assurance Objectives (QAOs) are related data quality planning and evaluation tools for all field sampling and laboratory analysis activities. It is necessary to have a consistent approach for developing and using DQOs and QAOs to ensure sufficient quality data is generated so that correct decisions are made from this study.

### **Data Quality Category**

In this study, the DFG and the UCD ATL use standard US Environmental Protection Agency (US EPA 2001, US EPA 2002a) or other reference methods approved by the Regional Board. Data are analyte-specific. These methods have standardized QC and documentation requirements, providing supporting information necessary to verify all reported results.

# **Quality Assurance Objectives**

Quality assurance objectives are the detailed QC specifications for precision, accuracy, representativeness, comparability and completeness (PARC). The QAOs presented in this QAPP represent the minimum acceptable specifications that should be considered routinely for field and analytical procedures. The QAOs are then used as comparison criteria during data quality review by the Regional Board to determine if the minimum requirements have been met and the data may be used as planned.

This section presents the QC checks that will be performed during field investigations and laboratory samples, including a discussion of frequency, acceptance criteria, and corrective action procedures. The lab will report the QC results to the DPR QA officer (Chemistry Laboratory Quality Control-SOP QAQC001.00, see Appendix F) on a continuous basis. The DPR QA Officer will review, summarize and submit the data to the project leader. If after being reviewed, a set of data is determined to be out of control, the DPR QA officer will notify the project leader and an appropriate course of corrective action will be prescribed.

The analyst or field scientist shall enter the corrective measures taken in the notebook, which will then be signed by the supervisor or QA officer. No additional analytical data will be generated until the problem has been identified and corrected.

# 14.2 Field Quality Control (QAOs)

Field QC samples are used to assess accuracy and precision of sampling procedures and equipment used in sampling. For these studies, we will collect grab samples where no equipment is used. Therefore, field QC samples will consist of field blanks but not equipment blanks. Field QC will also include field duplicate samples. Field staff will collect these QA samples equally among all sites and collection timings. The frequency and acceptance limits of field quality control samples for this project are summarized in <u>Table 12</u>.

#### 14.2.1 Field Blanks

Field blanks demonstrate that sampling procedures do not result in contamination of the environmental samples, ensuring accuracy of the data. Field blanks will consist of distilled water directly poured from a main container into sample bottles (per SOP QAQC011.00; see Appendix C). If any analytes of interest are detected at levels greater than the Reporting Limit (see <u>Table 7</u>) for the parameter, the DPR QA officer will notify the field sampling

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 28 of 49

crew so that the source of contamination can be identified (if possible) and corrective measures taken prior to the next sampling event. If the concentration in the associated samples is less than five times the value in the field blank, the results for the environmental samples may be unacceptably affected by contamination and should be qualified as below detection at the reported value.

# 14.2.2 Field Duplicate Samples

Field duplicates demonstrate the precision of the field sampling and analytical processes. The field staff will prepare field duplicates and the laboratory will analyze the duplicates along with the associated environmental samples. Field duplicates will consist of two aliquots from the same composite sample, or of two grab samples collected in rapid succession. If an RPD of greater than 25% is obtained, the duplicate samples will be reanalyzed. If an RPD greater than 25% is confirmed by reanalysis, environmental results will be qualified as estimated. The sampling crew should be notified so that the source of sampling variability can be identified (if possible) and corrective measures taken prior to the next sampling event.

# 14.3 Laboratory Quality Control (QAOs)

All laboratories will have the latest revision of the SWAMP QAMP. In addition, the following documents and information will be current and available:

- Laboratory QA Plan: Clearly defined policies and protocols specific to a particular laboratory, including personnel responsibilities, laboratory acceptance criteria and corrective actions to be applied to the affected analytical batches, qualification of data, and procedures for determining the acceptability of results.
- Laboratory Standard Operating Procedures (SOPs): Containing instructions for performing routine laboratory procedures.
- Laboratory Analytical Methods Manual: Step-by-step instructions describing exactly how a method is implemented in the laboratory for a particular analytical procedure. Contains all analytical methods utilized in the particular laboratory.
- Instrument Performance Information: Information on instrument baseline noise, calibration standard response, analytical precision and bias data, detection limits, etc. This information is usually recorded in logbooks or laboratory notebooks.

# 14.3.1 Laboratory (C. dubia and H. azteca) Toxicity Testing

All UCD ATL procedures follow a stringent QA/QC plan approved by the contract laboratory manager and consistent with the US EPA QA guidelines and the QAMP established for the SWAMP program. Laboratory QC during toxicity testing is necessary to ensure that the results from these tests are precise and accurate. UCD ATL personnel will assess laboratory precision and accuracy by using field duplicates, field blanks, laboratory controls, and positive reference toxicant tests (see <u>Table 13</u>). Specific QA/QC followed by UCD ATL is found in Appendix K. Briefly, these methods are described below.

Field blanks consist of analyte-free control water (Sierra Springs<sup>TM</sup> EPA moderately hard water amended to EPA moderately hard standards) prepared in the laboratory or analyte-free sediment. These bottles are transported to the field where the analyte-free matrix is transferred into a clean sampling bottle (provided by DPR field staff). We will collect one field blank during the first sampling period. Field duplicate samples will consist of two grab samples taken simultaneously or in rapid succession.

Laboratory controls are treatment vials containing pesticide free test matrix to which test organisms are added. This negative control determines if the invertebrates in the respective test are growing and responding normally. Positive reference toxicant tests are used to determine if a species are responding typically. These tests are conducted at the UCD ATL with known concentrations of an internal standard compound, usually NaCl. Using an internal standard gives a positive control, and allows interpretation of the data across tests.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 29 of 49

# 14.3.2 Laboratory Chemical Analyses

Laboratory QC is necessary to assess the accuracy and precision of analytical results. For water quality analyses, QC samples prepared in the contract laboratory will typically consist of method blanks, laboratory fortified control samples (LCS), laboratory duplicate samples, surrogates, blind spike samples, and matrix spikes and matrix spike duplicates (MS/MSD). The frequency and acceptance limits of laboratory quality control samples for this project are listed in <u>Table 14</u>.

# Method Blanks

Method blanks demonstrate that the analytical procedures do not result in sample contamination. The contract laboratory will prepare and analyze method blanks at a rate of at least one for each analytical batch. Method blanks will consist of deionized water processed along with the batch of environmental samples. If the result for a method blank is greater than the acceptance limits (Table 14), the source(s) of contamination should be corrected and the associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as below detection at the reported blank value.

#### Instrument Blanks

Instrument blanks demonstrate accuracy of the analytical analyses (i.e., that there is no contamination due to the instrumentation). Instrument blanks will consist of deionized water processed through the analytical instruments. If the result for an instrument blank is greater than the acceptance limits, the source of the contamination should be found and corrected, and the associated samples reanalyzed.

# Laboratory Fortified Control Samples (LCS)

The purpose of analyzing laboratory control samples is to demonstrate the accuracy of the analytical method. Laboratory control samples will consist of laboratory fortified (spiked) method blanks. The analytical chemists spikes (fortifies) the method blank with a known concentration of an analyte or several analytes. If recovery of any analyte is outside the acceptable range, the analytical process is not being performed adequately for that analyte. In this case, if the blind spike samples and the matrix spikes are also outside the acceptable range, the LCS and associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as biased low or high.

# Laboratory Duplicate Samples

Laboratory duplicate samples demonstrate precision of the analytical method. Laboratory duplicate samples consist of an extraction of a second LCS and subsequent analyses. If the RPD for the analyte in the laboratory duplicate sample and the LCS is greater than the <u>precision criteria</u> the analytical process is not being performed adequately for that analyte. In this case, the laboratory duplicate should be reanalyzed. If reanalysis is not possible, the associated sample results should be quantified as not reproducible due to analytical variability.

# Surrogate Samples

Surrogate samples are used to determine the accuracy of analytical procedures. Surrogate samples are samples that are spiked with a pure compound (i.e., triphenyl phosphate for OPs, dibromooctafluorobiphenyl for pyrethroids) just prior to processing. All samples, including the QA samples, will be spiked with surrogates.

# **Blind Spike Samples**

Blind spike samples, used to determine accuracy, are blank matrix water samples that are spiked (fortified) with a known concentration of analyte(s). However, these samples are different from LCS because they are spiked by a chemist other than the chemist performing the analysis. Blind spike samples, unknown to the analytical chemist, are then disguised as field samples and submitted by the QA officer with the field samples.

If recovery of any analyte in the blind spike is outside the acceptable range for accuracy (see Table 14), the analytical process is not being performed adequately for that analyte. The QA officer is to immediately contact the lab supervisor or lab QA officer. The source of the error needs to be determined by checking fortification calculations, standards and replicate spikes if they exist. If the matrix spikes are also outside the acceptable range, the associated samples and QA samples should be reanalyzed. If source of error is not determined and reanalysis is not possible, the associated sample results should be qualified as biased low or high.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 30 of 49

### Matrix Spikes and Matrix Spike Duplicates

Matrix spikes and matrix spike duplicates (MS/MSD) demonstrate the performance of the analytical method in a particular sample matrix, both for accuracy and precision. In this study, we will provide the lab with American River water and delta background sediment.

A MS/MSD consists of the environmental matrix fortified with a known concentration of an analyte. This is much like a <u>LCS</u>, but the environmental matrix (analyte-free river water or analyte-free sediment) is used in the place of deionized water. Approximately five percent of all the samples will be MS/MSD samples.

If the matrix spike (MS) recovery of any analyte is outside the acceptable range, there may be a problem analyzing the analyte in the presence of that particular matrix. If recovery of the LCS is acceptable, then the analytical process is being performed accurately for that analyte and the problem may be (but is not always) attributable to the sample matrix. An attempt will be made to correct the problem (by dilution) and then re-analyzing the samples and the matrix spikes. If the matrix problem cannot be corrected, we will qualify the results for that analyte as appropriate (low or high biased) due to matrix interference.

If the matrix spike duplicate (MSD) RPD for any analyte is greater than the precision criterion, the results for that analyte will have failed the precision acceptance criteria. If the RPD for <u>laboratory duplicates</u> is acceptable, the analytical process is being performed adequately for that analyte, and the problem may be attributable to the sample matrix. An attempt will be made to correct the problem (by dilution, concentration, etc.) and then re-analyzing the samples and the matrix spike duplicates. If the matrix is found to be the problem and cannot be corrected, we will qualify the results for that analyte as not reproducible due to matrix interference. Since reasons for precision and accuracy failure vary greatly, we will rely upon the laboratory supervisor and chemist's expertise to characterize the problems and to document the reasons for the Project QA Officer.

Table 12. Field QC samples (Element 14).

Type of QC Sample	Approximate Frequency	Acceptance Criteria
Field blanks	5% of samples	< RL
Field duplicate samples	5% of samples	RPD < 25%

Table 13. Laboratory toxicity (C. dubia and H. azteca) testing QC samples (Element 14).
See Appendix K for expanded details.

Laboratory QC	Approximate	Acceptance Limits		
	Frequency/Number	C. dubia	H. azteca	
Field Duplicate Samples	5% (One per study)	RPD < 25%	RPD < 25%	
Field Blank Samples	5% (One at the start of the study)	90% survival in	80% survival and measurable growth in	
Laboratory Controls	Each test	controls	controls	
Reference toxicant tests	Monthly for <i>C. dubia</i> ; Two per study for <i>H. azteca</i>	<u>+</u> 2 standard deviations around UCD ATL running mean		

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 31 of 49

# 14.3.3 Laboratory Analyses for grain size, TSS, and TOC

Laboratory QC is applied to grain size, TSS, and TOC to ensure precision and accuracy of the data. If the criteria are not met (<u>Table 15</u>) the QA officer will work with laboratory personnel to identify and eliminate sources of contamination. After corrections, data may need to be reanalyzed.

Laboratory QC	Approximate Frequency/Number	Acceptance Limits
Method blank	1 per extraction batch or 1 per 20 samples, whichever is more frequent	<rl< td=""></rl<>
Instrument blank	$\leq 12$ hours of instrument operation	<rl< td=""></rl<>
Laboratory fortified (spiked) control sample	1 per extraction batch	70 – 130%
Laboratory duplicate samples	5% of LCS	≤25% RPD
Surrogate samples	In all samples and QC	50-150%
Blind spike samples <sup>1</sup>	5%	Based on the widest, $70 - 130\%$ or $\pm 3$ standard deviations based on actual lab data
Matrix spike	5% (1 pair per extraction set or	$\pm 3$ standard deviations based on actual lab data
Matrix spike duplicate	per 20 samples, whichever is more frequent)	<u>≤</u> 25% RPD

Table 14. Laboratory QC samples (Element 14).

<sup>1</sup>For water samples only. No blind spikes for sediment samples.

Table 15. Grain size, TSS, and TOC QC samples (Element 14).

Type of QC Sample	Approximate Frequency	Acceptance Criteria
Method blanks	One per batch	< RL
Replicate samples	One per batch or 5%	RPD < 25%
Laboratory Reference Material	One per batch or 5%	Within 95% CI of the certified value

# 15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

The testing, inspection and maintenance of laboratory and field equipment is documented in Table 16. Ultimately, the project leader is responsible for the inspection, maintenance and documentation of field equipment and the analytical laboratory supervisor is likewise responsible for the laboratory equipment.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 32 of 49

# **15.1 Field Instrument/Equipment**

Field measurement equipment will be checked for operation in accordance with the manufacturer's specifications. Equipment will be inspected when first handed out and when returned from use for damage. Spare parts, including batteries, additional bolts, nuts, washers and other hardware for sampling equipment, should be taken into the field to be used during sampling to make repairs if needed. Spare parts will be kept in the study box which is taken to the field so that it will be available for use by the field staff. Additional spare parts are kept in the laboratory at the West Sacramento facilities. The equipment should be maintained in accordance with its SOPs, which include procedures specified by the manufacturer and those specified by the method. The field staff is responsible for ensuring that all instrumentation is operating properly prior to use. If problems are encountered, they will be documented in the field data sheets. The faulty instrumentation/equipment will be scheduled for repair and sequestered and tagged until repaired and qualified for re-use. Extra water quality meters are available for use in the West Sacramento laboratory.

# 15.2 Laboratory (C. dubia and H. azteca) Toxicity Testing

Laboratory instruments and equipment, and growth chambers or growth rooms will be checked for operation in accordance with manufacture's or SOP specifications. The equipment should be maintained in accordance with the laboratory's SOPs, which include procedures specified by the manufacturer and those specified by the method. The laboratory staff is responsible for ensuring that all instrumentation is operating properly prior to use. If problems are encountered, they will be documented in the equipment maintenance logs and not used until it is repaired and qualified for re-use.

# 15.3 Laboratory Instrument/Equipment

Laboratory instrument/equipment testing, inspection, and maintenance will be conducted in accordance with the procedures specified in the laboratory's QA Manual. The manual discusses the schedule, procedures, criteria, and documentation in place at the laboratory to prevent instrument and equipment failure and to minimize downtime. For each instrument or piece of equipment the laboratory maintains the following:

- Instrument/equipment inventory list;
- Instrument/equipment major spare parts list or inventory;
- External vendor service agreements (if applicable);
- Instrument-specific preventive maintenance logbook or file.

The laboratory documents all preventive maintenance for a piece of equipment in dedicated logbooks or files. Minor/inexpensive spare parts are kept in the laboratory for the chemists use. Major/expensive spare parts for equipment are purchased as necessary to repair equipment. Backup equipment is available to conduct analysis until arrival of ordered parts.

# 16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Field staff will calibrate field equipment used during the course of this study on a regular basis. Proper maintenance, calibration, and operation of each instrument will be the responsibility of field personnel assigned to a particular field activity. In addition, relevant manuals will be kept with field personnel during the performance of field activities and all equipment will receive routine maintenance checks to minimize equipment breakdown in the field. Any items found to be inoperable will be taken out of use and a note stating the time and date of this action will be made in the daily field records. An equipment calibration daily log form for selected equipment is provided in Appendix E. See Table 17 for a summary of the calibration requirements for field equipment.

Laboratory personnel maintain specific calibration practices as part of the lab SOPs. All instruments and equipment used during the field investigations will be maintained, calibrated, and operated according to the manufacturer's guidelines and recommendations, and lab SOPs. All laboratory equipment and instruments specific to each analysis are included in method-specific SOPs that are included in Appendixes G, H, I, J and L. See Table 17 for a summary of the calibration requirements for laboratory equipment.

Equipment / Instrument	Maintenance Activity, Testing Activity or Inspection Activity	Responsible Person	Frequency	SOP Reference
YSI 85 Oxygen, Conductivity, Salinity & Temperature Meter	Verify accuracy. If accuracy check fails, check and use back-up meter	Field Staff	Prior to daily use	EQWA003.00 EQWA004.00
YSI 60 pH Meter	Verify accuracy. Rinse probes prior to use.	Field Staff	Prior to daily use	EQWA002.00
Dohrmann DC-85A TOC Analyzer	Inspect Teflon tubing, acid trap, mist trap, and gas scrubber	Laboratory Staff	Prior to use	METH005.00
Agilent 6890 GC- ECD	Replace injector septum, insert, clip column	Laboratory Staff	Injector septum- weekly, Insert-2 months or as needed	Follow manufacturer's maintenance schedule
Agilent 6890 GC- FPD	Replace injector septum, insert, clip column	Laboratory Staff	Injector septum- weekly, Insert-2 months or as needed	Follow manufacturer's maintenance schedule
Varian Saturn 2000 GC-MS	Replace injector septum, insert, clip column, clean trap electrodes/source	Laboratory Staff	Injector septum- weekly, Insert-2 months or as needed Clean trap electrodes/source -3 months or as needed	Follow manufacturer's maintenance schedule

Table 16	Tastina	in an a sti an	and maintananas	of a a man line a		and analatical	in atomatica anata 1	$(\mathbf{E})$ and $(\mathbf{E})$
	Testing	inspection	, and maintenance	or sampling	eaunnmeni	and anaiviicai	instruments (	Element 151
10010 10.	1.00000	,	,	or sampring	, • • • • • • • • • • • • • • • • • • •			

Whenever possible, the laboratory uses recognized procedures for calibration, such as those published by U.S. EPA or ASTM. Equipment or instruments that fail calibration or become inoperable during use are tagged to indicate they are out of calibration and the problem summarized in the instrument-specific logbook or file (see Section 15.2). Such instruments or equipment are repaired and successfully recalibrated prior to reuse.

Equipment / Instrument	SOP reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
YSI 85 Oxygen, Conductivity, Salinity & Temperature Meter	EQWA003.00 EQWA004.00	Calibrate for DO per SOP.	Prior to each sampling event	Field staff
YSI 60 pH Meter	EQWA002.00	Calibrate pH meter with appropriate buffers for pH of measured water	Prior to each sampling event	Field staff
Dohrmann DC-85A TOC Analyzer	METH005.00	Calibrate according to section 3.0 in SOP; run a minimum of four injections of KHP	Prior to sampling event	Laboratory staff
Agilent 6890 GC-ECD	DPR: PY-Water	Recalibrate pyrethroid curves and analyze samples in external standard mode.	Beginning of each analytical run	Laboratory staff
Agilent 6890 GC- FPD	DPR: OP - Water	Recalibrate OP curves and analyze samples in external standard mode	Beginning of each analytical run	Laboratory staff
Varian Saturn 2000 GC-MS	DPR: PY-Water DPR: OP - Water	Recalibrate pyrethroid curves and OP curves and analyze samples in external standard mode.	Beginning of each analytical run	Laboratory staff

Table 17. Calibration of sampling equipment and analytical instruments (Element 16).

# 17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Supplies and consumables that may be used during field investigations include sample bottles, hoses, materials for decontamination activities, deionized or distilled water, potable water, and the like. Project team members obtaining supplies and consumables are responsible for assuring that the materials obtained are intact and in good condition, are available in adequate supply, and are stored appropriately until use. Project team members will reject these supplies and consumables if they observe any obvious signs of contamination (torn packages, etc.). Project team members will direct any questions or identification of any problems regarding supplies and consumables to the Project Leader for resolution.

Laboratory personnel will demonstrate that solvents, reagents, and other materials used in sample analysis by the laboratories are free from interferences or contamination by conducting method blanks initially and periodically with each sample lot. Inspection protocols and acceptance criteria for laboratory analytical reagents and other consumables are documented in the DFG laboratory QA Program Plan (Appendix L).

The supervisor of the toxicity lab will be responsible for acquiring, growing, and inspecting test organisms. The supervisor of the toxicity lab will also be responsible for ordering and inspecting supplies used in the laboratory toxicity testing.

# 18. NON-DIRECT MEASUREMENTS (EXISTING DATA)

The only non-direct data used in this study will be stream flow discharge from USGS as described in Element 6. USGS data is provisional until quality of the data is verified by the USGS. Data are reviewed periodically to ensure accuracy of the data. Verified data is published usually within six months of the end of the year. We will only use verified USGS data for this report (Carter and Davidson, 1968; Wahl et.al., 1995). Any USGS data that has not been verified prior to the deadlines of our report writing will be flagged as provisional data. According to USGS quality guidelines, any decisions that come from using provisional data must be subject to review after the data has been verified by the USGS.

We do not anticipate the using any other non-direct measured data for this project as this data may be of unknown quality. Historical reports may be cited, but only as reference as the data quality objectives for these studies may be different from this program.

# **19. DATA MANAGEMENT**

The objective of data management is to ensure that all data is properly collected and stored; in essence, not lost misplaced, or improperly transferred during the course of the study. All data will be maintained as described in <u>Element 9</u> and below.

The Project Leader is ultimately responsible for proper field data collection, data accumulation, and data storage. Specifically, to ensure proper data management, the Project Leader will ensure the following are completed:

- Project documents are copied (e.g., field data sheets, field logs, chain of custody forms, lab reports);
- Toxicity and chemical data are analyzed according to the specified procedures mentioned in this QAPP for data quality, and that this data is entered into EXCEL spreadsheets;
- Field data sheets are collected and the data entered into EXCEL spreadsheets;
- All data entered into EXCEL is verified, properly coded, and inspected for data transcription errors and corrected as appropriate;
- Flow rate data from USGS Gauge Stations is retrieved and stored;
- Data from contract laboratories is reviewed for completeness and accuracy;
- Contract laboratories have retained copies of data and reports sent to the Project Leader;
- Project files are maintained.

Data will be formatted (EXCEL) so that it can be uploaded into the SWAMP database ("SWAMP compatible"). For this, all QC data will be compared with SWAMP QA criteria and any data out of compliance will be flagged with the appropriate SWAMP data qualifier(s). All required fields will be completed and all data entries will comply with SWAMP business rules. However, we may not enter data from study 244 into the SWAMP database, as it is an "edge of field" study and not a typical surface water study. After uploading and checking the data, we will electronically transfer the data files to SWAMP Data Management Team, who will review the data prior to uploading the data into the SWAMP database.

The Project Leader will establish a project file for the storage of original data, historical data, written documents, and data collected or generated during this work. The format for the file may include the following categories:

- Correspondence
- Contracts
- Figures and Maps
- Laboratory Data and QA/QC Documents
- Photographs
- Schedules

- Budgets
- Field Data
- Permits
- Chains of Custody
- Reports

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 36 of 49

Original documents will be maintained in the project file. All materials will be dated, carry the initials of the person responsible for the preparation of the document, and bear the project number. The Project Leader maintains overall responsibility for the project files and assures that appropriate documents are filed.

# **GROUP C:** Assessment and Oversight

# 20. Assessments & Response Actions

Measurement data must be consistently assessed and documented to determine whether project QAOs have been met and to identify potential limitations on data use. In these studies, we will assess the field sampling procedures and the laboratory generated data from field sampling.

*Field Sampling.* At each sampling date, the Project Leader will assess the field procedures. Any corrective action will be carried out by the field sampling crew and reported to the QA Officer. In addition, the Project QA Officer or other designated members of the project team (where appropriate) will assess the field operations. The QA Officer will evaluate the field staff's sampling procedures to determine that: 1) sampling operations are being conducted in accordance with the respective monitoring plan and this QAPP, and 2) sample labels, field data sheets, field measurements, and COC records are complete and accurate. Audits may be unannounced. The QA Officer will report the results to the Project Leader; any necessary corrective actions will be taken.

*Laboratory Analysis.* The contract laboratories are responsible for properly following procedures and operating the analytical systems within the statistical control limits. These procedures include proper instrument maintenance, calibration of the instruments, and the running the laboratory QC sample analyses at the required frequency (e.g., method blanks, laboratory control samples, etc.). The contract laboratories will report associated QC sample results with the sample results so the project staff can evaluate the analytical process performance.

All analytical data will be supported by a data package. The data package contains the supporting QC data for the associated field samples. Data verification documentation will include the following information:

- A completed data review worksheet;
- A comprehensive narrative detailing all QC exceedances, explaining qualifications of data results. In cases where data are qualified due to quantifiable QC exceedances, the bias (high or low) will be identified;
- Data summary tables in tabular format reporting all data results with the qualifiers that were added during the data validation review. These tables will include sample ID, laboratory ID, date sampled, sample type (e.g., field duplicate, field blank), units, concentration of analytes, and validation qualifiers;
- Resubmittal requests sent to the laboratory indicating missing information, verification of analytical information, etc.

The contract laboratories have ongoing internal audit programs to monitor the adherence of policies, procedures, and standards. Internal audit programs typically include systems audits, performance evaluations, data audits, and spot assessments. Laboratory personnel who are independent of the area(s) being evaluated conduct internal audits. The laboratory also participates in external audits conducted by regulatory agencies and other clients.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 37 of 49

Assessment Activities. DPR scientists will have frequent and regular contact with the contract laboratories when the water and sediment samples are being analyzed. Frequent communication will allow for assessment of the DQOs and will promptly identify any problems requiring corrective actions early on in the study. All project data will be reviewed; the 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 qualifiers flags to the data as necessary to reflect limitations identified by the process;
- Calculating completeness by matrix and analyte;
- Identified problems reported to the Project Leader, with appropriate recommendations for corrective action;
- Assign data qualifier flags as needed, based on the established QC criteria;

*Corrective Actions.* During the course of sample collection and analysis in this study, DPR staff, the laboratory supervisors and analysts, QA officers, and contractor project supervisor and team members will ensure that all measurements and procedures are followed as specified in this QAPP, and measurements meet the prescribed and acceptance criteria. If a problem arises, prompt action to correct the immediate problem and identify its root causes is imperative. Any related systematic problems must also be identified. The Project QA officer has the power to halt all sampling and laboratory work if the deviations noted are considered detrimental to data quality.

Problems about analytical data quality that require corrective action are documented in the laboratories' QA/QC Guidance. Problems about field data quality that may require corrective action are documented in the field data sheets.

### **21. REPORTS TO MANAGEMENT**

DPR will prepare a final technical report after conducting data validation. The report will follow the format described in DPR SOP ADMN007.00. The elements described below will be addressed and included in the report:

- Description of the project including the number of samples, analyses, completeness and any significant problems or occurrences that influence data use.
- The QA/QC activities performed during this project.
- QC sample results, type and number of samples including the results that did not meet the project objectives, and the impact on usability.
- Tables of analytical results.

Data summary and final reports will be issued by DPR according to Table 18.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 38 of 49

Table 18. (Element 21) QA management reports.

Type of Report	Frequency (daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Dates(s)	Person(s) Responsible for Report Preparation	Report Recipients
Statistical Analysis of lab QC's	once	06/30/2008	Carissa Ganapathy	DPR Project Leader
Draft of final report	once	08/01/08	Sheryl Gill	SWRCB Grant Manager, CURES Contract Manager
Final technical report	once	09/30/2008	Sheryl Gill	SWRCB Grant Manager, CURES Contract Manager

# **GROUP D: DATA VALIDATION AND USABILITY**

### 22. DATA REVIEW, VERIFICATION, AND VALIDATION

Data verification is the process of reviewing data and accepting, qualifying, or rejecting data on the basis of sound criteria using established EPA guidelines. To verify the data, we will systematically review the analytical results and associated QC methods (i.e., the DQOs cited in Element 7 and the QA/QC practices cited in Elements 13, 14, 15, and 16). We will separate the data into three categories:

- 1. Data meeting all data quality objectives;
- 2. Data meeting failing precision criteria;
- 3. Data failing to meet accuracy criteria.

We will report data from category 1 as useable without qualification. Data in category 3 is of poor quality and we will not use or report it. Data in category 2 is of suspect and we will assess all aspects of it. If we find sufficient evidence supporting data quality, we will move the data into the first category. However, we will flag the data with a "J" (see Table 19), meaning that the results are an estimated value, but still considered valid data.

Data meeting all data quality objectives but with failures of QA/QC will be set aside until the impact of the failure on data quality is determined. Once determined, we will move the data into either the first or third category.

In cases where field blank results exceed the acceptance criteria, we will qualify and report the data according to the descriptions below:

- If the measured field sample concentrations are greater or equal to five times the field blank, we will report the data with no qualifications;
- If the measured field sample concentrations are less than five times the field blank level, we will qualify the data as "less than" the measured value (e.g., if a field blank is equal to 1.0  $\mu$ g/L, a measured field concentration of 4  $\mu$ g/L would be reported as < 4.0  $\mu$ g/L);
- Any data qualifications resulting form QC analyses will be reported with the field data as appropriate.

The results of the data verification and any corrective actions implemented are recorded on a QA/QC worksheet. The data reviewer will initial and date the QA/QC worksheet. The Project Leader will provide secondary review of the QA/QC worksheet and will also initial and date the QA/QC worksheet. The initialed and dated QA/QC worksheet will be attached to the final analytical laboratory report that is retained in the project files.

### 23. VERIFICATION AND VALIDATION METHODS

Contract laboratories QA Officers will use this QAPP for validating the data generated by the laboratory. The QA Officers will ensure that the analytical methods have been performed according to the method prescribed and to the project specifications, and that the results have been correctly calculated and reported. The DFG laboratory will conduct data validation prior to submitting the data to DPR. Specific items that are to be reviewed during data validation are:

- Chain of custody records, sample temperatures, holding times;
- 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.

Table 19. Definitions of data qualifier (Element 22).

Qualifier	Explanation of Qualifier		
Organic Analyses <sup>1</sup>			
U	The compound was analyzed for, but was not detected above the reported sample quantitation limit.		
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.		
N	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification".		
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.		
UJ	The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.		
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.		
Inorganic Analyses <sup>2</sup>			
U	The analyte was analyzed for, but was not detected above the reported sample quantitation limit.		
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.		
J+	The result is an estimated quantity, but the result may be biased high.		
J-	The result is an estimated quantity, but the result may be biased low.		
UJ	The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.		
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting Quality Control (QC) criteria. The analyte may or may not be present in the sample.		

<sup>1</sup>US EPA, 1999.

<sup>2</sup>US EPA, 2002b.

QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 41 of 49

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

The analytical process includes verification or a QA review of the data. This includes:

- Verifying the calibration samples for compliance with the laboratory and project criteria;
- Verifying that the batch QC were analyzed at a proper frequency and the results were within specifications;
- Comparing the raw data (e.g. chromatogram) with reported concentration for accuracy and consistency;
- Verifying that the holding times were met and that the reporting units and quantitation limits are correct;
- Determining whether corrective action was performed and control was re-established and documented prior to reanalysis of QC or project samples;
- Verifying that all project and QC sample results were properly reported and flagged
- Preparing batch narratives that adequately identify and discuss any problems encountered.

Specific Quality Control procedures are documented in the laboratory quality assurance manual (Appendixes K, L). After the data have been reviewed and verified, the laboratory reports are signed for release and distributions. Raw data and supporting documentation is stored in confidential files by laboratory document control.

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

### 24. RECONCILIATION WITH USER REQUIREMENTS

The final activity of the data verification process is to assess whether the data meets the DQOs. The Project Leader will assess the usability of the verified data by comparing the data to the verification criteria and DQOs. From this assessment, the Project Leader will provide an overall summary of data quality. Data quality will be defined as acceptable or as uncceptable. Data may be classified as unacceptable due to problems with accuracy, precision, sensitivity, completeness, or representativeness. The Project Leader will also give clear guidance to any of the data that have been qualified as estimated (J qualifier).

Because of cumulative effects of QC exceedances, some specific results may be determined to be unusable. Alternatively, based upon the EPA guidelines and best professional judgment, specific results may be determined to be usable for DQOs when they are not significantly outside the QC criteria.

If the data are sufficient to achieve project objectives, the Project Leader will release the data and work can proceed. If the data are insufficient, corrective action will be required.

We will put the data from both studies into "SWAMP comparable" format. Data from study 243 will be made available directly for upload into the SWAMP database. However, currently we do not plan to upload data from study 244 into the SWAMP database, as it is an "edge-of-field" study. If a future decision is made to include this information, the data will be properly formatted for upload.

### **25.** LITERATURE CITED

California EPA, State Water Resources Control Board. 2002. CWA Section 303(d) List. Accessed on July 24, 2007 at <u>http://www.swrcb.ca.gov/tmdl/303d\_lists.html</u>

California EPA, Central Valley Regional Water Quality Control Board, 2005. Amendments to the Water Quality Control Plan for the Sacramento and San Joaquin River Basins for the Control of Diazinon and Chlorpyrifos Runoff into the Lower San Joaquin River, Final Staff Report, October. Accessed on June 21, 2007 at www.swrcb.ca.gov/rwqcb5/programs/tmdl/sjrop/final-staff-report/staff-report.pdf

Carter, R.W. and J. Davidson. 1968. General procedures for gaging streams. U.S. Geological Survey Techniques Water Resources Investigations, Book 3, A6, 13 p. Accessed on September 27, 2007 at <a href="http://pubs.usgs.gov/twri/twri3-A6/pdf/twri3-A6">http://pubs.usgs.gov/twri/twri3-A6</a>, A6, 13 p. Accessed on September 27, 2007 at <a href="http://pubs.usgs.gov/twri/twri3-A6/pdf/twri3-A6">http://pubs.usgs.gov/twri/twri3-A6</a>, A6, 13 p. Accessed on September 27, 2007 at

Dias, J. 2007a. CA DPR SOP number ADMN003.01: Preparing and Approving Protocols. Accessed on August 22, 2007 at <u>http://www.cdpr.ca.gov/docs/empm/pubs/sop.htm</u>

Dias, J. 2007b. CA DPR SOP ADMN007.00: Preparing and Approving Study Memoranda and Reports. Accessed on August 22, 2007 at <u>http://www.cdpr.ca.gov/docs/empm/pubs/sop.htm</u>

Nichol, G. and E. Reyes, 2004. Surface Water Ambient Monitoring Program (SWAMP). Electronic Template for SWAMP-Compatible Quality Assurance Project Plans. Accessed on August 7, 2007 at <a href="http://www.swrcb.ca.gov/swamp/gapp.html">http://www.swrcb.ca.gov/swamp/gapp.html</a>

Puckett, M. 2002. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program (SWAMP). Prepared for California State Water Resources Control Board, Division of Water Quality, Sacramento, CA. First version, December 2002. Accessed on June 21, 2007 at http://www.waterboards.ca.gov/swamp/docs/swamp\_qapp.doc

U.S. Environmental Protection Agency, 1971. National Exposure Research Laboratory (NERL), Microbiological and Chemical Exposure Assessment Research Division (MCEARD). Method 160.2, Residue, Non-Filterable (Gravimetric, Dried at 103 – 105° C). Accessed on June 21, 2007 at http://web1.er.usgs.gov/nemi/method\_summary.jsp?param\_method\_id=5213

U. S. Environmental Protection Agency, 1999. Contract Laboratory Program National Functional Guidelines for Organic Data Review, OSWER 9240.1-05A-P, PB99-963506, EPA 540/R-99-008. Accessed on June 21, 2007 at <a href="http://www.epa.gov/superfund/programs/clp/download/fgorg.pdf">http://www.epa.gov/superfund/programs/clp/download/fgorg.pdf</a>

U.S. Environmental Protection Agency, 2001, EPA Requirements for Quality Assurance Project Plans, EPA QAA/R-5, EPA/240/B-01/003, March. Accessed on June 21, 2007 at <u>http://www.epa.gov/quality/qs-docs/r5-final.pdf</u>

U.S. Environmental Protection Agency, 2002a, EPA Guidance for Quality Assurance Project Plans, EPA QA/G-5, EPA/240/R-02/009. Accessed on June 21, 2007 at <u>http://www.epa.gov/quality/qs-docs/g5-final.pdf</u>

U. S. Environmental Protection Agency, 2002b. Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, OSWER 9240.1-35, EPA 540-R-01-008. Accessed on June 21, 2007 at <a href="http://www.epa.gov/superfund/programs/clp/download/inorgfg10-08-04.pdf">http://www.epa.gov/superfund/programs/clp/download/inorgfg10-08-04.pdf</a>

Wahl, K.L., Thomas, W.O., Jr., and Hirsch, R.M., 1995 The stream-gaging program of the U.S. Geological Survey: U.S. Geological Survey Circular 1123, 22 p. Accessed on September 27 at <a href="http://pubs.usgs.gov/circ/circ1123/">http://pubs.usgs.gov/circ/circ1123/</a>

Study #243 and Study #244 California Department of Pesticide Regulation Environmental Monitoring Branch 1001 I Street, Sacramento, CA 95812 QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 43 of 49

### Appendix A. Study #243 Monitoring Plan

Study 243 Monitoring Plan: http://www.cdpr.ca.gov/docs/emon/surfwtr/protocols/study243protocol.pdf

### Appendix B. Study #244 Monitoring Plan

Study 243 Monitoring Plan: http://www.cdpr.ca.gov/docs/emon/surfwtr/protocols/study244protocol.pdf

### Appendix C. DPR Standard Operating Procedures

All DPR protocol information can be found at: http://www.cdpr.ca.gov/docs/emon/pubs/sop.htm

EQWA002.00 (SOP for pH meter) http://www.cdpr.ca.gov/docs/emon/pubs/sops/eqwa002.pdf	FSOT007.00 (SOP for sampling pesticide application equipment) http://www.cdpr.ca.gov/docs/emon/pubs/sops/fsot007.pdf
EQWA003.00 (SOP for DO meter)	FSWA002.00 (SOP for surface water monitoring)
http://www.cdpr.ca.gov/docs/emon/pubs/sops/eqwa003.pdf	http://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa002.pdf
EQWA004.00 (SOP for conductivity meter)	FSWA016.00 (SOP for conducting sediment samples)
http://www.cdpr.ca.gov/docs/emon/pubs/sops/eqwa004.pdf	http://www.cdpr.ca.gov/docs/emon/pubs/sops/FSWA016.pdf
FSWA008.00 (SOP for sampling surface water runoff)	FSOT005.00 (SOP for mass deposition sheets)
http://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa008.pdf	http://www.cdpr.ca.gov/docs/emon/pubs/sops/fsot005.pdf
FSSO002.00 (SOP for soil sampling)	QAQC011.00 (SOP for field blanks)
http://www.cdpr.ca.gov/docs/emon/pubs/sops/fsso002.pdf	http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc011.pdf

## Appendix D. Sample Tracking and Transport Standard Operating Procedures

QAQC003.02 (SOP for sample tracking) http://www.cdpr.ca.gov/docs/emon/pubs/sops/QAQC003.02.pdf QAQC004.01 (SOP for transport of samples) http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc0401.pdf

Example of a Chain of Custody form for Sample transport:



Study #243 and Study #244 California Department of Pesticide Regulation Environmental Monitoring Branch 1001 I Street, Sacramento, CA 95812 QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 45 of 49

# Appendix E. Example Field Forms

# Field Data Sheet – Study Number 243

Date:	Time:	Field	Crew
	Orestimba Creek at Rive		
	<i>Other</i> =		-
Weather Co	onditions:		
Water Para			
рН		Temperature	${}^{m{\mathscr{C}}}$ (pH meter)
	Oxygen: mg/L		
Specific E	C*µS/cm OK	R mS/cm (circle one)	
Salinity	ppt		
Stream Con	ditions:		
	v: Staff Plate (Stream Heigh		
	<b>ty</b> (1 - no flow; 2 – low; 3 – 1		
Sample Nur	nbers:		
SEDIMENT			
I-CHEM	500 ml wide mouth jar		
(500 ml, fu	ell jar) PY =	<i>B</i> =	
PSMJ (Se	ediment) – Pint Mason size	ed jar	
(125 ml, ¼	full) Grain size =	<i>TOC</i> =	
1 LPP (P	olypropylene) Hyalella (1	)=	Hyalella (2) =
WATER - 1	-Liter Amber (1LAMBR	<b>(</b> )	
<i>OP</i> =	BU =	=	<i>Other</i> =
PY =	C. di	ubia (1) =	<i>Other</i> =
TOO	<i>C. di</i>	ubia (2) =	

FIELD INSTRUMENT CALIBRATION SHEET					
Project Name:	Project Number:				
Date:					
Equipment Type:					
Manufacturer:					
Model Number:					
Calibration (as necessary, minimum twice p	er day):				
CALIBRATION #1	Time:				
Calibration Standard:					
Instrument Reading:					
CALIBRATION #2	Time:				
Calibration Standard:					
Instrument Reading:					
CALIBRATION #3	Time:				
Calibration Standard:					
Instrument Reading:					
CALIBRATION #4	Time:				
Calibration Standard:					
Instrument Reading:					
	Date(s) Instrument Used:				
Name of person(s) who calibrated instruments:					
Calibration Standards Used:					
(1)					
(2)					
(3)					
(4)					
Source of Calibration Standards:					
Miscellaneous Comments:					
	Calibrated by:				
	Canorated by.				

Study #243 and Study #244 California Department of Pesticide Regulation Environmental Monitoring Branch 1001 I Street, Sacramento, CA 95812 QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 48 of 49

### Appendix F. Laboratory Quality Control Procedures

Chemistry Laboratory Quality Control SOP: <u>http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc001.pdf</u>

### Appendix G. Analytical Methods - Water

Pyrethroids in Water: http://www.cdpr.ca.gov/docs/emon/pubs/anl\_methds/imeth\_299.pdf

Organophosphorous Pesticides in water: http://www.cdpr.ca.gov/docs/emon/pubs/anl\_methds/imeth\_307.pdf

### Appendix H. Analytical Methods - Sediment

Pyrethroids in Sediment: http://www.cdpr.ca.gov/docs/emon/pubs/anl\_methds/imeth\_292.pdf

### Appendix I. Mass Deposition Analysis SOP



## Appendix J. TOC Determination and Sediment Size Analysis SOP

SOP to determine TOC: http://www.cdpr.ca.gov/docs/emon/pubs/sops/meth005\_00.pdf

SOP to determine Sediment Grain Size:



QAPP for studies 243 and 244 Revision 2.4 11/23/2009 Page 49 of 49

### Appendix K. Laboratory Methods and QA/QC for *C. dubia* and *H. azteca* Toxicity Tests





### Appendix L. CDFG Laboratory Quality Assurance Program Plan

State of CA, Department of Fish and Game, Office of Spill Prevention and Response, Laboratory Quality Assurance Plan

