

# Quality Assurance Project Plan

Prepared by  
**Bryn Phillips, UC Davis Marine Pollution Studies Laboratory**

**AGREEMENT NUMBER:** 06-352-553-0

**PROJECT NAME:** Watershed-scale Evaluation of Agricultural BMP Effectiveness Protecting Critical Coastal Habitats

**Principal Investigator:** Ron Tjeerdema (University of California Davis)

**Project Grant Manager:** Mary Adams (Central Coast Regional Water Quality Control Board)

Version 1.2  
November 14, 2007

## **GROUP A: PROJECT MANAGEMENT**

### **1. TITLE AND APPROVAL SHEETS**

Quality Assurance Project Plan

For

PROJECT NAME: Watershed-scale Evaluation of Agricultural  
BMP Effectiveness Protecting Critical Coastal  
Habitats

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Agreement Number: 06-352-553-0

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Date: September 14, 2007

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NAME OF RESPONSIBLE ORGANIZATION : Central Coast Regional Water Quality  
Control Board

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## APPROVAL SIGNATURES

## GRANT ORGANIZATION:

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date*:</u>
Project Manager	John Hunt		
QA Officer	Bryn Phillips		

CENTRAL COAST REGIONAL WATER QUALITY CONTROL BOARD

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date*:</u>
Contract Manager	Mary Adams		
QA Officer	Karen Worcester		

\* This is a contractual document. The signature dates indicate the earliest date when the project can start.

\*\* If the QAPP is being prepared under the jurisdiction of the State Water Resources Control Board (SWRCB) rather than a Regional Board, substitute the appropriate SWRCB information for the RWQCB information.

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## STANDARD OPERATING PROCEDURES

All toxicity analyses for this project follow the SWAMP standard operating procedures (SOPs) listed below. The SWAMP toxicity testing and water quality SOPs were written by the MPSL Granite Canyon and Water Pollution Control Laboratory staff, who maintain, update, and distribute SOPs for the SWAMP program. SOPs are available to the Contract Manager or designee on request.

Number	Procedure and Regulatory Citation	Revision Date
<b>General Laboratory Procedures</b>		
1.1	Data Handling	December 2, 2004
1.3	Glassware Cleaning	September 14, 2007
1.4	Pipette Use	September 14, 2007
1.5	Sample Handling	September 14, 2007
<b>Toxicity Testing Procedures</b>		
2.4	<i>Ceriodaphnia dubia</i> 96-Hour Acute Toxicity Test U.S. EPA (2002) 821-R-02-012	September 14, 2007
2.20	<i>Hyalella azteca</i> 10-d Water Toxicity Test U.S. EPA (2002) 821-R-02-012	September 14, 2007
2.7	<i>Hyalella azteca</i> 10-d Sediment Toxicity Test U.S. EPA (2000) 600/R-99/064	September 14, 2007
2.13	Toxicity Identification Evaluation (TIE) - Water	November 1, 2007
2.18	Toxicity Identification Evaluation (TIE) - Sediment	November 1, 2007
<b>Water Quality Procedures</b>		
3.4	Dissolved Oxygen, pH, Conductivity (Hach SensION 156)	September 14, 2007
3.2	Ammonia (Hach DR/2010 Spectrophotometer)	September 14, 2007
3.6	Salinity (Refractometer)	September 14, 2007
3.1	Alkalinity (Digital Titration)	September 14, 2007
3.5	Hardness (Digital Titration)	September 14, 2007
3.3	Diazinon and Chlorpyrifos (ELISA)	September 14, 2007

### 3. DISTRIBUTION LIST

<b>Name (Affiliation)</b>	<b>Title</b>	<b>Contact Information</b>	<b>QAPP No.</b>
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John Hunt (UCD-GCML)	Project Manager & Toxicity Laboratory Director	Tel: (831) 624-0947 Fax: (831) 626-1518 Email: jwhunt@ucdavis.edu	2
Kathryn Kuivila (USGS)	Chemistry Laboratory Manager (organics)	Tel: (916) 278-3052 Fax: (916) 278-3013 Email: kkuivila@usgs.gov	3
Bryn Phillips	Project QA Officer	Tel: (831) 624-0947 Fax: (831) 626-1518 Email: <a href="mailto:bmphillips@ucdavis.edu">bmphillips@ucdavis.edu</a>	4
Karen Worcester (CCRWQCB)	Regional QA Officer	Tel: (805) 549-3333 Fax: (805) 788-3576 Email: kworcester@waterboards.ca.gov	5

#### 4. PROJECT/TASK ORGANIZATION

##### 4.1 Involved Parties and Roles

The following agencies are involved in this project as the principal investigators or subcontracting laboratories. Personnel involved in this project are listed in Table 1.

**Table 1. (Element 4) Personnel responsibilities.**

<b>Name</b>	<b>Title</b>	<b>Affiliation and Contact Information</b>
Mary Adams	Project Contract Manager	Central Coast Regional Water Quality Control Board 895 Aerovista Place, Suite 101, San Luis Obispo, CA 93401 Tel: (805) 542-4768 Fax: (805) 788-3506 Email: madams@waterboards.ca.gov
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Ken Davis	Grain Size/TOC Laboratory Manager	Applied Marine Sciences 502 North Highway 3 – Suite B, League City, TX 77573 Tel: (281) 554-7272 Fax: (281) 554-6356 Email: kdavis1ams@aol.com
Sheila Holt	Benthic Analysis Laboratory Manager	Weston Solutions, Inc. 2433 Impala Dr., Carlsbad, CA 92010 Tel: (760)795-6914 Fax: (760) 931-1580 Email: Sheila.Holt@westonsolutions.com



## 4.2 Quality Assurance Officer Role

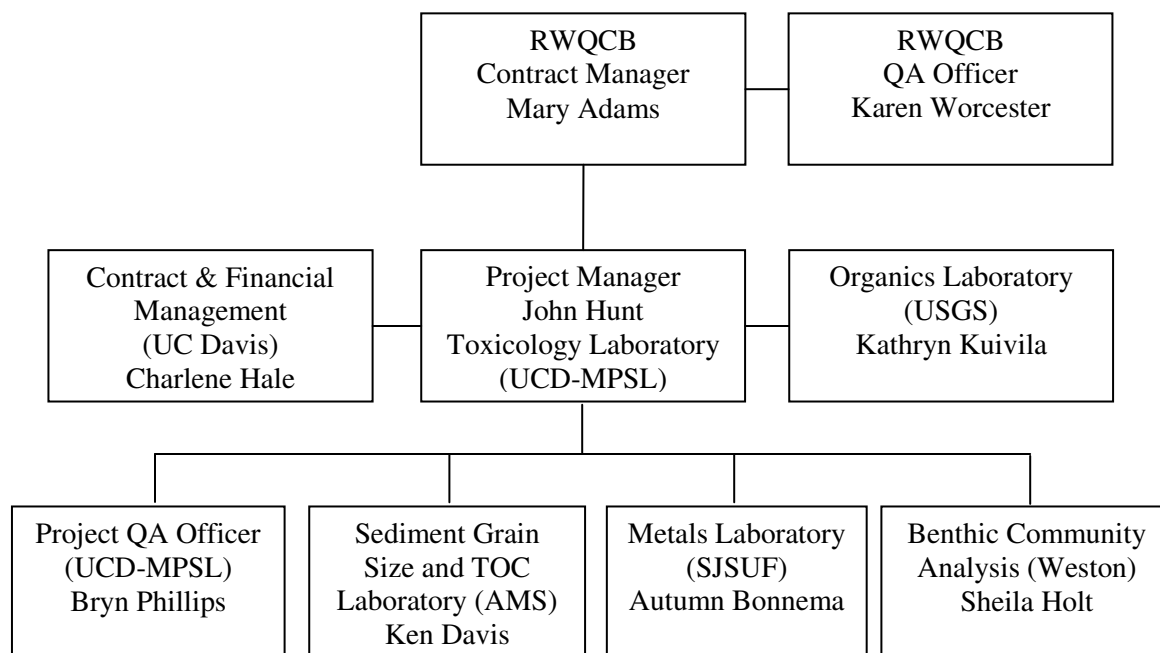
MPSL's QA Officer or designee will conduct a QA/QC review of all field-monitoring data and laboratory data produced under Tasks 2 through 5 of this contract.

## 4.3 Persons Responsible for QAPP Update and Maintenance

Mary Adams and John Hunt will be responsible for maintaining and updating the official approved QAPP. Either person can make changes.

## 4.4 Organizational Chart and Responsibilities

Figure 1. (Element 4) Organizational chart



## 4.5 Project Members in Advisory Roles

All project members who will advise on the project will participate in the delivery of project products, as listed above.

## **5. PROBLEM DEFINITION/BACKGROUND**

### **5.1 Problem statement.**

Coastal estuaries are among the most ecologically important and critically threatened habitats in California. Along California's Central Coast, the three largest watersheds drain to coastal estuaries that provide essential habitat for early life stages of commercial marine fish species, threatened anadromous fish species, migratory birds, and other wildlife. Each of these watersheds contains year-round, intensively cultivated agricultural land that supports a \$5 billion/year industry producing most of the nation's lettuce, artichokes, and crucifer crops. Farm groups are initiating management practices to control pesticide runoff, but there is currently no designated effort to document the cumulative loading and effects of pesticides in these coastal estuaries. This project is designed to provide a scientific, statistically rigorous baseline assessment to support future evaluations of the watershed-wide effectiveness of BMP implementation.

### **5.2 Decisions or outcomes**

The Pajaro, Salinas, and Santa Maria River estuaries will be monitored over a two-year period to measure contaminant concentrations and effects in estuarine water, sediment, and biota, and to link contaminant profiles with those from the main rivers and adjacent tributaries. Biological measurements at the molecular, organismal, and community levels will be measured synoptically to determine associations with contaminants. Each estuary will be sampled using a proportional placement design with sufficient numbers of sites and surveys to allow detection of the change expected to occur as management practices are implemented over time. Samples will be collected during three storm events, and during multiple dry season surveys. Measurements will include pyrethroid, organophosphate (OP), and organochlorine (OC) pesticides, as well as PCBs, PAHs, and metals. Endocrine disruption will be measured in resident fish, toxicity will be measured in water and sediment, and estuarine benthic communities will be assessed.

### **5.3 Water quality or regulatory criteria**

This project addresses the narrative toxicity water quality objective in the Central Coast Region Basin Plan (Basin Plan, 1995), as well as numerical objectives for pesticides. These objectives have been exceeded in many Central Coast streams, including those in the vicinity of this project. The primary beneficial use to be addressed by this project is aquatic life protection in streams and downstream estuaries, which provide critical habitat for many commercially important marine fish species and other wildlife.

The purpose of this study is to characterize pesticide concentrations and effects in the estuaries and their tributaries; it is not primarily designed to determine compliance with standards or objectives. However, data from this study could be used to support regulatory action, such as TMDL development. No action limits are set as part of this study design.

## **6. PROJECT/TASK DESCRIPTION**

### **6.1 Work statement and project products.**

1. Stakeholders Data Exchange on Individual and Cumulative Management Practices (MP) Effectiveness.
  - 1.1 Compile publicly available information from Regional Water Board Agricultural Waiver Farm Plan Checklists.
  - 1.2 Request from the Regional Water Board the proportion of farms participating in water quality short courses, and the proportion of farms with erosion control practices, irrigation management plans, pesticide management practices, and nutrient management practices in the three (3) Central Coast major watersheds. This information will be compiled to indicate the level of agricultural water quality management activity occurring in the three project watersheds. This will be included in the final report as part of the interpretation of linkages between farm water quality management and estuary condition.
  - 1.3 Exchange data with the Central Coast Resource Conservation Districts (RCDs) to determine the mean and variation in measured MP reduction of pesticides and toxicity from available studies of individual MPs implemented in the three (3) Central Coast watersheds.
  - 1.4 Estimate the potential cumulative, watershed-wide reduction in pesticide loading based on the proportion of MPs implemented and the average MP effectiveness in reducing pesticide concentrations.
  - 1.5 Create a template for continued estimations of pesticide runoff reductions over time, which can be adapted for use as part of future assessments of watershed-wide changes in pesticide transport. This template will be incorporated in the final report, and will serve as a reference for collecting similar data in the future for comparisons of management activity over time.
2. Estuary Field Sampling
  - 2.1 Determine sampling locations in each estuary based on proportional placement within suitable habitat for each measurement per the Monitoring Plan.
  - 2.2 Locate sediment collection sites in depositional, brackish water areas and water collection sites in well-mixed brackish water areas.
  - 2.3 Collect fish and sand crab specimens in brackish and marine areas where species congregate.

- 2.4 Prepare field logs and data sheets for recording information including: date/time, Global Positioning System (GPS) coordinate of sample collection, name of sampler, weather conditions, etc.
- 2.5 Convene coordination meetings with USGS, UCD, and Regional Board project participants to ensure consistent collection procedures and adherence to QAPP and SAP amongst field staff.
- 2.6 Collect water, sediment, and tissue samples in the field per the approved Monitoring Plan.
- 2.7 Collect sufficient samples to conduct duplicate analyses on ten percent (10%) of all samples to determine measurement precision according to the QAPP.

### 3. Analysis of Estuarine Samples

- 3.1 Analyze a minimum of ninety nine (99) estuarine water samples to determine concentrations of current-use and legacy pesticides, dissolved organic carbon, dissolved oxygen, pH, suspended sediment concentration, hardness, temperature, turbidity, salinity, nitrate, phosphate, and toxicity to estuarine amphipods per the approved QAPP.
- 3.2 Chemically analyze a minimum of seventy eight (78) estuarine bed sediment samples to determine concentrations of current-use and legacy pesticides, polycyclic aromatic hydrocarbons (PAHs), trace metals, total organic carbon, grain size, and sediment toxicity to infaunal amphipods per the approved QAPP.
- 3.3 Analyze a minimum of thirty three (33) estuarine bed sediment samples to identify benthic organisms for determination of community structure. A minimum of five (5) sites will be a representative subset of the eight (8) sites sampled for chemistry and toxicity per 3.2.
- 3.4 Conduct toxicity identification evaluations (TIEs) on a minimum of six (6) bed sediment samples and three (3) water samples, to identify chemicals causing observed toxicity.
- 3.5 Conduct analyses of physiological metabolic indicators (metabolomics) and endocrine disruption on seven (7) samples of organ and muscle tissue from representative fish species collected in the estuaries.
- 3.6 Chemically analyze a minimum of seven (7) representative fish samples from species collected in the estuaries to determine concentrations of current-use and legacy pesticides, polycyclic aromatic hydrocarbons (PAHs), and trace metals.
- 3.7 Chemically analyze a minimum of seven (7) representative samples of sand crabs collected at the estuary outlets to determine concentrations of organochlorine,

organophosphate, pyrethroid, and other new-use pesticides, polycyclic aromatic hydrocarbons (PAHs), and trace metals.

#### 4. Field Sampling in Tributaries to the Estuaries

- 4.1 Select sampling locations at public crossings of tributary streams near each estuary per the Sampling Plan. These will include the main stems of the Pajaro, Salinas, and Santa Maria Rivers, as well as at least one (1) other tributary proximate to each estuary, likely including the Beach Road Drain, the Blanco Drain, and Orcutt Creek.
- 4.2 Collect water, suspended sediment, and bed sediment samples in field.
  - 4.2.1 Collect water at each tributary during three (3) storm events and six (6) dry season surveys.
  - 4.2.2 Collect bed sediment at each tributary after one (1) storm event and two (2) dry season surveys.
  - 4.2.3 Collect suspended sediment samples at each tributary during three (3) storm events, using a high-volume pump and flow-through centrifuge.
- 4.3 Collect sufficient samples to conduct duplicate analyses on ten percent (10%) of all samples to determine measurement precision, according to the QAPP.

#### 5. Analysis of Samples from Tributaries to the Estuaries

- 5.1 Chemically analyze a minimum of fifty nine (59) tributary water samples to determine concentrations of current-use and legacy pesticides, dissolved organic carbon, dissolved oxygen, pH, suspended sediment concentration, hardness, temperature, turbidity, salinity, nitrate, phosphate, and toxicity to estuarine amphipods.
- 5.2 Measure current-use and legacy pesticides and dissolved organic carbon in both the suspended sediments and the associated water on a subset of at least eighteen (18) water samples primarily collected during storm events (4.2.1). These measurements will further understanding of pesticide partitioning between water and sediment and identify important transport mechanism(s) to the estuaries.
- 5.3 Chemically analyze a minimum of eighteen (18) tributary bed sediment samples (4.2.2) to determine concentrations of current-use and legacy pesticides, polycyclic aromatic hydrocarbons (PAHs), trace metals, total organic carbon, grain size, and sediment toxicity to infaunal amphipods.

#### 6 Data Management

- 6.1 Coordinate with the SWAMP Data Management Team at Moss Landing to determine the appropriate means and timing for data transfer to the SWAMP data base.
- 6.2 Verify at the laboratory level to determine compliance with quality assurance requirements detailed in the project SWAMP-comparable QAPP.

## 7. Data Analysis and Interpretation

- 7.1 Determine the frequency of detection for each pesticide analyte from samples collected. Prepare graphics showing the chemicals detected and their frequency of detection in estuaries and tributaries.
- 7.2 Determine the magnitude (concentration) of pesticides detected from samples collected. Prepare graphics showing the chemicals detected and their concentrations in estuary and tributary samples.
- 7.3 Determine frequency and spatial distribution of chemicals of primarily urban origin (PAHs and metals), to characterize the relative magnitude of urban runoff influence among the three estuaries and their tributaries from samples collected.
- 7.4 Compare chemical concentrations in water and sediment samples collected to assessment thresholds, such as Basin Plan Objectives, sediment quality guidelines, water quality criteria, and established median lethal concentrations for aquatic organisms.
- 7.5 Compare detected chemical concentrations among water, suspended sediment, bed sediment, and tissue phases, to further understanding of the chemical fate, transport, and potential routes of exposure to wildlife.
- 7.6 Compare tissue concentrations in resident fish and prey species (sand crabs) with physiological indicators of fish health (metabolic indicators and endocrine disruption).
- 7.7 Compare chemical concentrations, toxicity, and benthic community conditions in the estuaries with those recently observed in Northern California estuaries by the Environmental Protection Agency Environmental Monitoring and Assessment Program (EMAP).
- 7.8 Calculate mean and variance values for detected chemical concentrations, toxicity, benthic community metrics, and physiological measures.
- 7.9 Prepare a summary report of data in graphs and maps to show trends and spatial connections to further understanding of impacts and transport processes and submit to the Grant Manager.
- 7.10 Conduct statistical tests (e.g., Analysis of Variance) to determine the significance of differences:
  - among sites within estuaries, using laboratory replication and survey replication;
  - among surveys at each estuary, using laboratory replication and site replication;
  - among estuaries, using site and survey replication;

- 7.10 Compare the chemical composition of estuary samples and tributary samples to identify similarities, and to document linkages between current inputs and estuary conditions.
- 7.11 Prepare summary report summarizing available information about the proportion of agricultural MPs implemented, and about the average (and range of) effectiveness of the evaluated MPs in reducing pesticide loads for each watershed.
- 7.12 Compare information summarized in report (7.11) with current conditions in the three (3) estuaries to identify patterns and to establish the baseline for detection of change in the watersheds and estuaries over time as implementation programs grow. The study design also allows comparisons among the estuaries, which can be linked to existing practices and differential rates of MP implementation.

The project will provide quarterly progress reports, during the life of the project. At the end of the project, UC Davis and the RCD will provide draft and final reports.

## **6.2. Constituents to be monitored and measurement techniques**

Below is a summary of the Field Monitoring Plan that is included in Appendix A.

Samples are to be collected during twelve dry events and three storm events. A storm event will be defined as a minimum half-inch precipitation in the watershed. Sediment samples will be collected after, rather than during, the storm event in order to allow sediments to settle and to avoid the effects of storm scouring. Quality assurance duplicates will be collected randomly throughout the fifteen events (10% of samples).

### *Estuary Field Sampling and Analysis*

Sampling locations in each estuary will be chosen based on proportional placement within suitable habitat for each measurement. Sediment collection sites will be in depositional, brackish water areas and water collection sites in well-mixed brackish water areas. Two locations will be chosen for water sample collection and eight locations will be chosen for sediment collection.

Estuarine water samples will be collected during every event.

- Field analysis on these samples will include measurements of dissolved oxygen, pH, conductivity/salinity, temperature, and turbidity.
- Toxicity will be analyzed with 10-d survival protocol for *Hyalella azteca* (U.S. EPA 2002), and laboratory water quality measurements will include dissolved oxygen, pH, conductivity/salinity, hardness, alkalinity, nitrate, and phosphate. If conductivity measurements are suitably low, samples will also be analyzed using the 4-d acute survival protocol for *Ceriodaphnia dubia* (U.S. EPA 2002), based on the organism's higher sensitivity to Diazinon.
- Chemical analysis will include current use and legacy pesticides, and dissolved organic carbon.

Estuarine sediment will be collected during two (2) dry events and after one (1) storm event.

- Toxicity will be analyzed with 10-d growth and survival protocol for *Hyaella azteca* (U.S. EPA 2000), and laboratory water quality measurements will include dissolved oxygen, pH, conductivity/salinity, hardness, and alkalinity.
- Chemical analysis will include current use and legacy pesticides, metals, polycyclic aromatic hydrocarbons, and total organic carbon.
- Physical analysis will include grain size.
- Collection and analysis of benthic invertebrates will occur at five stations during two dry events.

Fish and sand crab specimens will be collected in brackish and marine areas during two (2) dry events.

- Chemical analysis of fish and crabs will include current use and legacy pesticides, metals, and polycyclic aromatic hydrocarbons.
- Physiological metabolic indicators (metabolomics) and endocrine disruption (vitellogenin) will be measured on fish.

#### *Tributary Field Sampling and Analysis*

Sampling locations in two tributaries will be located at public crossings near each estuary. These will include the main stems of the Pajaro, Salinas, and Santa Maria Rivers, as well as at least one (1) other tributary proximate to each estuary. Tributary sampling sites include:

Pajaro- Monterey Drainage Ditch, Beach Street Ditch

Salinas- Blanco Drain

Santa Maria- Orcutt Creek at Sand Plant

Tributary water samples are to be collected during six (6) dry season events and three (3) storm events.

- Field analysis on these samples will include measurements of dissolved oxygen, pH, conductivity/salinity, temperature, and turbidity.
- Depending on the conductivity of the samples, toxicity will be analyzed with either a 4-d acute survival protocol for *Ceriodaphnia dubia* (U.S. EPA 2002) or a 10-d survival protocol for *Hyaella azteca* (U.S. EPA 2002). Laboratory water quality measurements will include dissolved oxygen, pH, conductivity/salinity, hardness, alkalinity, nitrate, and phosphate.
- Chemical analysis will include current use and legacy pesticides, and dissolved organic carbon.

Tributary sediment samples are to be collected during two (2) dry season events and after one (1) storm event.

- Toxicity will be analyzed with 10-d growth and survival protocol for *Hyaella azteca* (U.S. EPA 2000), and laboratory water quality measurements will include dissolved oxygen, pH, conductivity/salinity, hardness, and alkalinity.
- Chemical analysis will include current use and legacy pesticides, metals, polycyclic aromatic hydrocarbons, and total organic carbon.
- Physical analysis will include grain size.



Suspended sediment samples at each tributary are to be collected during three (3) storm events, using a high-volume pump and flow-through centrifuge.

- Chemical analysis will include current use and legacy pesticides, and dissolved organic carbon.

Toxicity identification evaluations (TIEs) will be conducted on a minimum of six (6) bed sediment samples and three (3) water samples, to identify chemicals causing observed toxicity.

### *Sampling and Sample Handling*

Sample collection, sample handling, and laboratory methods will be the same as those employed by the California Surface Water Ambient Monitoring Program (SWAMP) using SWAMP protocols. Methods for collection of field samples and sample handling are further outlined in the project QAPP (attached).

### *Sampling Equipment*

Water samples will be collected in one-liter or 2.5 amber glass bottles, cleaned according to the SWAMP comparable protocols. Sediment samples will be collected directly from the substrate or from a petite Ponar grab sampler using polycarbonate core tubes or polyethylene scoops. Separate core tubes or scoops will be used for each site. Sediment will be immediately transferred to either two-liter glass jars or polyethylene-lined plastic buckets for standard testing. All materials that come into contact with the samples will be cleaned according to the SWAMP comparable protocols.

## **6.3 Project schedule**

**Table 2. (Element 6) Project schedule timeline.**

<b>Item</b>	<b>Activity and/or Deliverable</b>	<b>Deliverable Due Date</b>
<b>1</b>	<b>Stakeholders Data Exchange</b>	October 2007-Nov 2009
	1.1 Data from Regional Board Ag Waiver Farm Plan Checklists	
	1.2 Data from agricultural water quality management activity	
	1.3 Data from RCDs on previous MP studies	
	1.4 Estimation of pesticide reduction in each watershed	
	1.5 Creation of template for ongoing pesticide reduction estimation	
<b>2</b>	<b>Estuary Field Sampling</b>	October 2007-Sept 2009
	2.1 Determine sampling locations	October 2007
	2.2 Locate sediment and water collections sites	October 2007
	2.3 Collect fish and crab specimens	
	2.4 Prepare field logs and data sheets	October 2007
	2.5 Coordination meetings among USGS, UCD and Regional Board	
	2.6 Collect sediment, water, and tissue samples	
	2.7 Collect 10% quality assurance samples	

**Table 3. (Element 6) Project schedule timeline (continued)**

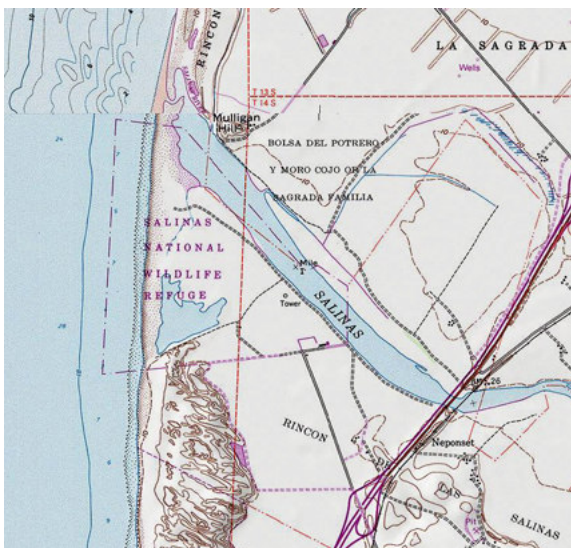
<b>3</b>	<b>Analysis of Estuarine Samples</b>	October 2007-Sept 2009
	3.1 Analyze water samples for toxicity and chemistry	
	3.2 Analyze sediment samples for toxicity and chemistry	
	3.3 Analyze sediment samples for benthic organisms	
	3.4 Conduct toxicity identification evaluations (TIEs)	
	3.5 Analyze fish tissue for metabolomics and VTG	
	3.6 Analyze fish tissue for chemistry	
	3.7 Analyze sand crab tissue for chemistry	
<b>4</b>	<b>Tributary Field Sampling</b>	October 2007-Sept 2009
	4.1 Determine sampling locations	October 2007
	4.2 Collect sediment, water, and suspended sediment samples	
	4.3 Collect 10% quality assurance samples	
<b>5</b>	<b>Analysis of Tributary Samples</b>	October 2007-Sept 2009
	5.1 Analyze water samples for toxicity and chemistry	
	5.2 Analyze suspended sediment samples for chemistry	
	5.3 Analyze sediment samples for toxicity and chemistry	
<b>6</b>	<b>Data Management</b>	Ongoing
	6.1 Coordinate with SWAMP Data Management Team	
	6.2 Verify data with SWAMP-comparable QAPP	
<b>7</b>	<b>Data Analysis and Interpretation</b>	July 2008-Dec 2009
	7.1 Determine frequency of pesticide detection	
	7.2 Determine magnitude of pesticide detection	
	7.3 Determine frequency and spatial distribution of urban chemicals	
	7.4 Compare chemical concentrations to assessment thresholds	
	7.5 Evaluate chemical fate, transport, and exposure routes	
	7.6 Compare tissue concentrations with physiological indicators	
	7.7 Comparison of project data to EMAP data	
	7.8 Calculate summary statistics for all measured parameters	
	7.9 Prepare summary data report and submit to Grant Manager	
	7.10 Conduct statistical tests	
	7.11 Prepare summary report on effectiveness of MPs	
	7.12 Compare 7.9 and 7.11	
	Draft Project Report	January 11, 2010
	Final Project Report	February 1, 2010

## 6.4 Geographical setting

	<b>Pajaro River</b>	<b>Salinas River</b>	<b>Santa Maria River</b>
County	Santa Cruz/Monterey	Monterey	San Luis Obispo/Santa Barbara
Watershed	Pajaro River	Salinas River	Santa Maria River
Water Body	Pajaro River Watsonville Slough	Salinas River	Santa Maria River
Regional Water Board	Region 3, Central Coast	Region 3, Central Coast	Region 3, Central Coast
Estuary Coordinates	36.8527, -121.8076	36.7453, -121.8006	34.9689, -120.6467



Pajaro River Estuary



Salinas River Estuary

Santa Maria River Estuary



## 6.5 Constraints

Accessing certain areas may be a seasonal constraint based on the variable weather patterns and the dynamic nature of lagoons. The presence or absence of a sand berm closing the lagoon off from direct tidal influence may affect sampling site selection. For example, certain areas where sediment samples were taken before a berm breach may not be suitable sediment sampling sites if the lagoon topography and hydrology have changed dramatically.

Weather patterns could also be a possible constraint for USGS suspended sediment sampling. These sampling sites require nearby vehicle access because of the heavy equipment involved.

Initial surveys conducted by MPSL recorded the presence of appropriate species for the biomarker study. However, seasonal availability of appropriate fish species could be a potential constraint.

## 7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Measurement quality objectives

Measurement or Analyses Type	Applicable Measurement Quality Objective
Water Toxicity	Meet acceptability criteria relative to: reference toxicant tests, ancillary test condition measures, and completeness
Water Trace Organics	Accuracy, Precision, Completeness, Comparability, Sensitivity

Sediment Toxicity	Meet acceptability criteria relative to: reference toxicant tests, ancillary test condition measures, and completeness
Sediment Benthic Community Analysis	Sorted samples are re-inspected to insure a 95% removal of specimens. Taxonomic identifications are reanalyzed on 10% of the samples by secondary taxonomists to insure accuracy of identifications
Sediment grain size and TOC	Accuracy, Precision, Comparability, Completeness, Sensitivity
Sediment Trace Metals	Accuracy, Precision, Comparability, Completeness, Sensitivity
Sediment Trace Organics	Accuracy, Precision, Comparability, Completeness, Sensitivity

Accuracy will be determined by measuring one or more Certified Reference Materials or Standard Reference Materials. At least one reference sample per batch is required. Additional analyte recovery measurements may be made by laboratory spiking of a replicate sample with a known concentration of the analyte. The target level of addition is targeted to be at least twice the original sample concentration.

Precision measurements will be determined on field and/or laboratory replicates. At least one replicate per batch is required. The relative percent difference (RPD) between two replicate samples or the relative standard deviation (RSD) between more than two replicate samples will be less than the DQOs listed in Tables 3 and 4 for each analyte of interest. Following are the calculations:

$$RPD = \frac{ABS(\text{rep 1} - \text{rep 2}) \times 100}{\text{Average}(\text{rep 1}, \text{rep 2})}$$

$$RSD = \frac{STDEV(\text{all replicate samples}) \times 100}{\text{Average}(\text{all replicate samples})}$$

ABS is the absolute value      STDEV is the standard deviation

Comparability is necessary so that data derived from this project can be combined with data from other projects. Such combinations are useful for wider scale assessments, such as between regions, or between different time periods. The standard for data comparability will be the ability to enter the data into the statewide SWAMP data base, so that it can be integrated with high quality data from other studies. Data from previous studies will not be used for analyses in this study, and no acceptance criteria for previous data are identified. As described in Tables 3 and 4, data from this project will be generated using SWAMP comparable QA/QC procedures for performance based methods, including all necessary standards, blanks, and reference materials.

All data reported for this project will be produced according to this QAPP and will be SWAMP comparable.

Representativeness is a qualitative measure of the degree to which the sampling approach characterizes the target population. This study is designed to provide baseline data for the presence and impacts of agricultural pesticide use. Water from the estuaries will be collected from two stations during fifteen events, providing sufficient replication to address temporal variation. Sediment from the estuaries will be collected from eight stations during six events, providing sufficient replication to address spatial variation. Additional sampling in the tributaries and during storm events will provide additional replication to address spatial and temporal variability. Because water quality can be more ephemeral, temporal replication was increased to address temporal variability. Sediment quality tends to be more static, therefore increased spatial replication was emphasized.

Completeness is a measure of the number of analyses generating useable data for each analysis divided by the number of samples collected for that analysis. Based on past experience with numerous projects of this type, we expect to produce acceptable data from > 95% of the samples collected.

Method sensitivity is measured as the target Method Detection Limit. The MDLs for this project are given in Table 7. These limits are sensitive enough to resolve biologically relevant differences in ambient chemical concentrations.

#### **Suggested Standard Reference Material:**

Grain size: NIST 1003b glass spheres (8 to 58 um diameter), constant-density spheres having a range of diameters. Precision and accuracy of the sedigraph (particle size analyzer) is evaluated with a garnet standard reference material (Micromeritics, Inc.).

TOC: Laboratory Control Material

Trace Elements: NRC MESS-3 or NIST 1646

Trace Organics: NIST 1941a or similar

**Table 3. (Element 7) Measurement quality objectives for field water measurements.**

Parameter	Accuracy	Precision	Recovery	Target Reporting Limit	Completeness
Conductivity	± 0.5%	± 10%	NA	0.1 µS/cm	No SWAMP requirement; will use 90%
Dissolved Oxygen	± 0.5 mg/L	± 10%	NA	0.1 mg/L	No SWAMP requirement; will use 90%
pH	± 0.5 units	± 10%	NA	0.1 pH unit	No SWAMP requirement; will use 90%
Temperature	± 0.5 °C	± 5%	NA	0.1 °C	No SWAMP requirement; will use 90%
Turbidity	± 10%	± 10%	NA	0.1 mg/L	No SWAMP requirement; will use 90%

**Table 4a. (Element 7) Measurement quality objectives for laboratory water measurements.**

Parameter	Accuracy	Precision	Recovery	Completeness
Toxicity Testing	Meet all performance criteria in method relative to reference toxicant.	Meet all performance criteria in method relative to sample replication.	NA	90%
Toxicity Water Quality	See Table 3			
ELISA	$\pm 20\%$ of nominal concentration of laboratory prepared solution	Coefficient of variation $\pm 20\%$ for duplicates	SWAMP requires the evaluation of a matrix spike, but no limits.	No SWAMP requirement – suggest 90%
Organic Analytes	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material. If not available then with 50% to 150% of true value	Field replicate or MS/MSD $\pm 25\%$ RPD. Field replicate minimum.	Matrix spike 50% - 150% or control limits at $\pm 3$ standard deviations based on actual lab data.	No SWAMP requirement – suggest 90%
Metal Analytes	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material. If not available then with 50% to 150% of true value	Field replicate or MS/MSD $\pm 25\%$ RPD. Field replicate minimum.	Matrix spike 50% - 150% or control limits at $\pm 3$ standard deviations based on actual lab data.	No SWAMP requirement – suggest 90%
Sediment Total Organic Carbon and Sediment Grain Size	CRM within the 95% CI stated by the provider. Laboratory Control Material (LCM) $\pm 20\%$ to 25% of stated value. No accuracy criteria for grain size.	Replicates within $\pm 20\%$	No SWAMP requirement although possible for TOC. Consider $\pm 25\%$ recovery (75% - 125%)	No SWAMP requirement – suggest 90%

**Table 4b. (Element 7) Measurement quality objectives for laboratory measurements for sediment grain size and TOC**

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	Contamination by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material	Accuracy	TOC: One per batch Grain Size: NA.	Within 95% confidence interval of the certified value	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	Precision	One per batch	RPD or RSD < 20% precision (grain size) < 3% (TOC)	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Laboratory control material (LCM)	Accuracy & Precision	One per batch of 20 or fewer samples.	Within 20–25% consensus value	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation



**Table 4b. (Element 7) Measurement quality objectives for laboratory measurements for trace organics and metals in water and sediment.**

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	Contamination by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material (CRM)	Accuracy          Precision	One per batch of 20 or fewer samples.	As a group: 70% of the analytes within 35% of the 95% confidence interval. Individually: No analyte outside 30% of 95% confidence interval for 2 consecutive analyses.  RPD (if n=2) < 35% RSD (if n>2) < 35% RSD of last 7 CRMs < 35%	Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	Precision	One per batch of 20 or fewer samples.	RPD < 35%	Recalibrate and reanalyze. If problem persists eliminate source of imprecision and reanalyze.
Matrix Spike	Accuracy	One per batch of 20 or fewer samples.	> 50% recovery if no CRM limits apply, otherwise use CRM limits.	Check CRM or LCS recovery. Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Surrogate Spike or Internal Standard	% Recovery used to adjust sample results	One per sample	Set by analyzing laboratory (reported in QA report). (Report surrogate recovery and acceptance criteria in final report)	Check CRM or LCS recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

## **8. SPECIAL TRAINING NEEDS/CERTIFICATION**

### **8.1 Specialized training or certifications.**

No specialized training or certifications is required for this project. The main subcontractor will conduct field surveys and water and sediment toxicity analyses (UCD-MPSL, contact: John Hunt). UCD-MPSL is the primary toxicology laboratory for the Surface Water Ambient Monitoring Program (SWAMP). In cooperation with CDFG-MPSL, UCD-MPSL authored the toxicology section of the SWAMP QAPP. Water and sediment toxicity test methods and TIE procedures follow standard U.S. EPA procedures. Additional TIE procedures, particularly for pyrethroid pesticides and sediments, will in some cases require use of novel techniques for which no standardized protocols have been described.

Chemistry for organic contaminants will be analyzed by the U.S. Geological Survey (USGS - Sacramento, contact: Kathryn Kuivila). This lab has recently been developing new techniques to measure pyrethroids in ambient sediments. Sediment chemistry for metal contaminants will be analyzed by the San Jose State University Foundation (SJSUF – Moss Landing, CA, contact: Autumn Bonnema). Sediment grain-size and total organic carbon will be analyzed by Applied Marine Sciences (AMS - League City, TX, contact: Ken Davis). Benthic community analysis will be conducted by Weston Solutions, Inc (WSI – Carlsbad, CA, contact: Sheila Holt).

In general, water and sediment samples will be collected, homogenized, split into fractions, and sent to the analytical laboratories using appropriate sample handling protocol outlined in the SWAMP QAPP.

### **8.2 Training and certification documentation.**

A complete listing of laboratory accreditation certificates is available directly from the subcontractors. The contractor's QA Officer is responsible for overseeing training.

### **8.3 Training personnel.**

No new training is required for this project. Training records for individual laboratory tasks are maintained at laboratories and are available on request. The contractor's QA Officer is responsible for ensuring training requirements are satisfied.

## **9. DOCUMENTS AND RECORDS**

The following documents, records, and electronic files will be produced:

- Quality Assurance Project Plan (submitted to contract manager in paper and electronic formats)
- Monitoring Plan (submitted to contract manager in paper and electronic formats)
- Field Sampling Sheets (internal documentation available on request)
- Chain of Custody Forms (exchanged for signatures with chemistry lab, and kept on file)

- Lab Sample Disposition Logs (internal documentation available on request)
- Calibration Logs for measurements of water quality standards (internal documentation available on request)
- Refrigerator Logs (internal documentation available on request)
- Meter and Spectrophotometer Maintenance Logs (internal documentation available on request)
- Test Organism Culture Logs (internal documentation available on request)
- Culture Water Lot Logs (internal documentation available on request)
- Pipette Calibration Logs (internal documentation available on request)
- Thermometer Calibration Logs (internal documentation available on request)
- Quarterly Progress Reports (submitted to contract manager in electronic format)
- Draft Interpretive Report with Data Tables (submitted to contract manager in electronic format)
- Final Interpretive Report with Data Tables (submitted to contract manager in paper and electronic formats)
- Data Appendix (submitted to contract manager in paper and electronic spreadsheet formats)

Copies of this QAPP will be distributed by the RCD project manager to all parties directly involved in this project. Any future amended QAPPs will be distributed in the same fashion. All originals of the first and subsequent amended QAPPs will be held at the RCD. Copies of versions, other than the most current, will be discarded so as not to create confusion.

Draft and final reports will be provided to the CCRWQCB Project Manager Mary Adams. The final report will include summary data tables and an appendix that contains all project data in electronic SWAMP compatible spreadsheet format. All laboratory logs and data sheets will be maintained at MPSL for five years following project completion, and are available for review by the Contract Manager or designee during that time. Copies of the database will be maintained without discarding. Laboratories will provide electronic copies of tabulated analytical data (including associated QA/QC information outlined below) in the SWAMP database format or a format agreed upon by the Contract Manager and the UCD-MPSL Project/Data Manager or designee. All electronic records are backed-up after each batch of data is entered.

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

### **10. SAMPLING PROCESS DESIGN**

Water and sediment from three central California river estuaries and their tributaries will be monitored for toxicity and chemistry. Fifteen surveys will take place, twelve during dry weather and three during storm events. This project is designed to provide a scientific, statistically rigorous baseline assessment to support future evaluations of the watershed-wide effectiveness of BMP implementation.

Sampling dates will be determined throughout the project based on timing of weather events and coordination with project participants. Sufficient water and sediment will be collected during each sampling event to allow splits to be sent for chemical analysis if toxicity is observed.

Please refer to the Monitoring Plan (Appendix A) already provided to the RWQCB Project Manager for further description of the sampling design and sample collection methodology.

The following data will be critical to the baseline assessment: water toxicity and chemistry; sediment toxicity, chemistry, grain size, and TOC; tissue chemistry from indigenous fish and sand crabs; and water and suspended sediment chemistry. Ancillary data collected for additional information and quality assurance will include field observations and water quality, toxicity test conditions, calibration, and other QA data.

Samples are to be collected during twelve dry events and three storm events. A storm event will be defined as a minimum half-inch precipitation in the watershed. Storm events will be scheduled accordingly, but dry events will proceed at regular intervals over the course of the project.

### **11. SAMPLING METHODS**

Sampling methods will be similar to those outlined in the SWAMP QAPP. Preparation of sampling equipment is the responsibility of Bryn Phillips (UCD-MPSL) and Kelly Smalling (USGS). Should problems arise during sample collection, these individuals will confer and determine the logical course of action to obtain quality samples.

The sample containers used for water and sediment samples are listed in Table 5. Sample containers are cleaned and prepared by the analyzing laboratory, or are factory pre-cleaned. Each container is given a permanent sample label written in waterproof ink. At a minimum, each sample label includes station name and code, sample date, Lab ID, analysis required, and collector's initials.

It is critical that sample contamination be avoided during collection. All sampling equipment is composed of a non-contaminating material and is thoroughly cleaned before each use (Puckett

2002, Appendix D, MPSL SOP 1.3). Sampling personnel wear nitrile gloves whenever taking or processing samples to avoid contact contamination. In addition, airborne contamination is avoided by keeping sample containers appropriately covered when not in use. Sampling methods follow those outlined in the SWAMP QAPP.

Approximately 5 liters of water will be collected at each station. Two 2.5 liter amber glass bottles will be rinsed three times with site water and then filled by submerging both simultaneously below the surface to avoid collecting the surface microlayer. Both bottles will be filled simultaneously from the same spot so that all 5 liters will be considered a single composite sample for purposes of later splitting between chemistry and toxicity labs.

Approximately 2 liters of fine-grained sediment will be collected from depositional areas at each site. The surficial 5 cm of bedded sediments will be sampled using a polycarbonate core tube or polyethylene scoop either directly from the substrate or from a petite Ponar grab sampler. Core samples are taken by inserting the core into the sediment to the 5 cm mark, sealing the bottom by hand, and then removing from the sediment. Overlying water is gently poured off before the sediment section is placed in the sample container. Sediment will then be placed in an iced cooler for transport to UCD-MPSL.

Water toxicity tests will use the 10-d acute survival protocol for *Hyalella azteca* (U.S. EPA 2002, MPSL SOP 2.20) and/or the 4-d acute survival protocol for *Ceriodaphnia dubia* (U.S. EPA 2002, MPSL SOP 2.4). Sediment toxicity tests will use the 10-d growth and survival protocol for *Hyalella azteca* (U.S. EPA 2000, MPSL SOP 2.7).

If samples are found to be significantly toxic to test organisms, up to nine samples will undergo toxicity identification evaluations (TIEs). TIEs will be conducted to identify possible causes of toxicity, and may include recently developed methods for identifying pyrethroids.

MPSL water samples will be collected by hand. Sediment samples will be collected by hand, or from an inflatable boat utilizing a petite Ponar grab sampler. If any problems occur or difficulties are encountered, solutions will be devised in the field in coordination with the Project Manager.

Water and suspended samples will be collected by USGS and processed using the methods described in Leblanc and others (2004), and Smalling and others (2005). Briefly, samples will be collected from multiple points and depths along a stream transect using a high-volume peristaltic pump fitted with Teflon tubing. The collected water will be pumped into pre-cleaned 20-L stainless steel soda kegs. The volume collected will range from about 300 to 900 L, depending on suspended-sediment concentrations. The objective is to process a sufficient volume of water to obtain at least 20 grams of suspended sediment.

The water sample will be pumped through a Westphalia continuous-flow centrifuge operating at 9,500g at the rate of 2 L/min to segregate the liquid and solid phases and concentrate the suspended sediments ( $> 0.3 \mu\text{m}$ ) into a slurry. The centrifuge flow rate is based on a study of particle trapping efficiency by Horowitz and others (1989) who found that 2 L/min using the Westphalia centrifuge yields in the optimum particle trapping efficiency. The water exiting the

centrifuge represents the liquid phase and will be analyzed for dissolved pesticides. The sediment slurry remaining in the centrifuge will be further dewatered at the laboratory using a high-speed refrigerated centrifuge operating at 10,000 revolutions per minute. The segregated water and sediment samples will be stored at 4 °C and -20 °C, respectively prior to analysis.

**Table 5. (Element 11) Sampling methods summary**

Matrix	Analytical Parameter	Sampling SOP #	Sample Volume	Field Container	Subsample Container and Method	Maximum Holding Time: Preparation/analysis
Water	Trace Organics	SWAMP Appendix D	2.5 L for all analyses	I-Chem amber glass bottle	New 1000 mL I-Chem™, amber glass bottles with Teflon™ liner, certified trace organics clean by I-Chem™ and provided by UCD-MPSL. Fill with water to top, leave no head-space.	7 Days Refrigerated
	Toxicity				NA	48 Hours Refrigerated
Sediment	Trace Organics	SWAMP Appendix D	2L for all analyses	I-Chem glass wide-mouth jar	New 250 mL I-Chem™, wide-mouth, glass with Teflon™ liner, certified trace organics clean by I-Chem™ and provided by UCD-MPSL. Fill 2/3 full with sediments.	12 Months Frozen
	Trace Metals				New 250 mL I-Chem™, wide-mouth, polyethylene with Teflon™ liner, certified trace metal clean by I-Chem™ and provided by UCD-MPSL. Fill 3/4 full with sediments.	12 Months Frozen
	Toxicity				NA	14 Days Refrigerated
	Grain Size				New 250 mL I-Chem™, wide-mouth, polyethylene with Teflon™ liner, certified trace metal clean by I-Chem™ and provided by UCD-MPSL. Fill 3/4 full with sediments.	28 Days Refrigerated
	Total Organic Carbon				New 250 mL I-Chem™, wide-mouth, polyethylene with Teflon™ liner, certified trace metal clean by I-Chem™ and provided by UCD-MPSL. Fill 3/4 full with sediments.	12 Months Frozen
Tissue	Trace Organics and Benthic Community Analysis	SWAMP Appendix D		I-Chem glass wide-mouth jar	New 250 mL I-Chem™, wide-mouth, glass with Teflon™ liner, certified trace organics clean by I-Chem™ and provided by UCD-MPSL.	12 Months Frozen

## 12. SAMPLE HANDLING AND CUSTODY

Sample handling will follow MPSL SOP 1.5. All samples will be stored on wet ice immediately after collection (see Tables 6 and 7 for container and analyte list).

The samples are checked periodically to ensure that they are appropriately protected. Ice is added as required. Additionally, coolers containing wet ice are drained periodically to remove melt water.

A sample record is maintained in the laboratory sample log by UCD-MPSL for each site. The sample record contains the following information: station name, station number, Granite Canyon code, date sampled and received, time sampled, volume, and date removed. The log also contains a comments field to include information on conditions that could possibly influence sample analysis or data interpretation, or to note the general performance of sampling equipment.

The laboratory sample log and the chain of custody forms allow tracing of the complete history of a sample from time of collection to final entry of data in the database.

[illegible]

Samples will be shipped in insulated coolers. All caps and lids will be checked for tightness prior to shipping.

All samples will be handled, prepared, transported and stored in a manner so as to minimize bulk loss, analyte loss, contamination, or biological degradation. Sample containers will be clearly labeled with an indelible marker.

Ice chests are sealed with tape before shipping. Samples are placed in the ice chest with enough dry or wet ice to completely fill the ice chest. Forms are placed in an envelope and taped to the top of the ice chest or they may be placed in a plastic bag and taped to the inside of the ice chest lid. It is assumed that samples in tape-sealed ice chests are secure whether being transported by staff vehicle, by common carrier, or by commercial package delivery.

The receiving laboratory has a sample custodian who examines the samples for correct documentation, proper preservation and holding times. In this study, sample collection will be done by MPSL and USGS personnel, so samples will not change custody between field collection and laboratory storage. Sample temperature will not be checked, because transport time will be too short for sample temperatures to reach 4°C in the iced coolers. For all samples transported from MPSL to other labs, temperature will be checked at the receiving lab by pouring a small amount of sample into a beaker and immediately measuring with a thermometer.

Contract laboratories will follow sample custody procedures outlined in their QA plans. Contract laboratory QA plans are on file with the respective laboratory.

All samples remaining after successful completion of analyses will be disposed of properly only after written confirmation from the UCD-MPSL Project Manager that data have been received, reviewed and validated.

It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals.

Chain-of-custody procedures require that possession of samples be traceable from the time the samples are collected until completion and submittal of analytical results. A complete chain-of-custody form is to accompany the transfer of samples to the analyzing laboratory and to be forwarded to the UCD-MPSL Project Manager with the data reporting package.

For samples collected by USGS, each sample container will be labeled with a unique sample identification code that includes the date, location, and time the sample was collected. Samples will be stored in a cooler immediately after collection. The chests will contain sufficient ice to maintain sample temperature below 4°C until relinquished to analytical laboratory personnel.



**Table 6. (Element 12). Sample handling and custody**

Parameter	Container	Volume	Initial Preservation	Holding Time
Water Trace Organics	I-Chem™, amber glass bottles with Teflon™ liner, certified trace organics clean	1L	Temperature	7 Days Refrigerated
Water Toxicity	I-Chem amber glass bottle	2.5L	Temperature	48 Hours Refrigerated
Sediment Trace Organics	I-Chem™, wide-mouth, glass with Teflon™ liner, certified trace organics clean	250 mL	Temperature	12 Months Frozen
Sediment Trace Metals	I-Chem™, polyethylene jar with Teflon™ liner, certified trace metals clean	250 mL	Temperature	12 Months Frozen
Sediment Toxicity	I-Chem glass wide-mouth jar	2L	Temperature	14 Days Refrigerated
Sediment Grain Size	I-Chem™, polyethylene jar with Teflon™ liner, certified trace metals clean	250 mL	Temperature	28 Days Refrigerated
Sediment Total Organic Carbon	I-Chem™, polyethylene jar with Teflon™ liner, certified trace metals clean	250 mL	Temperature	12 Months Frozen

### 13. ANALYTICAL METHODS

All toxicity testing and laboratory and field water quality methods follow original SWAMP Standard Operating Procedures (SOPs). The SWAMP toxicity testing and water quality SOPs were written by the MPSL staff, and the MPSL staff maintains, updates, and distributes these SOPs for the SWAMP program. SOPs are available to the Contract Manager or designee on request. Current versions of these SOPs are posted on the SWAMP FTP site.

For samples analyzed by USGS:

Water samples will be analyzed for pesticides by extracting one liter of sample water onto Oasis HLB solid-phase extraction (SPE) cartridges. Prior to extraction, all water samples will be spiked with <sup>13</sup>C-atrazine, and <sup>13</sup>C-diazinon as recovery surrogates. The SPE cartridges will be dried with carbon dioxide, eluted with 12 mL of ethyl acetate, and deuterated internal standards will be added to the eluant. All sample extracts will be analyzed by gas chromatography-mass spectrometry (GC-MS). Additional details are given in Crepeau and others, 2000.

Sediment samples will be extracted based on modifications to methods described by LeBlanc et al. (2004) and Smalling et al. (2005). Briefly, sediment samples will be extracted using microwave-assisted solvent extraction (MASE) or Accelerated Solvent Extraction (ASE) with dichloromethane and acetone. Sample matrix will be removed using column chromatography with either packed Florisil or pre-packed Alumina/Carbon SPE cartridges, depending on the compound class. Finally, sulfur will be removed using a gel-permeation/high-pressure liquid

chromatography system (GPC/HPLC). Sample extracts will be analyzed for current-use pesticides by GC-MS, and legacy pesticides will be analyzed by gas chromatography/micro-electron capture detection (GC-ECD) with GC-MS confirmation. In addition, moisture content, percent organic carbon, and percent nitrogen will be measured for each sediment sample (Smalling and others, 2005). A sub-set of all sediment samples will be sent to the National Water Quality Laboratory for PAH analysis using Schedule 2505 (Olson and others, in press).

Fish and sand crab samples will be extracted using procedures described in Riedel and others (2002) with minor modifications. Briefly, approximately 5 grams weight tissue will be extracted with dichloromethane using a Dionex Model 200 accelerated solvent extractor (ASE) at 100 °C and 2000 psi. Extractable lipid on a wet-tissue basis will be determined gravimetrically on each sample to the nearest 0.001 g using a microbalance. Lipids and other interferences will be removed using GPC/HPLC followed by florisil packed column chromatography. All data will be normalized to total extractable lipids and will be reported on a µg/kg lipid weight basis in order to compare data between species.

All sample extracts (1 µL injection volume) will be analyzed using either a Varian Saturn 2000 gas chromatograph/mass spectrometer (GC/MS) with ion-trap detection or an Agilent 6890 gas chromatograph with a micro-electron capture detector (GC-µECD). Analyte separation on the GC/MS is achieved using a 30 m x 0.25 mm i.d. x 0.25 µm film thickness HP-5MS capillary column (Agilent Technology, Folsom, CA), with Helium as the carrier gas. The temperature of the injector is set at 275 °C, and the trap, manifold and transfer line temperatures are set at 220, 80, and 280 °C respectively. The GC oven program will be as follows: 80 °C (hold 0.5 min), ramp to 120 °C at 10 °C/min; , ramp to 200 °C at 3 °C/min (hold 5 min), ramp to 219 °C at 3 °C/min (hold 5 min), ramp to 300 °C at 10 °C/min (hold 10 min). Complete details of the analytical method are described in Crepeau et al. (2000) and LeBlanc et al. (2004). Analyte separation on the GC/µECD is achieved using a 30 m x 0.25 mm i.d. x 0.25 µm film thickness DB-XLB fused-silica capillary column (Agilent Technology, Folsom, CA), with helium as the carrier gas. The split/splitless injector and detector temperatures are 250 and 330 °C, respectively. The initial GC oven temperature of 75 °C (0.5 min. hold) is followed by an increase to 300 °C at 10 °C/min.

Expected laboratory turnaround times, from sample receipt to data availability, are as follows:

Water toxicity tests:	30 days
Sediment toxicity tests:	30 days
Organic chemistry:	4 months
Metals chemistry:	4 months
Sediment grain size:	30 days
Sediment TOC:	30 days
Benthic Analysis:	6 months

Sediment samples will be disposed of by the MPSL staff via drying sediments in dedicated containers at MPSL, transferring the dried sediment to plastic 55-gallon drums, and transporting them to the Monterey Regional landfill where they will be disposed of as non-hazardous waste. This is part of a continuing program with Monterey Regional that involves regular testing. Tissue samples will be disposed of through regular commercial waste pickup from MPSL and

USGS. Water samples will be disposed of in the MPSL water treatment system under general permit with the Central Coast Regional Water Quality Control Board.

**Table 7a. (Element 13) Toxicity testing parameters, methods, and reporting units**

Toxicity Tests (UCD-MPSL)	MPSL SOP	Method Reference	Reporting Units
Sediment Toxicity - <i>Hyalella azteca</i>	MPSL SOP 2.7	US EPA 600/R-99/064	
Amphipod Survival			%
Amphipod Growth			mg/individual
Water Toxicity - <i>Ceriodaphnia dubia</i>	MPSL SOP 2.4	US EPA 821-R-02-012	
Daphnid Survival			%
Water Toxicity - <i>Hyalella azteca</i>	MPSL SOP 2.20	US EPA 821-R-02-012	
Amphipod Survival			%
Water Quality	MPSL SOP 3.1-3.6		
QA/QC measures: precision and accuracy			%

**Table 7b. (Element 13) Sediment physical parameters, methods and reporting units**

Sediment Quality Parameters (AMS)	Methods	Reporting Units
% clay (<5 µm)	ASTM D422	% dry weight
% silt (5 µm – 74 µm )		% dry weight
% sand (74 µm - 2 mm)		% dry weight
% gravel (>2 mm)		% dry weight
Total Organic Carbon	US EPA 9060A	%

**Table 7c. (Element 13) List of compound with corresponding water and sediment method detection limits (MDLs). MDLs for tissue analysis will be developed as part of this project.**

<b>Compound</b>	<b>Water (ng/L)</b>	<b>Sediment (µg/kg)</b>	<b>Compound</b>	<b>Water (ng/L)</b>	<b>Sediment (µg/kg)</b>
<b>Anilines</b>			<b>Pyrethroids</b>		
Ethalfuralin	3.0	1.2	Allethrin	18.0	10.0 <sup>1</sup>
Pendamethalin	2.3	1.5	Bifenthrin	4.7	2.3
Trifluralin	2.1	1.1	Cyfluthrin	5.2	7.9
<b>Azoles/Triazoles</b>			Cypermethrin	5.6	5.6
Cyproconazole	11.2	4.0 <sup>1</sup>	Deltamethrin	3.5	1.1
Fipronil	2.9	1.0 <sup>1</sup>	Esfevalerate	3.9	1.8
Fipronil desulfinyl	1.6	1.0 <sup>1</sup>	Fenpropathrin	4.1	1.4
Fipronil sulfide	1.8	1.0 <sup>1</sup>	λ-Cyhalothrin	2.0	1.6
Fipronil sulfone	3.5	1.0 <sup>1</sup>	Permethrin	3.4	1.2
Metconazole	14.7	4.0 <sup>1</sup>	Resmethrin	5.7	5.9
Myclobutanil	9.2	4.0 <sup>1</sup>	Sumithrin	5.1	2.9
Propiconazole	8.8	4.0 <sup>1</sup>	τ-Fluvalinate	5.3	1.1
Tebuconazole	10.2	4.0 <sup>1</sup>	Tetramethrin	2.9	4.0 <sup>1</sup>
Tetraconazole	8.2	4.0 <sup>1</sup>	<b>Strobilurins</b>		
<b>Carbamates</b>			Azoxystrobin	9.3	10.0 <sup>1</sup>
Carbaryl	6.5	2.2	Pyraclostrobin	15.9	20.0 <sup>1</sup>
Carbofuran	3.1	5.3	Trifloxystrobin	3.9	4.0 <sup>1</sup>
<b>Chloroacetanilides</b>			<b>Thiocarbamates</b>		
Alachlor	1.7	1.4	Butylate	1.8	1.1
Metolachlor	1.5	1.7	Cycloate	1.1	0.8
<b>Organochlorines</b>			EPTC	1.5	1.4
Pentachloronitrobenzene	4.7	2.0 <sup>1</sup>	Molinate	3.2	0.6
Pentachloroanisole	3.1	2.0 <sup>1</sup>	Pebulate	2.3	0.9
p,p DDD	3.6	1.3	Thiobencarb	1.9	1.6
p,p DDE	4.1	1.5	<b>Triazines/Triazones</b>		
p,p DDT	4.0	1.9	Atrazine	2.3	1.7
<b>Organophosphates</b>			Hexazinone	8.4	2.3
Chlorpyrifos	2.1	0.8	Prometryn	1.8	1.9
Diazinon	0.9	0.6	Simazine	5.0	1.4
Malathion	3.7	2.2	<b>Miscellaneous</b>		
Methidathion	7.2	1.5	Chlorothalonil	12.1	4.0 <sup>1</sup>
Methylparathion	3.4	2.0	Dacthal (DCPA)	2.0	1.5
Phosmet	4.4	2.4	Iprodione	8.7	4.0 <sup>1</sup>
			Methoprene	15.6	4.0 <sup>1</sup>
			Napropamide	11.3	1.6
			Oxyfluorfen	3.1	2.5
			Piperonyl butoxide	2.3	1.3

<sup>1</sup> Limit of detection only (LOD)

**Table 7d. (Element 13) Limit of detection (LOD) for organochlorines analyzed only in sediment samples. MDLs for tissue analysis will be developed as part of this project.**

<b>Compound</b>	<b>LOD (µg/kg)</b>
α-Chlordane	1.0
α-HCH	1.0
Aldrin	1.0
β-HC	1.0
cis-Nonachlor	1.0
δ-HCH	1.0
Dieldrin	1.0
Endosulfan I	1.0
Endosulfan II	1.0
Endosulfan sulfate	1.0
Endrin	2.0
Endrin aldehyde	1.0
α-Chlordane	1.0
γ-HCH	1.0
Heptachlor	1.0
Heptachlor epoxide	1.0
Hexachlorobenzene	1.0
Isodrin	1.0
Methoxychlor	2.0
Oxychlordane	1.0
trans-Nonachlor	1.0

**Table 7e. (Element 13) Total Reporting Limits (TRL) for PAHs in sediment samples. TRLs for tissue analysis will be developed as part of this project.**

<b>PAH</b>	<b>TRL (µg/kg)</b>
Dibenz[a,h]anthracene	10
Chrysene	10
2-Methylanthracene	10
4H-	
Cyclopenta[def]phenanthrene	10
Fluorene	10
1-Methyl-9H-fluorene	10
Acenaphthene	10
Acenaphthylene	10
Anthracene	10
Benz[a]anthracene	10
Nitrobenzene-d5	0.1
Benzo[a]pyrene	10
Benzo[b]fluoranthene	10

Benzo[e]pyrene	10
Benzo[ghi]perylene	10
Benzo[k]fluoranthene	10
2-Fluorobiphenyl	0.1 pct
Fluoranthene	10
Indeno[1,2,3-cd]pyrene	10
Naphthalene	10
1,2-Dimethylnaphthalene	10
1,6-Dimethylnaphthalene	10
2,3,6-Trimethylnaphthalene	10
2,6-Dimethylnaphthalene	10
2-Ethylnaphthalene	10
Perylene	10
Phenanthrene	10
1-Methylphenanthrene	10
Pyrene	10
1-Methylpyrene	10
Terphenyl-d14	0.1 pct

**Table 7f. (Element 13) Reporting Limits (RL) and Detection Limits (DL) for trace metals in all samples (SJSUF).**

<u>H2O</u>		Ag	Al	As	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	Co
		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
	DL	0.01	4.00	0.3	0.01	0.1	0.02	0.01	0.03	0.003	0.2	0.05	
	RL	0.05	10	0.50	0.02	0.20	0.04	0.03	0.06	0.02	0.50	0.20	
<u>Tissue</u>		Ag	Al	As	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	Co
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
dry weight	DL	0.02	6.2	0.13	0.01	0.55	0.43	0.17	0.02	0.01	0.62	4.0	0.003
	RL	0.06	20	0.40	0.03	1.5	1.2	0.50	0.06	0.03	1.8	12.0	0.02
wet weight		0.003	1.0	0.02	0.002	0.10	0.07	0.03	0.003	0.002	0.10	0.70	
		0.01	3.0	0.06	0.006	0.30	0.20	0.10	0.010	0.006	0.30	2.00	
<u>Sediment</u>		Ag	Al	As	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
dry weight	DL	0.07	42	0.32	0.03	0.11	1.08	0.39	0.55	0.26	0.32	3.0	
	RL	0.20	125	1.0	0.10	0.30	3.0	1.0	1.5	0.75	1.0	9.0	

## 14. QUALITY CONTROL

**Table 8a. (Elements 14 and 16) Field analytical quality control and instrument calibration**

Parameter	Element 14 Quality Control	Element 16 Instrument Calibration Frequency
Conductivity	Accuracy and Precision <10%	Calibrate prior to first measurement. Standard verification at every station or every 10 samples.
Dissolved Oxygen	Accuracy and Precision <10%	Calibrate prior to first measurement. Standard verification at every station or every 10 samples.
pH	Accuracy and Precision <10%	Calibrate prior to first measurement. Standard verification at every station or every 10 samples.
Temperature	Accuracy and Precision <1%	Internal Instrument Calibration
Turbidity	Accuracy and Precision <1%	Internal Instrument Calibration

**Table 8b. (Elements 14 and 16) Laboratory analytical quality control and instrument calibration frequency**

Parameter	Element 14 Quality Control	Element 16 Instrument Calibration/Frequency
Toxicity testing in water and sediment	Reference toxicant and negative controls with each test. General water quality measurements – dissolved oxygen, pH, conductivity, and ammonia. All performance criteria outlined in method SOP.	All performance criteria outlined in method SOP.
Organic chemistry in water, sediment and tissue	Blanks – Laboratory and field blanks. No detectable amount of substance in blanks. Frequencies – Accuracy, precision, recovery, and blanks at 1 in 20 (5%) with at least one in every batch. <i>MDL study – prior to first use and annually thereafter. Procedure according to 40CFR Part 136.3 appendix B.</i> <i>Surrogate spike (similar structure or isotopically labeled) – determined by project manager.</i> All quality assurance and quality control procedures and criteria specified by selected method.	External calibration with 3 – 5 standards covering the range of sample concentrations prior to sample analysis. At low end, the lowest standard at or near the MDL. Linear regression $r^2 \leq 0.995$ Calibration verification every 10 samples after initial calibration. Standard source different that that used for initial calibration. Recovery 90% - 110%, except for mercury 85% - 115%.
Metal chemistry in water and sediment	Blanks – Laboratory and field blanks. No detectable amount of substance in blanks. Frequencies – Accuracy, precision, recovery, and blanks at 1 in 20 (5%) with at least one in every batch. <i>MDL study – prior to first use and annually thereafter. Procedure according to 40CFR Part 136.3 appendix B.</i> <i>Surrogate spike (similar structure or isotopically labeled) – determined by project manager.</i> All quality assurance and quality control procedures and criteria specified by selected method.	External calibration with 3 – 5 standards covering the range of sample concentrations prior to sample analysis. At low end, the lowest standard at or near the MDL. Linear regression $r^2 \leq 0.995$ Calibration verification every 10 samples after initial calibration. Standard source different that that used for initial calibration. Recovery 90% - 110%, except for mercury 85% - 115%.
Total organic carbon in sediment and sediment grain size	Blanks – no detectable amount or <30% of lowest sample. Frequency – Accuracy for TOC every 15 samples; Precision one per batch; LCM for TOC 1 in 20 (5%) with at least one in every batch.	No SWAMP requirements. Suggest follow manufacturer's requirements for TOC analyzer. Check weights for balances.

If control limits are exceeded for any of the parameters in Table 8a, all measurements taken since the last acceptable standard check will be discarded, and the samples will be re-measured.



Toxicity tests that do not meet the quality control requirements cited above will be repeated by the MPSL staff. Data from organic chemistry, TOC, and grain size analyses that do not meet control requirements will either be re-analyzed by the USGS staff, or will be flagged in the data base, on a sample by sample basis, by the QA Officer in consultation with the SWAMP QA Team and Data Management Team.

Effectiveness of these corrective actions will be determined by reviewing the results of quality assurance measurements (controls, standard reference materials, etc.) in the repeated analyses. Analyses will be repeated until QA criteria are met.

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

Sampling equipment and sample storage containers are cleaned and inspected in the laboratory by UCD-MPSL prior to the start of the sampling event following SWAMP procedures (Puckett 2002, Appendix D). Pre-cleaned items include sample collection jars and bottles and sediment collection core tubes. Core tubes are wrapped in new plastic bags until used in the field.

Laboratory instruments and equipment are inspected and maintained by UCD-MPSL laboratory personnel according to the manufacturer. Bryn Phillips, the Laboratory QA Officer, is responsible for equipment testing, inspection and maintenance. Testing, inspection and maintenance, and spare parts supply are conducted as described in the following SWAMP SOPs:

- 1.5 Standard Operating Procedure for Pipette Use
- 3.1 Standard Operating Procedure for Alkalinity Measurement
- 3.2 Standard Operating Procedure for Ammonia Measurement by Spectrophotometer
- 3.3 Standard Operating Procedure for ELISA Measurement of Diazinon and Chlorpyrifos
- 3.4 Standard Operating Procedure for HACH SensION 156 (includes DO, pH, conductivity)
- 3.5 Standard Operating Procedure for Hardness Measurement
- 3.6 Standard Operating Procedure for Refractometer Measurements
- 3.7 Standard Operating Procedure for Sulfide Measurement

All instruments and equipment have back-up components. If instruments do not pass inspection, back-up components are put in place. If it is determined that data have been recorded with faulty instruments the corrective action is to cross out the data on the data sheet, re-analyze the samples, and make a record of the occurrence.

## **16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY**

Laboratory instruments and equipment will be calibrated and maintained by MPSL staff, under direction of Bryn Phillips, according to laboratory protocol the following SWAMP SOPs. All calibrations and corrective actions are documented in logbooks for each instrument or piece of equipment.

- 1.5 Standard Operating Procedure for Pipette Use  
Pipette calibration is checked once per month. If they are out of calibration, they are sent in for factory service.
- 3.1 Standard Operating Procedure for Alkalinity Measurement  
Alkalinity standards are checked quarterly. If standards do not read correctly, the digital titrator is replaced.
- 3.2 Standard Operating Procedure for Ammonia Measurement by Spectrophotometer  
The spectrophotometer is factory calibrated. Standard reference materials are measured with each batch of samples. If standards do not read correctly, the instrument is serviced, and samples are re-analyzed.
- 3.3 Standard Operating Procedure for ELISA Measurement of Diazinon and Chlorpyrifos  
A calibration curve is created for every batch of samples and external standard reference materials are analyzed.
- 3.4 Standard Operating Procedure for HACH SensION 156 (includes DO, pH, conductivity)  
All electrodes are calibrated with every batch of samples. Precision and accuracy measurements are taken throughout the analysis. If precision or accuracy are greater than 10%, the batch of samples is re-analyzed.
- 3.5 Standard Operating Procedure for Hardness Measurement  
Hardness standards are checked quarterly. If standards do not read correctly, the digital titrator is replaced.
- 3.6 Standard Operating Procedure for Refractometer Measurements  
The refractometer is calibrated quarterly.
- 3.7 Standard Operating Procedure for Sulfide Measurement  
A calibration curve is created for every batch of samples.

For USGS instruments, initial calibration curves will be generated on each instrument (GC/MS and GC/ $\mu$ ECD) using standard solutions containing all of the target pesticides before sample analysis begins. Computer software will be used to generate linear regression equations for pesticide response over the concentration range of the calibration curve (0.025-5.0 ng/ $\mu$ L for GC/MS and 1-100 pg/ $\mu$ L for GC/ $\mu$ ECD). Calibration curves will be accepted when the correlation coefficient is greater than 0.99. Calibration will be checked frequently by analyzing standards throughout the sample analysis, but at the very least once every 8 hours during the sample analysis period. Pesticide quantification in the environmental samples will continue as long as the calibration curves are verified to be acceptable.

## **17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES**

Supplies and consumables that may be used in this project include reference toxicant chemicals for toxicity testing, test organisms for toxicity testing, bottles of known cleanliness for chemical analyses, etc. All supplies and containers used in this study will be either certified for cleanliness (e.g. I-Chem jars and reagents), or thoroughly inspected prior to use (e.g. sampling gloves and equipment). Laboratories will determine that all supplies and consumables comply with acceptance criteria outlined in their Standard Operating Procedures prior to conducting analyses. Supplies and consumables are inspected upon receipt. Those products deemed

unacceptable are returned to the vendor for replacement. Bryn Phillips, the Laboratory QA Officer, is responsible for inspection and acceptance of supplies and consumables.

## **18. NON-DIRECT MEASUREMENTS (EXISTING DATA)**

It is not anticipated that this study will use environmental measurements generated by other organizations.

## **19. DATA MANAGEMENT**

University of California, Davis Marine Pollution Studies Laboratory (UCD-MPSL) and each sub-contractor will be responsible for the study's data handling and storage. The data produced during this study will be managed following Surface Water Ambient Monitoring Program (SWAMP) protocols outlined in the SWAMP 2.5 Database Manual, and be held in a SWAMP compatible database at UCD-MPSL. All data are tracked through a contract task spreadsheet that is maintained by Bryn Phillips, MPSL QA Officer.

Chemistry and ancillary parameter data will be transferred to UCD-MPSL in Microsoft Excel spreadsheets and compiled into the database. Data will be reviewed to ensure that they are consistent with the format of the database and other data records. The UCD-MPSL database is backed up on a weekly basis.

Field measurements using data Sonde equipment will be used in this study. When field equipment is used by MPSL personnel, Bryn Phillips verifies that all raw data is kept in the original Sonde file (and stored on a PC); and that statistical endpoints are calculated at the lab after downloading and trimming records logged out of the water.

Raw data generated from TIEs will be stored in Excel files and included in the draft and final report. The SWAMP database is not formatted to accept the types of data generated from TIEs, as these data are not always standardized, and may require interpretation to be used properly. Data from TIEs will be provided in electronic (Excel) format according to established procedures at UCD-MPSL. These data will be discussed and interpreted in accompanying Microsoft Word text files. Original raw data sheets and duplicates of these are stored in separate locations at MPSL. Excel data files are stored as original and back-up electronic files. All data are compiled, analyzed, and transmitted by Bryn Phillips (UCD-MPSL), and Bryn Phillips is responsible for overall data quality review.

## **GROUP C: ASSESSMENT AND OVERSIGHT**

### **20. ASSESSMENTS & RESPONSE ACTIONS**

The UCD-MPSL Project Manager, John Hunt, and the Quality Assurance Officer, Bryn Phillips, will assure that sample collection is performed according to clean sampling methods described in the QAPP. QA/QC review of the reported results by UCD-MPSL will evaluate if DQOs have been met and possible corrective action may be warranted to ensure high quality data is produced.

If corrective action is warranted, after UCD-MPSL has performed QA/QC review of the monitoring data, a subcontracting analytical laboratory may be asked to re-analyze samples that did not meet expected DQOs. Archived samples, maintained by MPSL may be used to provide additional sample for reanalysis.

Assessment of routine laboratory quality control is made on a daily basis, with immediate resolution and corrective action for any discrepancies from targets. These routine quality control assessments include checks of refrigerator and constant temperature room temperatures, precision and accuracy of ancillary toxicity testing measurements (such as dissolved oxygen or pH), and culture conditions for test organisms. These routine QC assessments and corrections are made by laboratory staff under the supervision of Bryn Phillips.

Assessments of toxicity test acceptability are made by Bryn Phillips on the day that tests are completed. These include assessments of test control performance, variability among replicates, and acceptability of test conditions of temperature and dissolved oxygen. Corrective actions include repetition of toxicity tests having unacceptable control performance, and evaluation of test condition variation relative to test performance. For example, small test-wide exceedences of temperature ranges may be flagged, but the toxicity data used for the project, if control response is acceptable; as opposed to using minor fluctuations in test condition as cause to repeat the test. All such decisions will be made in consultation with the Project Manager.

Quarterly reports to the RWQCB Project Manager will include an update on project status and all quality assurance assessments. These reports will include the results of the assessments and summaries of any corrective actions taken. These reports will be prepared and submitted on the following approximate dates: January 30, 2008, April 30, 2008, July 30, 2008, October 30, 2008, January 30, 2009, April 30, 2009, July 30, 2009, and October 30, 2009.

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

Interim and final reports will be submitted by UCD-MPSL to the Project Manager at the RWQCB according to the schedule outline in the Agreement and listed in Element 6, Table 2. Reports will be written by John Hunt, with review by Brian Anderson and Bryn Phillips. The reports will be received by Mary Adams, who will distribute them to others in the Regional Water Quality Control Board who manages various aspects of agricultural management practice implementation and evaluation.

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

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

Data generated for the field monitoring component of this project will be reviewed by UCD-MPSL QA Officer, or designee, against the measurement quality objectives cited in Element 7 and the quality assurance/quality control practices cited in Elements 14, 15, 16, and 17. When warranted reanalysis of sample material may be requested of the labs or data will be qualified appropriately.

### **23. VERIFICATION AND VALIDATION METHODS**

All data generated by or received at UCD-MPSL will be processed by Bryn Phillips at UCD-MPSL. Data reporting formats and expectations are written into all sub-contracts. Cover letters and data reports must accompany each external data submission. The first phase of data validation is accomplished by the laboratories generating the data. Quality assurance requirements for each data set are reviewed and evaluated, and data are flagged accordingly if quality assurance requirements are not met. Data are further validated by Bryn Phillips prior to entry into the database. Standard SWAMP database qualifiers (Version 2.5) will be used to convey the quality of the data to the end users. Verification of data is accomplished by evaluating it for completeness, correctness, and conformance/compliance against the method, procedural, or contractual requirements. Issues regarding data verification will be identified by Bryn Phillips of MPSL, who will receive and review data from the USGS and AMS Laboratories, and Mary Adams who will receive and review data from MPSL. These issues will be resolved through discussions among the principles identified in Table 1. Resolution will include re-sampling or re-analysis of samples if data quality issues cannot be resolved at the data transfer or data base level.

All Reports will be sent to the RWQCB project manager.

### **24. RECONCILIATION WITH USER REQUIREMENTS**

The goal of this project is to provide rigorous baseline data to characterize the current condition of three central coast estuaries with regard to pesticide occurrence and impacts, and to gather and aggregate information about the effectiveness of individual management practices being implemented in each watershed, to allow an evaluation of change in condition over the next 5 to 20 years as management practices are implemented. The key to project success is measurement of contaminant concentrations and effects with sufficient spatial and temporal replication that significant differences can be detected between the current baseline study and similar studies conducted after widespread management practice implementation 5 to 20 years from now. Comparable data are not now available to conduct a power analysis of the detectable effect size, or the level of replication necessary to detect management-relevant effects as statistically significant. However, contaminant concentrations and effects in sediments, which tend to vary spatially, will be measured during three surveys at eight sites

in each of the small (~ 10 to 20 acre) estuaries to describe the mean and variance of sediment condition. Contaminant concentrations and effects in water, which tend to vary temporally, will be measured during 15 surveys at two sites in each of the estuaries to describe the mean and variance of water condition. It is expected, though it cannot presently be quantitatively predicted, that this level of replication will allow statistical detection of a 20% difference in contaminant concentrations and effects. User requirements for detectable change also cannot be quantified. However, discussions with many resource managers have indicated that Regional Board managers would be willing to adapt and modify policies based on an observed 20% change in environmental condition. This project is designed to produce the level of statistical power to provide resource managers with the feedback they need to employ an adaptive management approach to watershed protection. Data will be interpreted in comprehensive reports aimed at giving farmers, technicians, and resource managers the information needed to evaluate and adapt MP program performance. Reports will focus on presenting data in a format most useful for follow-up assessments to detect change over time.

Data verification will be conducted by the Project QA Officer according to the SWAMP process for checking that data are present, accurately transcribed and properly calculated; and that the QC samples are analyzed at the correct frequency and meet the method/project criteria. The data will be validated by comparing them to project Data Quality Objectives. Data that do not meet QA requirements will be flagged according to SWAMP procedure before being submitted to the SWAMP database. All project data will be submitted in appropriate SWAMP format for inclusion in the CEDEN system to make it available to the general public and scientific community.

## REFERENCES

LeBlanc, L.A., Schroeder, R.A., Orlando, J.L. and Kuivila, K.A., 2004, Occurrence, distribution and transport of pesticides, trace elements and selected inorganic constituents into the Salton Sea Basin, California, 2001-2002. U.S. Geological Survey Scientific Investigations Report 2004-5117, 40 p.

Puckett, M. 2002. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program (SWAMP). California Department of Fish and Game, Monterey, CA. Prepared for the State Water Resources Control Board, Sacramento, CA. 145 pages plus Appendices.

Smalling, K.L., Orlando, J.L. and Kuivila, K.M., 2005, Analysis of pesticides in surface water and sediment from Yolo Bypass, California, 2004-2005, U.S. Geological Survey Scientific Investigations Report 2005-5220, 20p.

U.S. Environmental Protection Agency. 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. Office of Research and Development. EPA 600-R-99-096, Washington, DC, USA

U.S. Environmental Protection Agency. 2002. Methods for measuring the acute toxicity of effluents and receiving water to freshwater and marine organisms. Office of Research and Development. EPA-821-R-02-012, Washington, DC, USA

## **APPENDIX A: MONITORING PLAN**

### *MONITORING PLAN*

**AGREEMENT NUMBER:** 06-352-553-0

**PROJECT NAME:** Watershed-scale Evaluation of Agricultural BMP Effectiveness Protecting Critical Coastal Habitats

**Principal Investigator:** Ron Tjeerdema (University of California Davis)

**Project Grant Manager:** Mary Adams (Central Coast Regional Water Quality Control Board)

November 14, 2007



## FIELD MONITORING PLAN

**AGREEMENT NUMBER:** 06-352-553-0

**PROJECT NAME:** Watershed-scale Evaluation of Agricultural BMP Effectiveness Protecting Critical Coastal Habitats

**Principal Investigator:** Ron Tjeerdema (University of California Davis)

**Project Grant Manager:** Mary Adams (Central Coast Regional Water Quality Control Board)

**Project Manager:** John Hunt (UCD-GCML)

This field monitoring plan covers work to be performed under Contract Tasks 2 through 5:  
Field Sampling and Analysis of Estuaries and Tributaries.

### OBJECTIVE

The objective of this project is to provide a scientific, statistically rigorous baseline assessment to support future evaluations of the watershed-wide effectiveness of BMP implementation.

### APPROACH

The Pajaro, Salinas, and Santa Maria River estuaries will be monitored over a two-year period to determine organic pollutant loadings from the main rivers and adjacent tributaries, and to measure chemical concentrations in estuarine water, sediment, and biota. Biological measurements at the molecular, organismal, and community levels will be measured synoptically to determine associations with contaminants. Each estuary will be sampled using a proportional design with sufficient numbers of sites and surveys to allow detection of the change expected to occur as BMPs are implemented over time (20 to 50% indicator change). Samples will be collected during three storm events, and during multiple dry season surveys. Measurements will include pyrethroid, OP, and OC pesticides, as well as PCBs, PAHs, and metals. Endocrine disruption will be measured in resident fish, toxicity will be measured in water and sediment, and estuarine benthic communities will be assessed.

### PROJECT FUNDING

This project is funded by the Consolidated Grants Program of the California State Water Resources Control Board.

### BACKGROUND

Coastal estuaries are among the most ecologically important and critically threatened habitats in California. Along California's Central Coast, the three largest watersheds drain to coastal estuaries that provide essential habitat for early life stages of commercial marine fish species, threatened anadromous fish species, migratory birds, and other wildlife. Each of these watersheds contains year-round, intensively cultivated agricultural land that supports a \$5 billion/year industry producing most of the nation's lettuce, artichokes, and crucifer crops. Farm groups are initiating management practices to control pesticide runoff, but there is currently no designated effort to document the cumulative loading and effects of pesticides in these coastal estuaries.

## WORK PLAN

This project will include execution of the following tasks:

1. Stakeholders Data Exchange on Individual and Cumulative Management Practices (MP) Effectiveness.
2. Estuary Field Sampling
3. Analysis of Estuarine Samples
4. Field Sampling in Tributaries to the Estuaries
5. Analysis of Samples from Tributaries to the Estuaries
6. Data Management
7. Data Analysis and Interpretation

Task 1 will be performed by all participating parties. Tasks 2 through 5 will be performed by UC Davis and USGS. Task 6 will be performed by UC Davis. Task 7 will be performed by UC Davis and USGS.

Table 1. List of Participants

Project management and coordination with conservation practice implementation	Central Coast Regional Water Quality Control Board
Sample collection and toxicity testing	UC Davis Marine Pollution Studies Laboratory
Organic Chemistry	United States Geological Survey (USGS)
Metals Chemistry	San Jose State University Foundation (SJSUF)
Benthic Community Analysis	Weston Solutions, Inc (WSI)
Sediment Physical Parameters	Applied Marine Sciences (AMS)

## Sampling, toxicity testing, and chemical analysis strategy

Samples are to be collected during twelve dry events and three storm events. A storm event will be defined as a minimum half-inch precipitation in the watershed. Quality assurance duplicates will be collected randomly throughout the fifteen events. Sampling strategy, number of samples and various analyses are summarized in Table 2.

### Estuary Field Sampling and Analysis

Sampling locations in each estuary will be chosen based on proportional placement within suitable habitat for each measurement. Sediment collection sites in depositional, brackish water

areas and water collection sites in well-mixed brackish water areas. Two locations will be chosen for water sample collection and eight locations will be chosen for sediment collection.

Estuarine water samples will be collected during every event.

- Field analysis on these samples will include measurements of dissolved oxygen, pH, conductivity/salinity, temperature, and turbidity.
- Toxicity will be analyzed with *Hyalella azteca*, and if conductivities are suitably low, with *Ceriodaphnia dubia*. Laboratory water quality measurements will include dissolved oxygen, pH, conductivity/salinity, hardness, alkalinity, nitrate, and phosphate.
- Chemical analysis will include current use and legacy pesticides, and dissolved organic carbon.

Estuarine sediment will be collected during two (2) dry events and one (1) storm event.

- Toxicity will be analyzed with *Hyalella azteca*, and laboratory water quality measurements will include dissolved oxygen, pH, conductivity/salinity, hardness, and alkalinity.
- Chemical analysis will include current use and legacy pesticides, metals, polycyclic aromatic hydrocarbons, and total organic carbon.
- Physical analysis will include grain size.
- Collection and analysis of benthic invertebrates will occur at five stations during two dry events.

Fish and sand crab specimens will be collected in brackish and marine areas during two (2) dry events.

- Chemical analysis of fish and crabs will include current use and legacy pesticides, metals, and polycyclic aromatic hydrocarbons.
- Physiological metabolic indicators (metabolomics) and endocrine disruption (vitellogenin) will be measured on fish.

### **Tributary Field Sampling and Analysis**

Sampling locations in two tributaries will be located at public crossings near each estuary. These will include the main stems of the Pajaro, Salinas, and Santa Maria Rivers, as well as at least one (1) other tributary proximate to each estuary, including the Monterey Drainage Ditch, Beach Road Drain, the Blanco Drain, and Orcutt Creek.

Tributary water samples are to be collected during six (6) dry season events and three (3) storm events.

- Field analysis on these samples will include measurements of dissolved oxygen, pH, conductivity/salinity, temperature, and turbidity.
- Toxicity will be analyzed with *Ceriodaphnia dubia* or *Hyalella azteca*, depending on the conductivity of the samples. Laboratory water quality measurements will include dissolved oxygen, pH, conductivity/salinity, hardness, alkalinity, nitrate, and phosphate.
- Chemical analysis will include current use and legacy pesticides, and dissolved organic carbon.

Tributary sediment samples are to be collected during two (2) dry season events and one (1) storm events.

- Toxicity will be analyzed with *Hyalomma azteca*, and laboratory water quality measurements will include dissolved oxygen, pH, conductivity/salinity, hardness, and alkalinity.
- Chemical analysis will include current use and legacy pesticides, metals, polycyclic aromatic hydrocarbons, and total organic carbon.
- Physical analysis will include grain size.

Suspended sediment samples at each tributary are to be collected during three (3) storm events, using a high-volume pump and flow-through centrifuge.

- Chemical analysis will include current use and legacy pesticides, and dissolved organic carbon.

Toxicity identification evaluations (TIEs) will be conducted on a minimum of six (6) bed sediment samples and three (3) water samples, to identify chemicals causing observed toxicity.

Sufficient samples will be collected to conduct duplicate analyses on ten percent (10%) of all samples to determine measurement precision, according to the QAPP.

All sampling and analysis will be conducted according to the project Quality Assurance Project Plan, which is based on and compliant with the Quality Assurance Management Plan for the California Surface Water Ambient Monitoring Program (SWAMP).

Table 2a. Activity matrix key

Water Tasks (W)	Sediment Tasks (S)	Biology Tasks (F, C, B)	Suspended Tasks (X)
<b>Field Tasks:</b> Toxicity sample collection Chemistry sample collection SSC sample collection WQ: DO, pH, T, Turb, Cond	<b>Field Tasks:</b> Toxicity sample collection Chemistry sample collection GS sample collection	<b>Field Tasks:</b> Fish collection (F) Sand Crab collection (C) Benthic Collection (B)	<b>Field Tasks:</b> Collect suspended sediment Collect water
<b>Toxicity Analysis:</b> <i>Hyalomma azteca</i> and/or <i>Ceriodaphnia dubia</i> NO3, PO4, Hard, Alk	<b>Toxicity Analysis:</b> <i>Hyalomma azteca</i> Hard, Alk	<b>Laboratory Analysis:</b> Fish dissection Metabolomics and VTG	
<b>Chemistry Analysis:</b> DOC Pesticides	<b>Chemistry Analysis:</b> TOC Pesticides Metals PAHs	<b>Chemistry Analysis:</b> Pesticides Metals PAHs	<b>Chemistry Analysis:</b> DOC Pesticides

Table 2b. Activity matrix

Event	Dry 1	Dry 2	Dry 3	Dry 4	Dry 5	Dry 6	Dry 7	Dry 8	Dry 9	Dry 10	Dry 11	Dry 12	Storm 1	Storm 2	Storm 3	QA 1	QA 2	QA 3	Totals					
	W	W	WFC	W	W	SW	W	W	WFC	W	W	SW	W	W	SW	W	WFC	W	W	S	F	C	B	X
Santa Maria 1	W	W	WFC	W	W	SW	W	W	WFC	W	W	SW	W	W	SW	W	WFC	W	33	26	3	3	11	0
Santa Maria 2	W	W	W	W	W	SW	W	W	W	W	W	SW	W	W	SW	S	S							
Santa Maria 3						S						S			S	B								
Santa Maria 4						SB						SB			S	S								
Santa Maria 5						SB						SB			S	S								
Santa Maria 6						SB						SB			S	S								
Santa Maria 7						SB						SB			S	S								
Santa Maria 8						SB						SB			S	S								
Salinas 1	W	W	WFC	W	W	SW	W	W	WFC	W	W	SW	W	W	SW	W	W	W	33	26	2	2	11	0
Salinas 2	W	W	W	W	W	SW	W	W	W	W	W	SW	W	W	SW	S	S							
Salinas 3						S						S			S	B								
Salinas 4						SB						SB			S	S								
Salinas 5						SB						SB			S	S								
Salinas 6						SB						SB			S	S								
Salinas 7						SB						SB			S	S								
Salinas 8						SB						SB			S	S								
Pajaro 1	W	W	WFC	W	W	SW	W	W	WFC	W	W	SW	W	W	SW	W	W	W	33	26	2	2	11	0
Pajaro 2	W	W	W	W	W	SW	W	W	W	W	W	SW	W	W	SW	S	S							
Pajaro 3						S						S			S	B								
Pajaro 4						SB						SB			S	S								
Pajaro 5						SB						SB			S	S								
Pajaro 6						SB						SB			S	S								
Pajaro 7						SB						SB			S	S								
Pajaro 8						SB						SB			S	S								
Total													99	78	7	7	33	0						
SM Main	W	W	W	W	SW	W	W	W	W	W	W	SW	WX	SWX	WX	W	W		20	6	0	0	0	6
Orcutt	W	W	W	W	SW	SW	W	W	W	W	W	SW	WX	SWX	WX									
Salinas Main	W	W	W	W	SW	SW	W	W	W	W	W	SW	WX	SWX	WX	W	W		20	6	0	0	0	6
Blanco	W	W	W	W	SW	SW	W	W	W	W	W	SW	WX	SWX	WX									
Pajaro Main	W	W	W	W	SW	SW	W	W	W	W	W	SW	WX	SWX	WX	W	W		19	6	0	0	0	6
Beach St	W	W	W	W	SW	SW	W	W	W	W	W	SW	WX	SWX	WX				59	18	0	0	0	18
Total													59	18	0	0	0	18						

### **Sampling and Sample Handling**

Sample collection, sample handling, and laboratory methods will be the same as those employed by the California Surface Water Ambient Monitoring Program (SWAMP) using SWAMP protocols. Methods for collection of field samples and sample handling are further outlined in the project QAPP (attached).

### **Sampling Equipment**

Water samples will be collected in one-liter or 2.5 amber glass bottles, cleaned according to the SWAMP comparable protocols described in the project QAPP (attached). Sediment samples will be collected directly from the substrate or from a petite Ponar grab sampler using polycarbonate core tubes or polyethylene scoops. Separate core tubes or scoops will be used for each site. Sediment will be immediately transferred to either two-liter glass jars or polyethylene-lined plastic buckets for standard testing. All materials that come into contact with the samples will be cleaned according to the SWAMP comparable protocols described in the project QAPP (attached).

### **Toxicity Tests**

Water samples will be tested for toxicity using the 10-d survival protocol for *Hyalella azteca* (U.S. EPA 2002) and/or the 4-d acute survival protocol for *Ceriodaphnia dubia* (U.S. EPA 2002). Tests will follow standard EPA protocol, as described in the attached QAPP. Sediment samples will be tested using the 10-d growth and survival protocol for *Hyalella azteca* (U.S. EPA 2000). Endpoints and reporting units for both protocols are summarized in Table 2.

Toxicity identification evaluations (TIEs) will be performed on selected water and sediment samples that exhibit substantial toxicity. TIEs will be conducted to identify possible causes of toxicity including using methods developed to date for identifying pyrethroids.

### **Sediment Quality Parameters**

Sediment samples will be analyzed for grain size distribution and total organic carbon. Parameters and reporting units are summarized in Table 3.

### **Chemical Analyses**

The two OP pesticides diazinon and chlorpyrifos will be measured using enzyme-linked immunosorbent assays (ELISAs) according to specifications described in the project QAPP (attached). The ELISA reporting limits are 100 ng/L for chlorpyrifos and 60 ng/L for diazinon. The organophosphate, organochlorine, and carbamate pesticides to be measured in water are listed in Table 4.

Organochlorine and pyrethroid pesticides to be measured in sediment are listed in Tables 4 and 5. All chemical analyses will be accompanied by performance based quality assurance measures according to SWAMP protocols.

Table 3. Toxicity test and sediment quality parameters and reporting units.

Toxicity Tests (UCD-MPSL)	Reporting Units	Sediment Quality Parameters (AMS)	Reporting Units
Sediment Toxicity - <i>Hyalella azteca</i>		% clay (<5 µm)	% dry weight
Amphipod Survival	%	% silt (5 µm – 74 µm )	% dry weight
Amphipod Growth	mg/individual	% sand (74 µm - 2 mm)	% dry weight
Water Toxicity - <i>Ceriodaphnia dubia</i>		% gravel (>2 mm)	% dry weight
Daphnid Survival	%		
Daphnid Reproduction	young/individual	Total Organic Carbon	%
Water Quality			
QA/QC measures: precision and accuracy	%		

Table 4. List of compound with corresponding water and sediment method detection limits (MDLs). MDLs for tissue analysis will be developed as part of this project.

Compound	Water (ng/L)	Sediment (µg/kg)	Compound	Water (ng/L)	Sediment (µg/kg)
<b>Anilines</b>			<b>Pyrethroids</b>		
Ethalfuralin	3.0	1.2	Allethrin	18.0	10.0 <sup>1</sup>
Pendamethalin	2.3	1.5	Bifenthrin	4.7	2.3
Trifluralin	2.1	1.1	Cyfluthrin	5.2	7.9
<b>Azoles/Triazoles</b>			Cypermethrin	5.6	5.6
Cyproconazole	11.2	4.0 <sup>1</sup>	Deltamethrin	3.5	1.1
Fipronil	2.9	1.0 <sup>1</sup>	Esfevalerate	3.9	1.8
Fipronil desulfinyl	1.6	1.0 <sup>1</sup>	Fenpropathrin	4.1	1.4
Fipronil sulfide	1.8	1.0 <sup>1</sup>	λ-Cyhalothrin	2.0	1.6
Fipronil sulfone	3.5	1.0 <sup>1</sup>	Permethrin	3.4	1.2
Metconazole	14.7	4.0 <sup>1</sup>	Resmethrin	5.7	5.9
Myclobutanil	9.2	4.0 <sup>1</sup>	Sumithrin	5.1	2.9
Propiconazole	8.8	4.0 <sup>1</sup>	τ-Fluvalinate	5.3	1.1
Tebuconazole	10.2	4.0 <sup>1</sup>	Tetramethrin	2.9	4.0 <sup>1</sup>
Tetraconazole	8.2	4.0 <sup>1</sup>	<b>Strobilurins</b>		
<b>Carbamates</b>			Azoxystrobin	9.3	10.0 <sup>1</sup>
Carbaryl	6.5	2.2	Pyraclostrobin	15.9	20.0 <sup>1</sup>
Carbofuran	3.1	5.3	Trifloxystrobin	3.9	4.0 <sup>1</sup>
<b>Chloroacetanilides</b>			<b>Thiocarbamates</b>		
Alachlor	1.7	1.4	Butylate	1.8	1.1
Metolachlor	1.5	1.7	Cycloate	1.1	0.8
<b>Organochlorines</b>			EPTC	1.5	1.4
Pentachloronitrobenzene	4.7	2.0 <sup>1</sup>	Molinate	3.2	0.6
Pentachloroanisole	3.1	2.0 <sup>1</sup>	Pebulate	2.3	0.9
p,p DDD	3.6	1.3	Thiobencarb	1.9	1.6
p,p DDE	4.1	1.5	<b>Triazines/Triazones</b>		
p,p DDT	4.0	1.9	Atrazine	2.3	1.7
<b>Organophosphates</b>			Hexazinone	8.4	2.3
Chlorpyrifos	2.1	0.8	Prometryn	1.8	1.9
Diazinon	0.9	0.6	Simazine	5.0	1.4
Malathion	3.7	2.2	<b>Miscellaneous</b>		

Methidathion	7.2	1.5	Chlorothalonil	12.1	4.0 <sup>1</sup>
Methylparathion	3.4	2.0	Dacthal (DCPA)	2.0	1.5
Phosmet	4.4	2.4	Iprodione	8.7	4.0 <sup>1</sup>
			Methoprene	15.6	4.0 <sup>1</sup>
			Napropamide	11.3	1.6
			Oxyfluorfen	3.1	2.5
			Piperonyl butoxide	2.3	1.3

<sup>1</sup> Limit of detection only (LOD)

Table 5. Limit of detection (LOD) for organochlorines analyzed only in sediment samples. LODs for tissue analysis will be developed as part of this project.

<b>Compound</b>	<b>LOD (µg/kg)</b>
α-Chlordane	1.0
α-HCH	1.0
Aldrin	1.0
β-HC	1.0
cis-Nonachlor	1.0
δ-HCH	1.0
Dieldrin	1.0
Endosulfan I	1.0
Endosulfan II	1.0
Endosulfan sulfate	1.0
Endrin	2.0
Endrin aldehyde	1.0
α-Chlordane	1.0
γ-HCH	1.0
Heptachlor	1.0
Heptachlor epoxide	1.0
Hexachlorobenzene	1.0
Isodrin	1.0
Methoxychlor	2.0
Oxychlordane	1.0
trans-Nonachlor	1.0



Table 6. Total Reporting Limits (TRL) for PAHs in sediment samples. TRLs for tissue analysis will be developed as part of this project.

<b>PAH</b>	<b>TRL (µg/kg)</b>
Dibenz[a,h]anthracene	10
Chrysene	10
2-Methylanthracene	10
4H- Cyclopenta[def]phenanthrene	10
Fluorene	10
1-Methyl-9H-fluorene	10
Acenaphthene	10
Acenaphthylene	10
Anthracene	10
Benz[a]anthracene	10
Nitrobenzene-d5	0.1
Benzo[a]pyrene	10
Benzo[b]fluoranthene	10
Benzo[e]pyrene	10
Benzo[ghi]perylene	10
Benzo[k]fluoranthene	10
2-Fluorobiphenyl	0.1 pct
Fluoranthene	10
Indeno[1,2,3-cd]pyrene	10
Naphthalene	10
1,2-Dimethylnaphthalene	10
1,6-Dimethylnaphthalene	10
2,3,6-Trimethylnaphthalene	10
2,6-Dimethylnaphthalene	10
2-Ethylnaphthalene	10
Perylene	10
Phenanthrene	10
1-Methylphenanthrene	10
Pyrene	10
1-Methylpyrene	10
Terphenyl-d14	0.1 pct

Table 7. Reporting Limits (RL) and Detection Limits (DL) for trace metals in all samples (SJSUF)

<b><u>H2O</u></b>		<b>Ag</b>	<b>Al</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Mn</b>	<b>Ni</b>	<b>Pb</b>	<b>Se</b>	<b>Zn</b>	<b>Co</b>
	<b>DL</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>
	<b>RL</b>	<b>0.01</b>	<b>4.00</b>	<b>0.3</b>	<b>0.01</b>	<b>0.1</b>	<b>0.02</b>	<b>0.01</b>	<b>0.03</b>	<b>0.003</b>	<b>0.2</b>	<b>0.05</b>	
		<b>0.05</b>	<b>10</b>	<b>0.50</b>	<b>0.02</b>	<b>0.20</b>	<b>0.04</b>	<b>0.03</b>	<b>0.06</b>	<b>0.02</b>	<b>0.50</b>	<b>0.20</b>	
<b><u>Tissue</u></b>		<b>Ag</b>	<b>Al</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Mn</b>	<b>Ni</b>	<b>Pb</b>	<b>Se</b>	<b>Zn</b>	<b>Co</b>
		<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>
<b>dry weight</b>	<b>DL</b>	0.02	6.2	0.13	0.01	0.55	0.43	0.17	0.02	0.01	0.62	4.0	0.003
	<b>RL</b>	<b>0.06</b>	<b>20</b>	<b>0.40</b>	<b>0.03</b>	<b>1.5</b>	<b>1.2</b>	<b>0.50</b>	<b>0.06</b>	<b>0.03</b>	<b>1.8</b>	<b>12.0</b>	<b>0.02</b>
<b>wet weight</b>		0.003	1.0	0.02	0.002	0.10	0.07	0.03	0.003	0.002	0.10	0.70	
		0.01	3.0	0.06	0.006	0.30	0.20	0.10	0.010	0.006	0.30	2.00	
<b><u>Sediment</u></b>		<b>Ag</b>	<b>Al</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Mn</b>	<b>Ni</b>	<b>Pb</b>	<b>Se</b>	<b>Zn</b>	
		<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	
<b>dry weight</b>	<b>DL</b>	0.07	42	0.32	0.03	0.11	1.08	0.39	0.55	0.26	0.32	3.0	
	<b>RL</b>	<b>0.20</b>	<b>125</b>	<b>1.0</b>	<b>0.10</b>	<b>0.30</b>	<b>3.0</b>	<b>1.0</b>	<b>1.5</b>	<b>0.75</b>	<b>1.0</b>	<b>9.0</b>	

## **APPENDIX B: RELATED STUDIES**

### **CENTRAL COAST AGRICULTURAL WAIVER MONITORING**

Contact: Alison Jones ([ajones@waterboards.ca.gov](mailto:ajones@waterboards.ca.gov))

### **TMDL DEVELOPMENT FOR SANTA MARIA RIVER AND ORCUTT CREEK**

Contact: Katie McNeill ([kmcneill@waterboards.ca.gov](mailto:kmcneill@waterboards.ca.gov))

### **CENTRAL COAST AMBIENT MONITORING PROGRAM (CCAMP)**

Contact: Karen Worcester ([kworcester@waterboards.ca.gov](mailto:kworcester@waterboards.ca.gov))

### **RCD MONTEREY COUNTY VEGETATED TREATMENT SYSTEM EVALUATION**

Contact: Emily Hanson ([emily.hanson@rcdmonterey.org](mailto:emily.hanson@rcdmonterey.org))

## **APPENDIX C: DESCRIPTION OF QUALITY ASSURANCE/QUALITY CONTROL, AND REPORTING EXPECTATIONS**

### **Quality Assurance and Quality Control**

This study will employ similar laboratory methodologies as SWAMP, which is a performance-based program. Laboratories will use current SWAMP laboratory methods unless new methods are discussed, warranted, and approved by the project manager (or designee). Laboratories will review the SWAMP Quality Assurance Project Plan (QAPP).

All scientific activities undertaken by laboratories must adhere to quality assurance and quality control (QA/QC) procedures as developed in the QAPP. This will include requirements for documenting chain of custody for samples, proper sample storage and holding times, data validation methods, and analysis of quality control samples, laboratory blanks and spikes, laboratory replicates, and standard reference materials (when available). Laboratories will be required to provide concise and complete reports of analyses of quality control samples to verify that Measurement quality objectives (DQOs) are being met. If DQOs are not being met, re-analysis of samples may be necessary.

### **Reporting of Results**

Laboratory personnel will verify, screen, validate, and prepare all data, including QA/QC results, in accordance with the SWAMP QAPP and will provide (upon request) detailed QA/QC documentation that can be referred to for an explanation of any factors affecting data quality or interpretation. Any detailed QA/QC data not submitted as part of the reporting package (see below) should be maintained in the laboratory's database for future reference.

Laboratories will provide electronic copies of the cover letter and tabulated analytical data (including associated QA/QC information outlined below) in the SWAMP database format or a format agreed upon with the UCD-MPSL Project/Data Manager or designee.

### **Each electronic data report package will consist of the following components:**

1. A cover letter (electronic copy) transmitting the data report package. The following topics will be addressed in the narrative:
  - a. Identify Samples: Include the contract number, study, sample dates, matrix, and total number of field samples being submitted. Note if any of the contracted number of samples were not analyzed for any reason. Include a list of the type of QA samples included in the report package.
  - b. Clarify linkage between field samples and QA: Provide a list of which QA samples are associated with each set of field samples. Be sure to say if the QA samples are associated by batch or cruise
  - c. Summarize Methods used: Provide a short summary of the procedures and instrumentation used, including:
    - i. Pre-prep, extraction, and quantification methods (reference EPA methods where applicable). Include electronic copies of your SOPs with your data submission package.
    - ii. Type and frequency of QA samples run (e.g. blank, duplicate, matrix spike, SRMs). Include: (1) concentrations used for spiked samples or equivalent, and (2) concentration range used for generating instrument calibration curves. (Note: You may choose to reference the location of this information in the expanded report.)
    - iii. Sample size extracted and what units you are reporting the data in.
    - iv. Indicate if the data have been recovery corrected and if the MDLs were adjusted for sample size extracted. Also indicate if the data are reported in wet or dry weight.
    - v. PROVIDE DATA THAT HAVE NOT BEEN BLANK CORRECTED and clearly identify all blank samples that would be used to blank correct each sample batch. State that the data were not blank corrected in the cover letter and list those parameters that should be blank corrected prior to data usage.

- vi. A list of qualifier definitions.
  - d. Report on the QA/QC: Do the results meet the measurement quality objectives (DQOs) outlined in Tables 3 and 4 of the 1999 QAPP? Provide a brief summary table of precision, accuracy, and blank sample concentrations and explain any analytical problems and/or corrective actions taken. Examples of items to include are:
    - i. An explanation of any analyte accuracy and recovery calculations that were outside DQOs outlined in the QAPP.
    - ii. Any contamination of the blanks.
    - iii. Any analyte concentrations that were outside calibrated range.
    - iv. Lost/broken samples.
2. Tabulated electronic results in SWAMP database format unless another format is agreed upon with the project manager. Tabulated data will include the following information for each sample (when applicable):
- a. Sample identification: Unique sample-ID (provided on the COC and available electronically upon request - contact MPSL's Project/Data Manager), site code, site name, collection date, analysis date/s, sample type (field sample or QA/QC), matrix (water, sediment, tissue (include species))
  - b. Analytical methods: pre-prep., extraction, and quantification methods (codes should reference to SOPs submitted with the data submission package).
  - c. Analytical results: Parameter name, result, unit, and method detection limit (MDL) for all target parameters (see Table 1 for naming convention and reporting units). When applicable, state whether the results are reported in wet or dry weight, and submit the appropriate QA/QC data qualifiers with the results.
  - d. Required additional data include:
    - i. % solids
    - ii. Control results (for toxicity tests)
    - iii. Field and lab replicate results
    - iv. Quality assurance information for each analytical chemistry batch:
      - 1. SRM results, absolute concentrations measured, certified value, and % recovery relative to certified value.
      - 2. Matrix spike results (or similar samples): include target amount spiked for each analyte, actual recovery concentrations, and calculated % recovery.
      - 3. Method blank sample results in units equivalent to field sample results (e.g. if the field samples are reported as ng/g, method blanks are given in the same units). Clearly identify those samples recommended for blank correcting the results.
      - 4. Field and lab replicate results.

### **Waste Disposal**

After receipt of samples, laboratories will be responsible for proper storage of samples during the project, and disposal of samples after the project is complete. To the extent that any samples collected, or other materials used, are considered hazardous waste, laboratories will be responsible for disposing of these materials in accordance with all applicable Federal, State and/or Local laws.

### **Archiving**

Whenever possible, laboratories will retain sufficient amounts of sample or sample extract to allow for future re-analysis. Samples or extracts will be archived using appropriate storage techniques. Sample materials will not be discarded until all work described in this contract has been submitted to the RCD, validated, verified and RCD has paid the final invoice.