



**Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812
November 6, 2007**

**STUDY #243: SURFACE WATER QUALITY MONITORING - ORESTIMBA
AND DEL PUERTO CREEK WATERSHEDS**

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I. INTRODUCTION

The San Joaquin River (SJR) watershed is an important agricultural production area in the Central Valley of California. The SJR drains about 32,000 square miles through the San Joaquin Valley. Beneficial uses of waterways in the San Joaquin Valley have been threatened by elevated concentrations of pesticides resulting in the SJR listing in the Clean Water Act (CWA) § 303(d) list for impaired waters.

Surface water monitoring programs in California have focused on monitoring waterborne pesticides. Organophosphate (OP) insecticides have been found to be common pollutants in the SJR and its tributaries in the water phase. Less emphasis has been placed on monitoring soils and sediments, commonly associated with hydrophobic pyrethroid (PY) insecticides. However, PYs have been detected (Bacey et. al., 2004) and have been associated with toxicity to aquatic invertebrates (Amweg et.al., 2005; Weston et.al., 2004).

Determining the concentrations of OPs and PYs in water and sediment in the SJR and its tributaries is a first step towards managing the movement of insecticides into the SJR. This study is part of a large research grant project titled *Implementing IPM/BMPs to Reduce Organophosphate and Pyrethroid Runoff in Agricultural Land, San Joaquin Watershed*. A Proposition 50 Agricultural Water Quality Grant awarded to the Coalition for Urban/Rural Environmental Stewardship (CURES) funds the project. Researchers at the University of California, Davis (UCD), will utilize data collected in the study to support and calibrate the Better Assessment Science Integrating Point & Non-point Sources (BASINS)/ Soil and Water Assessment Tool (SWAT) environmental assessment models (US EPA, 2001). This model will calculate long-term water quality impacts of varying agricultural management practices. Sampling sites and frequencies were chosen to fill gaps in existing water quality monitoring data.

II. OBJECTIVE

The objectives of this study are three-fold:

- 1) collect water and sediment samples from Del Puerto and Orestimba Creeks, and associated water quality parameters;
- 2) determine the concentrations of OP and PY insecticides in these samples;
- 3) determine the toxicity of these samples to representative invertebrate organisms.

III. PERSONNEL

This is a cooperative study between several entities, including the Department of Pesticide Regulation (DPR), the Department of Fish and Game (DFG), and the University of California, Davis under the direction of the Coalition for Urban /Rural Environmental Stewardship (CURES). DPR Environmental Monitoring Branch staff, under the overall supervision of Marshall Lee, Senior Environmental Scientist, will conduct this study.

Other key personnel include:

- Project Leader: Mike Ensminger
- Field Coordinator: Rick Bergin
- Research Scientist: Frank Spurlock
- Chemists: California Department Fish and Game
- Aquatic Toxicity: University California Davis - Aquatic Toxicity Laboratory

Please direct questions regarding this study to Michael Ensminger, Associate Environmental Research Scientist, at (916) 324-4186 or mensminger@cdpr.ca.gov.

IV. STUDY PLAN

Study Sites

DPR will monitor surface water quality at two tributaries of the San Joaquin River. Sampling sites are Orestimba Creek at River Road near the town of Crow's Landing and Del Puerto Creek at Vineyard Road near the town of Patterson (Figure 1; click on link below to access).

Both sites have United States Geological Survey (USGS) gauging stations (access at <http://waterdata.usgs.gov/ca/nwis/current/?type=flow>) with easily obtainable flow data. Station numbers for Orestimba Creek and for Del Puerto Creek are 11274538 and 11274630, respectively.

Water Quality Parameters

Table 1 lists the water quality parameters that we will measure for each sampling event. Data will be formatted for inclusion in the Surface Water Ambient Monitoring Program (SWAMP) database (CA EPA SWRCB, 2005).

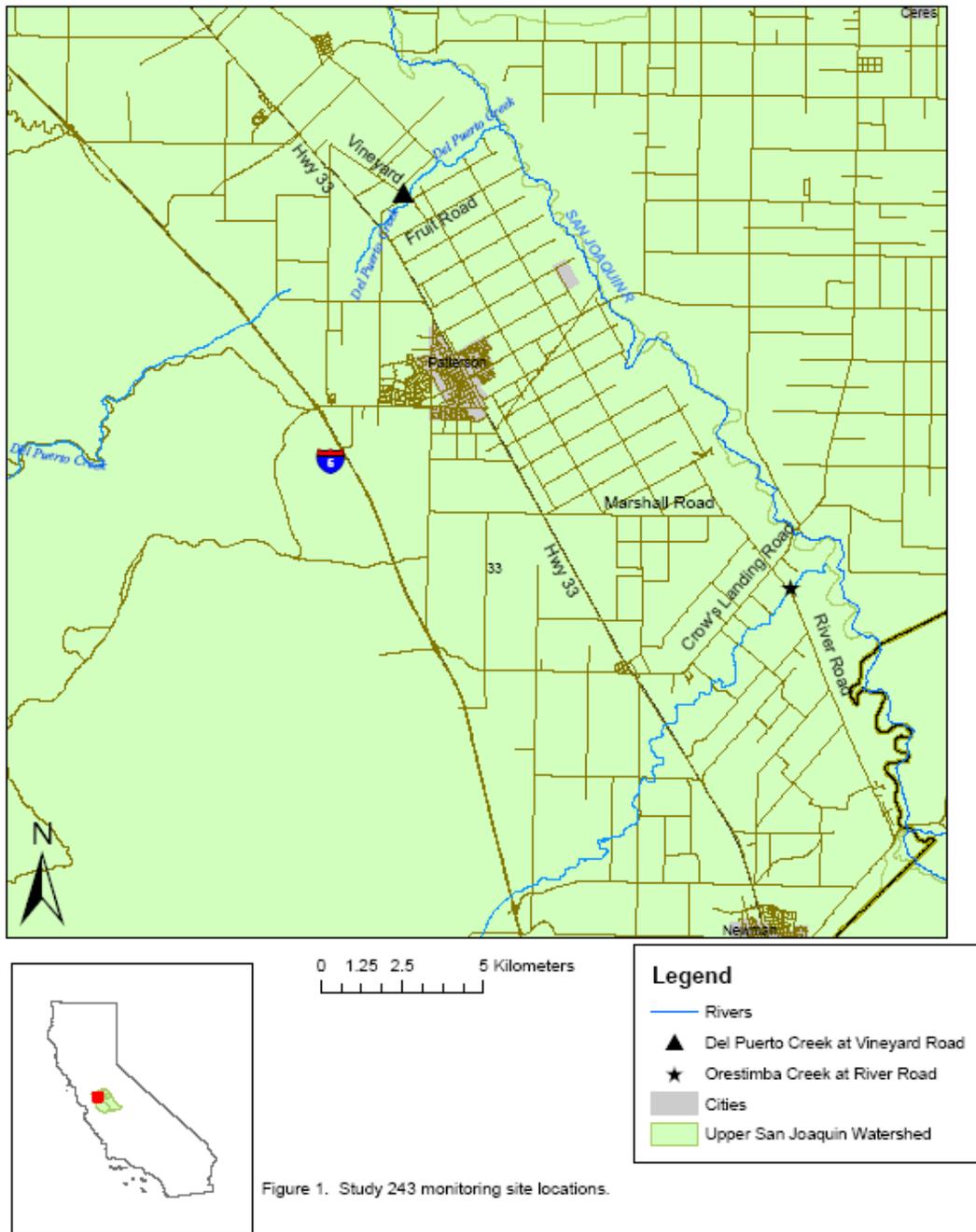


Figure 1. Study 243 monitoring site locations.

Figure 1. Sampling sites on Del Puerto Creek and Orestimba Creek.

Quality Assurance/Quality Control

Quality Assurance/Quality Control (QA/QC) will be conducted in accordance with approved Quality Assurance Project Plan. For field QC for analytical analyses, 15% of

the samples will be QC samples. QC samples will consist of field blanks, blind spikes, and field duplicate samples. QC for the UCD ATL toxicity tests will consist of field blanks, duplicate samples, laboratory controls, and reference toxicity tests.

Table 1. Water quality parameters for Study 243.

Water Chemistry	Sediment Chemistry	Toxicity
Organophosphate Screen	Pyrethroid Screen	Water
Pyrethroid Screen	Sediment Grain Size	<i>Ceriodaphnia dubia</i> (acute)
Total Suspended Solids	Total Organic Carbon	Sediment
Electrical Conductivity		<i>Hyalella azteca</i>
Dissolved Oxygen		
Temperature		
pH		

V. SAMPLING METHODS/CHEMICAL ANALYTICAL METHODS

Sampling Methods

A. Water

DPR staff will collect water samples for chemical analysis and for determining total suspended solids (TSS). DPR will collect these samples from center channel using an extendable pole directly into 1L amber glass bottles and sealed with Teflon® lined lids following CA DPR SOP FSWA002.00 (Bennett, 1997). Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed. Table 2 lists the water quality parameters to be measured or collected. For samples collected, Table 2 also lists sampling container and volume.

DPR staff will measure electrical conductivity (EC), dissolved oxygen (DO), temperature, and pH *in situ* at each sampling event using YSI® portable meters following CA DPR SOPs EQWA002.00, EQWA003.00, and EQWA004.00 (Garretson, 1998; Jones and Hoffman, 1999; Jones, 1999a, respectively).

B. Sediment

DPR staff will collect sediment samples for chemical analysis following CA DPR SOP FSWA016.00 (Mamola, 2005). DPR staff will collect sediment samples for chemical analysis, sediment grain size, total organic carbon (TOC), and invertebrate toxicity tests following Surface Water Ambient Monitoring Program guidelines for bed sediment sampling procedures (CA EPA SWRCB, 2002).

Table 2. Water quality parameters and volume to be collected at each sampling time.

Water	Container	Volume collected
OP Screen	1 L amber glass	1 Liter
PY Screen	1 L amber glass	1 Liter
<i>C. dubia</i> Toxicity	1 L amber glass	2 Liters
TSS	1 L amber glass	1 Liter
EC	<i>in situ</i>	NA
DO	<i>in situ</i>	NA
pH	<i>in situ</i>	NA
Sediment	Container	Volume collected
PY Screen	1 Pint glass mason	500 ml
Sediment Grain Size	1 Pint glass mason	125 ml
TOC	1 Pint glass mason	125 ml
<i>Hyalella</i> Toxicity	1 L polyethylene	2 Liters

NA = not applicable

Chemical Analyses

DPR staff will transport samples following the procedures outlined in DPR SOP QAQC004.01 (Jones, 1999b). A chain-of-custody record will be completed and accompany each sample.

The California Department of Fish and Game, Fish and Wildlife Water Pollution Control Laboratory (DFG) will conduct chemical analysis of all water and sediment samples. DFG will analyze all water samples for OP and PY insecticides, and will analyze sediment samples for PY insecticides. DFG will also determine sediment grain size for sediments collected.

The University of California at Davis Aquatic Toxicity Laboratory (UCD ATL) will conduct invertebrate aquatic and sediment toxicity tests according to US EPA guidelines (US EPA, 2000; US EPA, 2002). Specific methods can be found at the UCD ATL website (<http://www.vetmed.ucdavis.edu/apc/atl/>).

DPR staff will measure the following parameters:

- TSS via vacuum filtration of the samples and subsequent oven drying of the filtrate collected on tared, rinsed and oven-dried filters (US EPA, 1971);
- TOC analysis following CA DPR SOP METH005 (Gunasekara, 2006).

VI. DATA ANALYSIS

For this study, we are interested in detections or non-detections of pesticides in surface waters and in sediments. Pesticides will be reported as detected if they are found at concentrations equal to or greater than their RL (reporting limit). Table 3 lists the chemicals that DFG will analyze, with their respective MDL (minimum detection limit) and RL. DFG will report concentrations of OPs and PYs in water as micrograms per liter ($\mu\text{g/L}$) and report concentration of PYs in sediment as nanograms per gram of sediment (ng/g).

UCD ATL will use negative controls consisting of pesticide free matrix in all invertebrate toxicity tests. Invertebrate growth and survivability in the collected environmental samples will be compared to the results from the negative controls.

Table 3. Minimum detection limits (MDL) and reporting limits (RL) for Organophosphate (OP) and Pyrethroid insecticides.

OPs in Water	MDL ($\mu\text{g/L}$)	RL ($\mu\text{g/L}$)	Pyrethroids	Water		Sediment	
				MDL ($\mu\text{g/L}$)	RL ($\mu\text{g/L}$)	MDL (ng/g) Dry wt.	RL (ng/g) Dry wt.
Azinphos methyl	0.030	0.050	Bifenthrin	0.001	0.002	1.000	2.000
Chlorpyrifos	0.020	0.050	Cyfluthrin	0.002	0.004	3.000	5.000
Diazinon	0.005	0.020	Lambda- Cyhalothrin	0.001	0.002	2.000	5.000
Dimethoate	0.030	0.050	Cypermethrin	0.002	0.004	2.000	5.000
Disulfoton	0.010	0.050	Deltamethrin	0.002	0.004	na ¹	na
Malathion	0.030	0.050	Esfenvalerate	0.001	0.002	2.000	5.000
Methidathion	0.030	0.050	Fenpropathrin	0.002	0.004	na	na
Methyl parathion	0.010	0.050	Permethrin	0.003	0.005	1.000	2.000
Phosmet	0.030	0.050	DBOB ² (surrogate)	na	na	na	na
Triphenyl Phosphate (surrogate)	0.030	0.050					

¹na = data not available

²DBOB = dibromooctafluorobiphenyl

VII. TIMETABLE

Monitoring Frequency

Both sampling sites will be monitored monthly from December 2007 through June 2008. In addition, storm events will trigger three sampling events during the dormant season (Table 4). Water and sediment sampling for the invertebrate toxicity studies will follow a modified winter schedule, with only one storm event (Table 5). Other pertinent timelines (chemical analyses, report preparation, etc.) are shown in Table 6.

Table 4. Water and sediment sampling schedule for chemical analyses.

Sampling Type	2007	2008						Number of Sites	Number of Samples
	Dec	Jan	Feb	Mar	Apr	May	Jun		
Regular Sampling									
OP Water	X	X	X	X	X	X	X	2	14
PY Water	X	X	X	X	X	X	X	2	14
PY Sediment	X	X	X	X	X	X	X	2	14
TSS, Water	X	X	X	X	X	X	X	2	14
Grain Size, Sediment	X	X	X	X	X	X	X	2	14
TOC, Sediment	X	X	X	X	X	X	X	2	14
Storm Sampling									
OP Water	X	X	X					2	6
PY Water	X	X	X					2	6
PY Sediment	X	X	X					2	6
TSS, Water	X	X	X					2	6
Grain Size, Sediment	X	X	X					2	6
TOC, Sediment	X	X	X					2	6
								Total	120

Table 5. Water and sediment sampling schedule for invertebrate toxicity testing.

Sampling Type	2007	2008						Number of Sites	Number of Samples
	Dec	Jan	Feb	Mar	Apr	May	Jun		
Regular Sampling									
Water	X	X	X	X	X	X	X	2	14
Sediment	X	X	X	X	X	X	X	2	14
Storm Sampling									
Water		X						2	2
Sediment		X						2	2
								Total	32

Table 6. Additional timelines for Study 243.

Activity	Date (MM/DD/YYYY)		Deliverable Due Date
	Anticipated Date of Initiation	Anticipated Date of Completion	
Collect water samples	12/01/2007	06/30/2008	Within 7 days after sampling
Collect sediment sample	12/01/2007	06/30/2008	Within 40 days after sampling
Chemical analysis	12/01/2007	07/31/2008	Monthly
Invertebrate Toxicity Testing	12/01/2007	07/31/2008	Monthly
Summarize Data	03/31/2008	08/15/2008	08/15/2008
Statistical Analysis of lab QC's	12/01/2007	06/30/2008	06/30/2008
Draft Final Report	05/01/2008	08/31/2008	08/31/2008
Final Report	08/01/2008	09/30/2008	09/30/2008

VIII. LABORATORY BUDGET

The total cost for the chemical analyses, both from DFG and UCD ATL are listed below. Cost includes QC samples.

Instream Monitoring			
Chemical Analysis	No. of samples	Unit cost	
OP screen (water)	23*	294	\$6,762
Pyrethroid Screen (water)	23*	294	\$6,762
Pyrethroid Screen (sediment)	23*	412	\$9,476
Method Validation (PY Sed)	15	412	\$6,180
Subtotal			\$29,180
DFG Overhead		17.14%	\$5,001
Total, Chemical Analysis			<u>\$34,181</u>
Sediment Grain Size			
Grain Size	23*	136	\$3,128
DFG Overhead		17.14%	\$536
Total, Sediment Grain Size			<u>\$3,664</u>
Toxicity Testing			
<i>C. dubia</i> (acute)	28**	240	\$6,720
<i>H. azteca</i>	28**	900	\$25,200
Subtotal			\$31,920
UCD ATL Overhead		31.5%	\$10,055
Total, Toxicity Testing			<u>\$41,975</u>
Total Instream Costs			<u>\$79,820</u>

*Contains 3 QC samples (field duplicates, field blanks, and blind spikes).

**Of the 28 samples, 12 samples are QC samples

IX. CONTRACT INFORMATION

This study is part of a large research grant project titled Implementing IPM/BMPs to Reduce Organophosphate (OP) and Pyrethroid Runoff in Agricultural Land, San Joaquin Watershed. Information about the complete contract is listed below.

Contract Number: DPR# 06-0127R

Contractor: CURES (Coalition for Urban/Rural Environmental Stewardship)

Contract Manager: Sheryl Gill

Amount: \$299,000

Time period: December 2007 – September 2008

Brief summary of duties: Prepare a monitoring plan and a QAPP for studies 243 and 244; monitor surface water quality by taking water and sediment samples (study 243); analyze samples for the presence of OP and PY insecticides; perform a resident vegetation pilot study (study 244); prepare a written report of findings.

X. LITERATURE CITED

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