

**Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, California 95812
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**STUDY 207 (SWP02): MONITORING SURFACE WATERS OF THE SAN JOAQUIN RIVER
BASIN FOR SELECTED SUMMER-USE PESTICIDES.**

I. INTRODUCTION

In the San Joaquin Valley, a wide variety of pesticides are applied throughout the summer growing season (DPR, 2001a). Relatively little recent surface water monitoring has been conducted in the San Joaquin basin during the summer season. Such monitoring data are needed to characterize the current summer distribution and concentrations of pesticides in the San Joaquin River. Pesticides were selected for monitoring in this study based on (a) physiochemical properties indicating potential mobility, (b) their relatively high use, (c) potential aquatic toxicity, and/or (d) a lack of current monitoring data.

Pyrethroid insecticides: permethrin / esfenvalerate

Permethrin and esfenvalerate are used on a variety of crops in the San Joaquin basin. During May through August of 2000, the reported use of permethrin and esfenvalerate in the five-county San Joaquin basin area comprised of Fresno, Madera, Merced, San Joaquin, and Stanislaus counties was 56,463 and 6,478 pounds of active ingredient, respectively (DPR, 2001a). These pyrethroids were chosen for monitoring in this study because of a lack of summer monitoring data for these compounds in the San Joaquin Valley, and because of their potential for aquatic toxicity (Table 1).

Metolachlor and degradates

Metolachlor has been classified as a possible human carcinogen by U.S. EPA's Office of Pesticide Program's Carcinogenicity Peer Review Committee (U.S. EPA, 1996). Metolachlor also exhibits moderate to high aquatic toxicity (U.S. EPA, 2002), and its relatively low Koc value indicates that the herbicide is potentially mobile. Although the toxicological significance of the metolachlor degradation products (metolachlor ethanesulfonic acid and metolachlor oxanilic acid) is unknown at present, they also appear to be mobile, having been detected in the surface water of other states (Kalkhoff et al., 2000; Frey 2001).

During the summer there is relatively high use of metolachlor in the San Joaquin basin, primarily for control of broadleaf and annual grassy weeds in corn and beans. During May through August 2000, 63,899 pounds of metolachlor were applied in the five county San Joaquin River basin area (DPR, 2001a). Metolachlor has been detected in California surface water (DPR, 2001b), and degradation products of metolachlor have been detected in California groundwater (DPR, 2001c). The Department of Pesticide Regulation is unaware of the existence of any monitoring data for metolachlor degradation products in California surface water. While alachlor use is much less than metolachlor, alachlor and its degradates are included in the analytical method for metolachlor and degradates (Table 2).

Other potential surfacewater contaminants

A wide variety of herbicides and organophosphate insecticides, including diazinon and chlorpyrifos, are applied in the San Joaquin basin during the summer season (DPR, 2001a), and have been detected in San Joaquin Valley surface water (USGS, 1998). These include several of the pesticides listed in the organophosphate and triazine herbicide analytical screens shown in Table 2. Consequently all water samples will be analyzed using these two additional analytical methods to provide current information on the presence of these known contaminants during summer months.

II. OBJECTIVE

The purpose of this monitoring project is to determine if select pesticides used in the dry summer season in the San Joaquin valley are present in surface waters in measurable amounts, and if so, what typical range of concentrations may be observed. The results will be used to aid in the development of priorities for future monitoring and/or mitigation efforts.

III. PERSONNEL

This study will be conducted by staff from the Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Kean S. Goh, PhD., Agricultural Program Supervisor IV. Key personnel are listed below:

Project Leader:	Keith Starner
Field Coordinators:	Sheryl Gill
Senior Scientist:	Frank Spurlock
Laboratory Liaison:	Carissa Ganapathy
Chemists:	To be determined

Questions concerning this monitoring project should be directed to Keith Starner at (916) 324-4167.

IV. STUDY PLAN

Monitoring sites will be selected based on local historical pesticide use, and the priority will be given to water courses consisting primarily of agricultural drainage. Additionally, the site selection process will follow the general guidelines in Standard Operating Procedure (SOP) FSWA002.00 (Bennett, 1997).

Sampling will commence in early July 2002 and continue throughout the summer until late September 2002. Each site will be sampled once per week.

V. SAMPLING METHODS

At each sampling site, a single pyrethroid grab sample will be collected directly into a 1-liter amber glass bottle. Grab samples will be collected as close to center channel as possible using a grab pole consisting of a glass bottle at the end of an extendable pole, or other sampling equipment designed to collect a sample directly into a 1-liter glass bottle. Sample will not be transferred from the original sample bottle until analysis at the lab. Amber bottles will be sealed with Teflon-lined lids and samples will be transported and stored on wet ice or refrigerated at 4°C until extraction for chemical analysis. The pyrethroid sample will not be composited with the sample described below.

Additionally, a total of approximately 6 L of surface water will be collected using a D-77 depth-integrated sampler with a 3-liter Teflon bottle and nozzle. At sites where use of the D-77 sampler is impractical due to insufficient water depth or access, a wading rod with a 3-liter Teflon bottle and nozzle will be used to collect a depth-integrated sample. If stream depth is too shallow to collect a depth-integrated sample, grab samples will be collected using a 10-liter stainless steel bucket or using a grab pole consisting of a glass bottle at the end of an extendable pole. These samples will be collected as close to center channel as possible.

These surface water subsamples will be composited in a stainless steel container until approximately 6 L of water has been collected. This composited sample will then be stored on wet ice until delivered to the processing facility in West Sacramento. Upon arrival at West Sacramento, the samples will be split into amber glass bottles using a Geotech® 10-port splitter, then sealed with Teflon®-lined lids according to SOP FSWA004 (Ganapathy 1998).

Dissolved oxygen, pH, specific conductivity, and water temperature will be measured *in situ* at each site during each sampling period.

All samples will be transported and stored on wet ice or refrigerated at 4°C until extraction for chemical analysis.

VI. CHEMICAL ANALYSIS

Chemical analyses will be performed by the California Department of Food and Agriculture's Center for Analytical Chemistry. Quality control will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa, 1995). Ten percent of the total number of analyses will be submitted with field samples as field blanks and blind spikes.

Samples will be analyzed for permethrin and esfenvalerate; metolachlor, alachlor and their ethanesulfonic acid and oxanilic acid degradates; and a suite of organophosphate pesticides and a suite of herbicides. Method titles and reporting limits for this study are reported in Table 2.

For pyrethroid analyses (permethrin and esfenvalerate), the whole samples, including any suspended sediment, will be extracted in the sample bottle (*in toto*) and the pyrethroid residues will be reported on a whole sample basis (water plus suspended sediment).

VII. DATA ANALYSIS

Concentrations of pesticides and degradation products in water will be reported as micrograms per liter ($\mu\text{g/L}$), and summary statistics will be provided in the final report. Detections will be compared to pesticide application data, precipitation records, and water level gauging data. Aquatic toxicological benchmarks will be provided as an aid in interpreting the data.

VIII. TIMETABLE

Field Sampling:	July through September 2002
Chemical Analysis:	July through November 2002
Preliminary Memorandum:	April 2003
Final Report:	June 2003

X. REFERENCES

- ARSUSDA. 2001. Agricultural Research Service, U.S. Department of Agriculture. [Online] Available: <http://www.arsusda.gov/ppdb2.html>
- Bennett, K. 1997. Conducting Surface Water Monitoring for Pesticides. Environmental Hazards Assessment Program FSWA002.00. Department of Pesticide Regulation, Sacramento, CA
- DPR. 2001a. The California Department of Pesticide Regulation. Pesticide Chemistry Database.
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- DPR. 2001c. The California Department of Pesticide Regulation. Well Monitoring Database.
- Frey, J.W. 2001. Occurrence, Distribution, and Loads of Selected Pesticides in Streams in the Lake Erie-Lake St. Clair Basin, 1996-1998. US Geological Survey Water-Resources Investigations Report 00-4169.
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- Kalkhoff, Stephen J., Kimberlee K. Barnes, Kent D. Becher, Mark E. Savoca, Douglas J. Schnoebelen, Eric M. Sadorf, Stephen D. Porter, and Daniel J. Sullivan. 2000. Water Quality in the Eastern Iowa Basins, Iowa and Minnesota, 1996–98. US Geological Survey Water Resources Circular 1210.
- Segawa, R. 1995. Chemistry Laboratory Quality Control. Environmental Hazards Assessment Program QAQC001.00. Department of Pesticide Regulation, Sacramento, CA.
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Table 1. PYRETHROID AND METOLACHLOR PHYSICAL CHARACTERISTICS

Pesticide	Koc	Solubility (mg/l)	Half-life Soil (days)	Half-life Water (days)	Toxicity LC ₅₀ <i>Daphnia Magna</i> (ppb)
Esfenvalerate	1000-12,000 ^a	0.0002 ^a	14 - 75 ^a	stable ^a	0.15 ^c
Permethrin	10,471-86,000 ^a	0.006 ^a	6 - 106 ^a	3-42 ^b	0.1-0.3 ^c
Metolachlor	22-307 ^a	488-530 ^a	12-292 ^a	stable ^a	23,000-26,000 ^a

a–ARSUSDA b–DPR c–U.S.EPA 2002

**TABLE 2. CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE, CENTER FOR ANALYTICAL CHEMISTRY
 SYNTHETIC PYRETHROID, ORGANOPHOSPHATE, HERBICIDE RESIDUE ANALYTICAL SCREENS.**

Organophosphate Pesticides in Surface Water by GC Method: GC/FPD		Metolachlor/Alachlor and degradates in Surface Water by LC/MS Method: APCI/LC/MS/MS		Triazines/Herbicides in Surface Water by LC/MS Method: APCI/LC/MS/MS	
<u>Compound</u>	<u>Reporting Limit</u> <u>(µg/L)</u>	<u>Compound</u>	<u>Reporting Limit</u> <u>(µg/L)</u>	<u>Compound</u>	<u>Reporting Limit</u> <u>(µg/L)</u>
Azinphos methyl	0.05	Metolachlor	0.05	Atrazine	0.05
Chlorpyrifos	0.04	Alachlor	0.05	Bromacil	0.05
Diazinon	0.04	Metolachlor OXA	0.05	Diuron	0.05
DDVP (dichlorvos)	0.05	Metolachlor ESA	0.05	Hexazinone	0.05
Dimethoate	0.04	Alachlor OXA	0.05	Metribuzin	0.05
Disulfoton	0.04	Alachlor ESA	0.05	Norflurazon	0.05
Ethoprop	0.05			Prometon	0.05
Fenamiphos	0.05			Prometryn	0.05
Fonofos	0.04			Simazine	0.05
Malathion	0.04			AEA	0.05
Methodathion	0.05			ACET	0.05
Methyl Parathion	0.03			DACT	0.05
Phosmet	0.05				
		Pyrethroid Pesticides in Surface Water Method: GC/EC			
		<u>Compound</u>	<u>Reporting Limit</u> <u>(µg/L)</u>		
Thimet (Phorate)	0.05	Esfenvalerate	0.05		
Profenofos	0.05	Permethrin	0.05		
Tribufos	0.05				