Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, California 95812
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STUDY 219: MONITORING SURFACE WATERS AND SEDIMENTS OF THE SALINAS AND SAN JOAQUIN RIVER BASINS FOR SYNTHETIC PYRETHROID PESTICIDES.

I. INTRODUCTION

The Salinas and San Joaquin Valleys are important agricultural regions in California, with concomitant use of a wide variety of pesticides throughout the summer growing season (DPR, 2002). The effects of pesticides applied during the summer months on the quality of surface waters in these rives basins is not well documented. Surface water monitoring in the San Joaquin basin during the summer season has been spotty, and is virtually non-existent in the Salinas River Basin. There is very limited summer sampling data for pesticides – including pyrethroids in these river basins. Therefore, this study was designed to characterize the current summer season distributions and concentrations of selected pesticides in water and sediment. The pyrethroids were selected for monitoring based on three criteria: (a) their relatively high use, (b) their high potential aquatic toxicities, and (c) a lack of current monitoring data.

Pyrethroid insecticides: bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin and permethrin.

Pyrethroid insecticides are used on a variety of crops in the Salinas and San Joaquin River basins. During May through October 2001, the combined reported use (DPR 2002) of bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin and permethrin in Monterey County (primarily in the Salinas River Basin) was 383, 328, 1,602, 2,189, 242, and 25430 lbs active ingredient (AI) respectively. In the five-county San Joaquin basin area (Fresno, Madera, Merced, San Joaquin, and Stanislaus counties), combined use of these pyrethroid insecticides was 4,495, 3,973, 1,628, 4,491, 1399, and 12,728 pounds AI, respectively. Use by pesticide for each of the San Joaquin and Salinas River Basin Counties is presented in Table 1. These pyrethroids were chosen for monitoring in this study because of a lack of summer monitoring data for these compounds in the Salinas and San Joaquin Valleys, and because of their potential for aquatic or sediment toxicity (Table 2).

Organophosphate insecticides:

A wide variety of organophosphate insecticides, including diazinon and chlorpyrifos, are applied in both river basins basin during the summer season (DPR, 2002), and have been detected in San Joaquin Valley surface water (Foe, 1995; Kratzer 1997). These include several of the pesticides listed in the organophosphate analytical screens shown in Table 3. All water samples will be analyzed to provide current information on the presence of these known contaminants during summer months due to ongoing concerns over the impact of organophosphates on water quality.

II. OBJECTIVE

The purpose of this monitoring project is to determine if six pyrethroids used in the dry summer season in the San Joaquin Valley and Salinas Valley are present in the surface waters and/or sediments of these regions in measurable concentrations, and if so, what representative ranges of concentrations may be observed. The secondary objective is to provide recent summer season monitoring data for organophosphate in the two regions. The results will be used to aid in the development of priorities for future monitoring and/or mitigation efforts.

III. PERSONNEL

Staff from the Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Kean S, Goh, PhD., Agricultural Program Supervisor IV, will conduct this study.
Key personnel are listed below:

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

To resolve questions concerning this monitoring project please contact Kevin Kelley at (916) 324-4187.

IV. STUDY PLAN

Four monitoring sites in each basin will be selected based on local historical pesticide use, and priority will be given to tributary watercourses 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 May 2003 and continue throughout the summer through late September 2003. Sites 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 (Spurlock, 1999). 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.

Sediment will be collected following procedures outlined in Bacey (2003). Sediment samples will be collected using either a Hollow coring device or the Ekman dredge, depending on creek-bed or riverbed composition.

Dissolved oxygen, pH, specific conductivity, and water temperature will be measured *in situ* at each site at the time of sample collection. Gauging/flow data will also be collected.

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 (10%) of the total number of analyses will consist of field blanks and blind spikes, to be submitted to the laboratory with field samples.

All samples will be analyzed for bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, and permethrin, and aqueous samples only will also be analyzed for a suite of organophosphate pesticides. Method titles and reporting limits for this study are reported in Table 3.

For all pyrethroid water analyses, 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). Replicate samples will be collected at each sampling event and analyzed to determine suspended sediment concentration.

VII. DATA ANALYSIS

Concentrations of pesticides in water and sediment will be reported as micrograms per liter (µg/L) and µg/Kg, respectively. Summary statistics will be provided in the final report. Detections will be compared to pesticide application data, precipitation records, and any available toxicity data. Water level gauging and flow data will also be reported. Suspended sediment concentrations will be used along with K_{OC} data and estimated sediment organic carbon concentrations to estimate dissolved and sorbed pyrethroid concentrations in the whole water samples.

VIII. TIMETABLE

Field Sampling:	May through September 2003
Chemical Analysis:	May through November 2003
Preliminary Memorandum:	April 2004
Final Report:	June 2004

IX. BUDGET

Primary Analysis				**Cost** **(@ $300/sample)**
Organophosphate screen	8 sites x 21 weeks =	168 samples	=	50,400
Pyrethroids, Water	8 sites x 21 weeks =	168 samples	=	50,400
Pyrethroids, Sediment	8 sites x 21 weeks =	168 samples	=	50,400
Quality Control				
Blind spikes		33 samples	=	9,900
Field blanks		33 samples	=	9,900
Total				171,000

X. REFERENCES

Bacey, N. 2003. Sediment Collection SOP. In Prep.

Bennett, K. 1997. Conducting surface water monitoring for pesticides. Environmental Hazards Assessment Program FSWA002.00. Department of Pesticide Regulation, Sacramento, CA

DPR. 2003. CDPR Ecotox Database. Data assembled by Jon Shelgren, Registration Branch, Department of Pesticide Regulation, California Environmental Protection Agency.

DPR. 2002. Pesticide Use Reporting. Annual 2001 http://www.cdpr.ca.gov/docs/pur/purmain.htm

Foe, C. 1995. Insecticide concentrations and invertebrate bioassay mortality in agricultural return water from the San Joaquin basin. Central Valley Regional Water Quality Control Board.

Kratzer, C. 1997. Transport of diazinon in the San Joaquin River Basin, California. USGS Open-File report 97-411.

Laskowski, D.A. 2002. Physical and chemical properties of pyrethroids. Rev. Environ Contam Toxicol. 174:49-170

Segawa, R. 1995. Chemistry Laboratory Quality Control. Environmental Hazards Assessment Program QAQC001.00. Department of Pesticide Regulation, Sacramento, CA.

Spurlock, F., 1999. Sampling for Surface Water Runoff in Agricultural Fields. SOP FSWA008.00

Table 1. Pyrethroid Insecticide Applied in the Salinas River Basin and the San Joaquin River Basin during 2001. (DPR 2002)

	May	June	July	August	September	October	Total
BIFENTHRIN							
Fresno†	21.3	810.0	882.0	301.2	44.5	0.3	2,059.3
Madera†	0.0	9.4	10.4	43.7	0.0	0.0	63.6
Merced†	0.9	238.6	829.1	271.1	23.0	0.0	1,362.7
San Joaquin†	0.0	89.4	19.7	33.6	15.1	0.8	158.6
Stanislaus†	16.8	153.6	307.7	309.5	55.5	8.0	851.1
Monterey‡	18.2	55.2	136.3	73.1	81.9	18.8	383.4
CYFLUTHRIN							
Fresno	849.7	160.2	909.7	1162.0	107.1	89.5	3278.2
Madera	62.6	35.0	45.3	1.1	0.0	0.0	144.1
Merced	0.0	49.8	43.9	96.8	17.6	12.2	220.3
San Joaquin	0.4	0.0	1.3	0.0	0.0	0.0	1.7
Stanislaus	239.5	12.3	44.4	21.5	10.7	0.0	328.4
Monterey	0.2	0.2	0.5	0.5	0.1	0.5	2.0
CYPERMETHRIN							
Fresno	549.4	210.2	49.7	0.0	287.2	318.6	1,415.0
Madera	0.0	1.4	0.8	0.0	0.0	0.0	2.1
Merced	0.0	73.8	8.4	2.3	0.0	0.0	84.6
San Joaquin							
Stanislaus	19.7	19.7	17.2	22.6	21.6	21.7	122.4
Monterey	199.6	206.4	334.8	419.3	293.7	148.2	1,602.1
ESFENVALERATE							
Fresno	356.7	180.0	168.8	305.9	305.9	131.7	1,449.1
Madera	76.0	4.7	115.5	13.1	3.9	0.0	213.1
Merced	225.8	221.7	292.3	235.9	56.1	12.0	1,043.8
San Joaquin							
Stanislaus	437.1	317.2	892.6	134.8	4.2	0.0	1,785.9
Monterey	210.6	388.8	406.9	395.7	456.0	331.2	2,189.1
LAMBDA-CYHALOTHRIN							
Fresno	123.6	198.8	305.8	189.1	46.5	61.8	925.7
Madera							
Merced	114.8	37.0	30.0	10.7	32.2	6.5	231.2
San Joaquin							
Stanislaus	18.6	23.1	80.3	43.1	50.0	26.9	242.0
Monterey	440.8	378.9	350.2	369.6	485.1	255.5	2,280.1
PERMETHRIN							
Fresno	319.7	220.9	862.0	514.9	1413.3	3,493.8	6,824.7
Madera							
Merced	1,138.2	769.4	960.8	249.8	120.7	16.8	3,255.7
San Joaquin							
Stanislaus	632.7	411.8	1,515.9	78.7	5.5	2.6	2,647.1
Monterey	5,980.2	4,548.5	3,921.8	4,068.8	4,219.9	2,690.4	25,429.7

† San Joaquin River Basin Counties
‡ Salinas River Counties

Table 2. Pyrethroid Physical and Toxicological Characteristics

Pesticide	**K_{OC}**[†]	**Solubility** (mg/l)[†]	**Half-life Soil** (days)[†]	**Hydrolytic** (pH 7) **Half-life** (days)[†]	**Toxicity LC_{50}** *Daphnia Magna* (ppb)[‡]
Bifenthrin	237000	$1.4e^{-5}$	96-425	Stable	1.6
Cyfluthrin	124,000	$2.3e^{-3}$	12-34	183	0.16
Cypermethrin	310,000	$4.0e^{-3}$	28-55	274	1.25
Esfenvalerate		$6.0e^{-3}$	39-94	Stable	0.24
lambda-cyhalothrin	326,000	$5.0e^{-3}$	43	Stable	0.23
Permethrin	277,000	$5.5e^{-3}$	40-197	Stable	0.075

[†] Laskowski, 2002
[‡] DPR 2003.

TABLE 3. California Department Of Food And Agriculture, Center For Analytical Chemistry Synthetic Pyrethroid, Organophosphate, Analytical Screens.

Organophosphate Pesticides in Surface Water by GC Method: GC/FPD

Compound	***Reporting Limit (μg/L)***
Azinphos methyl	0.05
Chlorpyrifos	0.04
Diazinon	0.04
DDVP (dichlorvos)	0.05
Dimethoate	0.04
Disulfoton	0.04
Ethoprop	0.05
Fenamiphos	0.05
Fonofos	0.04
Malathion	0.04
Methidathion	0.05
Methyl Parathion	0.03
Phosmet	0.05
Thimet (Phorate)	0.05
Profenofos	0.05
Tribufos	0.05

Pyrethroid Pesticides in Surface Water; Method: GC/EC

Compound	***Reporting Limit (μg/L)***
Bifenthrin	†
Cyfluthrin	†
Cypermethrin	†
Esfenvalerate	†
Lambda-Cyhalothrin	†
Permethrin	†

Pyrethroid Pesticides in Sediment; Method: GC/EC

Compound	***Reporting Limit (μg/g)***
Bifenthrin	0.01
Cyfluthrin	0.01
Cypermethrin	0.01
Esfenvalerate	0.01
Lambda-Cyhalothrin	0.01
Permethrin	0.01

† Value not available at this time (Wednesday April 2, 2003)