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Study 271. Surface Water Monitoring for Pesticides in Agricultural Areas of California, 2011.

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I. INTRODUCTION

A wide variety of agricultural pesticides are applied in California throughout the year. In 2009, for example, over 300 pesticide active ingredients (AIs) were applied in agricultural areas of the state (CDPR 2011a). Pesticide active ingredients which are highly toxic to aquatic organisms and have significant use in California have been identified through assessments of toxicity and pesticide use data (US EPA 2009, Starner 2008a, Starner 2007). Surface water monitoring data for these pesticides are needed in order to assess the potential impacts of California pesticide use on aquatic systems.

Numerous pesticides possessing relatively high aquatic toxicity are applied intensively in several agricultural areas of the state (Figure 1). Recent monitoring results from these areas indicate that, for several AIs, concentrations exceeding water quality benchmarks can occur in aquatic environments; for several other AIs with significant aquatic toxicity, recent surface water monitoring data are lacking (Kozlowski *et al.* 2004, Anderson *et al.* 2005, Hunt *et al.* 2006, Orlando *et al.* 2008, Central Coast Water Quality Preservation, Inc. 2008, 2009, Starner 2008b, 2009, 2011, Phillips *et al.* 2010). These areas represent different climates, soil types, treated crops, and agricultural practices, factors which impact the potential for offsite movement of pesticides. Consistent monitoring over time is needed to understand the environmental fate of current-use pesticides under a variety of conditions.

II. OBJECTIVE

The objective of this study is to provide data for a long-term assessment of surface water pesticide contamination in high-use agricultural areas of California.

Results will provide useful data on the environmental fate of current-use pesticides under a variety of conditions for use in the development of management responses.

III. PERSONNEL

The study will be conducted by staff from the Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Kean S. Goh, Environmental Program Manager (Supervisor) I. Key personnel are listed below:

Project Leader:	Keith Starner
Field Coordinator:	Kevin Kelley
Senior Scientist:	Frank Spurlock
Laboratory Liaison:	Sue Peoples
Chemists:	California Department of Food and Agriculture, Center for Analytical Chemistry Staff Chemists

Questions concerning this monitoring project should be directed to Keith Starner at (916) 324-4167 or by email at kstarner@cdpr.ca.gov.

Note: All pesticide use data cited are agricultural use data from CDPR 2011a unless specified otherwise.

IV. STUDY PLAN

Monitoring in each area will be conducted during the season or seasons of historically high pesticide use (CDPR 2011a, Table 1). “Primary” sites are defined as those sites sampled at every sampling interval; six to ten primary sites will be sampled in each area. In addition to the primary sites, additional sites (“secondary” sites) may be sampled as appropriate based on current pesticide use in the areas. Some sites (primary or secondary) may be sampled multiple times during a single sample event to collect time-series pesticide concentration data. Locations of individual sampling sites will be determined based on recent surface monitoring results and the historical pesticide use patterns in the areas. Sampling will commence in March 2011 and continue through October 2011.

V. SAMPLING METHODS

At each sampling site, surface water grab samples for chemical analysis will be collected into 1-liter amber glass bottles. Grab samples will be collected using either a grab pole consisting of a glass bottle at the end of an extendable pole. Glass bottles will be sealed with Teflon-lined lids and samples will be transported and stored on wet ice or refrigerated at 4^{o}C until extraction for chemical analysis. Appropriate DPR QA/QC Standard Operating Procedures will be followed.

Dissolved oxygen, pH, specific conductivity, and water temperature will be measured *in situ* at each site during each sampling period. Flow data will be collected using a digital flow meter.

VI. CHEMICAL ANALYSIS

Chemical analysis will be performed by the California Department of Food and Agriculture’s Center for Analytical Chemistry. Analytical method analytes, method detection limits, and reporting limits for this study are given in Table 1. Details of the chemical analysis methods will be provided in the final report. Quality control will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa 1995).

VII. DATA ANALYSIS

Concentrations of pesticides in water will be reported as micrograms per liter (µg/L) / parts per billion (ppb) or nanograms per liter (ng/L) / parts per trillion (ppt). Concentrations of pesticides in sediment will be reported as micrograms per kilogram (µg/kg) / parts per billion (ppb) dry weight. Resulting data will be analyzed and reported as appropriate, potentially including the following:

Comparison of pesticide concentrations to aquatic toxicity benchmarks, water quality limits and other toxicity data (CCVRWQCB 2010, US EPA 2009); spatial analysis of data in order to identify correlations between observed pesticide concentrations and region-specific pesticide use and geographical features; assessment of results to determine potential additional monitoring in regions with similar pesticide use patterns.

VIII. TIMETABLE

Field Sampling:	February 2011 through October 2011
Chemical Analysis:	February 2011 through December 2011
Draft Report:	September 2012

IX. BUDGET

Sample analysis	Samples	Cost/Sample	Cost Estimate
Organophosphates	85	$650	$55250
Diazinon	85	425	36125
Carbamates	80	500	40000
Bensulide	80	510	40800
Imidacloprid	85	500	42500
Dinitroanilines	10	800	8000
Pyrethroids (sediment)	10	800	8000
Subtotal Analysis			**$230,675**

Continuing QC	Samples	Cost/Sample	Cost Estimate
Organophosphates	8	$650	$5200
Diazinon	8	425	3400
Carbamates	8	500	4000
Bensulide	8	510	4080
Imidacloprid	8	500	4000
Dinitroanilines	1	800	800
Pyrethroids (sed)	1	800	800
Subtotal QC			**$22,280**
Total			**$252,955**

X. REFERENCES

Anderson, B.S., Phillips, B.M., Hunt, J.W., Connor, V., Richard, N., Tjeerdema, R.S. 2006. Identifying primary stressors impacting macroinvertebrates in the Salinas River (California, USA): Relative effects on pesticides and suspended particles. Environmental Pollution 141 402-408.

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Starner, K. 2009. Spatial and Temporal Analysis of Diazinon Irrigation-Season Use and Monitoring Data. http://www.cdpr.ca.gov/docs/emon/surfwtr/swanalysis.htm

Starner, K. 2011. Pesticides in Surface Water from Agricultural Regions of California 2006-2007.

US EPA 2009. Aquatic Life Benchmark Table. Benchmark table updated April 2009. http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

Table 1. Monitoring Plan, 2011.

Area	**Analytical Screen**	**Season**	**Events**
Central/South Coast	Organophosphates	Spring though Fall	6
Central/South Coast	Carbamates	Spring through Fall	6
Central/South Coast	Bensulide	Spring through Fall	6
Central/South Coast	Imidacloprid	Spring through Fall	6
Central/South Coast	Pyrethroids	Summer	1
Imperial Valley	Organophosphates	Spring and Fall	2
Imperial Valley	Carbamates	Fall	1
Imperial Valley	Dinitroanilines	Spring	1
Imperial Valley	Bensulide	Fall	1
Imperial Valley	Imidacloprid	Spring and Fall	2

Table 2. Department of Food and Agriculture, Center for Analytical Chemistry analytical method details.

Organophosphate (OP) Insecticides in Surface Water by GC/FPD

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Chlorpyrifos	0.0008	0.01
Diazinon	0.0012	0.01
Dichlorvos	0.0098	0.05
Dimethoate	0.0079	0.04
Disulfoton	0.0093	0.04
Ethoprop	0.0098	0.05
Fenamiphos	0.0125	0.05
Malathion	0.0117	0.04
Methidathion	0.0111	0.05
Methyl Parathion	0.008	0.03
Phorate	0.0083	0.05

Carbamate (CB) Insecticides by LCMS.

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Oxamyl	0.0255	0.05
Methomyl	0.0265	0.05
Carbaryl	0.0136	0.05
Mesurol	0.0270	0.05

Dinitroaniline (DN) Herbicides/ Oxyfluorfen in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Oryzalin	0.01	0.05
Ethalfluralin	0.01	0.05
Trifluralin	0.01	0.05
Benfluralin	0.01	0.05
Prodiamine	0.01	0.05
Pendamethalin	0.01	0.05
Oxyfluorfen	0.01	0.05

Bensulide (BEN) in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Bensulide	0.014	0.05

Imidacloprid (IM) in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Imidacloprid	0.01	0.05

Pyrethroid Insecticides (PY) in Sediment

Chemical	***Method Detection Limit (µg/kg)***	***Reporting Limit (µg/kg)***
Resmethrin	0.87	1.5
Bifenthrin	0.108	1.0
Fenpropothrin	0.109	1.0
Lambda-cyhalothrin	0.115	1.0
Permethirn (cis)	0.116	1.0
Permethrin (trans)	0.135	1.0
Cyfluthrin	0.183	1.0
Cypermethrin	0.107	1.0
Fenvalerate/esfenvalerate	0.143	1.0
Deltamethrin	0.126	1.0

Figure 1. Agricultural Monitoring Regions, 2011