Department of Pesticide Regulation
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Study 278. Surface Water Monitoring for Pesticides in Agricultural Areas of California, 2012.

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I. INTRODUCTION

A wide variety of agricultural pesticides are applied in California throughout the year. In 2010, over 300 pesticide active ingredients (AIs) were applied in agricultural areas of the state (CDPR 2012). Many pesticide active ingredients with significant use in California agriculture are toxic to aquatic organisms (US EPA 2012). 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 in several agricultural areas of the state (Figure 1). Recent monitoring results from these areas indicate that for several AIs, including diazinon, chlorpyrifos, malathion, and dimethoate, concentrations exceeding water quality benchmarks frequently occur in aquatic environments. For several other classes of pesticides with significant aquatic toxicity, including strobilurin fungicides, diacylhydrazine insecticides, and neonicotinoid insecticides, recent surface water monitoring data are lacking (Kozlowski *et al.* 2004, Hunt *et al.* 2006, Orlando *et al.* 2008, Central Coast Water Quality Preservation, Inc. 2008 and 2009, Phillips *et al.* 2010, Anderson *et al.* 2010, Smalling and Orlando 2011, Starner *et al.* 2011, Starner 2011, Zhang *et al.* 2011, Starner and Goh, *in press*). These areas represent different California 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 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
Laboratory Liaison:	Sue Peoples
Chemists:	California Department of Food and Agriculture, Center for Analytical Chemistry Staff Chemists

Note: All pesticide use data cited are agricultural use data from CDPR 2012 unless specified otherwise.

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

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 sample sites continuously included in DPR's monitoring efforts and sampled at every sampling interval in the appropriate region. Primary site information is given in Table 2. Additional secondary sites will be sampled as appropriate; secondary sampling sites will be selected based on recent surface monitoring results and the historical pesticide use patterns 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. Sampling will commence in March 2012 and continue through October 2012.

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 3. 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). 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 2012, US EPA 2012); 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:	March 2012 through October 2012
Chemical Analysis:	March 2012 through December 2012
Draft Report:	September 2013

IX. BUDGET

Analysis	Cost/Sample($)	Samples	Cost Estimate
Organophosphates	600	80	48000
Diazinon	510	55	28050
Diacylhydrazines	720	45	32400
Strobilurins	840	45	37800
Imidacloprid/degrads	930	80	74400
Dinitroanilines (long)	960	10	9600
Pyrethroids	600	30	18000
Subtotal Analysis			248250

Continuing QC	Cost/Sample($)	Samples	Cost Estimate
Organophosphates	600	8	4800
Diazinon	510	4	2040
Diacylhydrazines	720	4	2880
Strobilurins	840	4	3360
Imidacloprid/degrads	930	8	7440
Dinitroanilines (long)	960	1	960
Pyrethroids	600	3	1800
Subtotal QC			23280

Total **271530**

X. REFERENCES

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Table 1. Monitoring Plan, 2012

Region	Season	Analytical Screen	Events
Central/South Coast	Spring through Fall	Organophosphates	6
		Imidacloprid	6
		Diacylhydrazines	3
		Strobilurins	3
		Pyrethroids	2
Imperial Valley	Spring and Fall	Organophosphates	2
	Spring	Dinitroanilines	1
	Fall	Imidacloprid	1
	Fall	Diacylhydrazines	1
Napa/Sonoma	Spring	Strobilurins	2
		Imidacloprid	2
		Diacylhydrazines	2

Table 2. Primary Sample Site Information

Region	Description	Latitude	Longitude	Code
C/S Coast - Pajaro	Watsonville Slough at Shell Rd	36.87154	-121.81734	27-63
C/S Coast - Pajaro	Beach Street Ditch	36.86871	-121.81584	44-18
C/S Coast-Salinas	Salinas River at Del Monte	36.73146	-121.78246	27-14
C/S Coast-Salinas	Tembladero Slough at Haro	36.75957	-121.7545	27-66
C/S Coast-Salinas	Alisal Crk at Hartnell	36.64352	-121.57837	27-70
C/S Coast-Salinas	Quail Crk at HWY 101	36.60917	-121.56303	27-7
C/S Coast-Salinas	Chualar Crk at Chualar River Rd	36.55803	-121.5292	27-8
C/S Coast - S. Maria	Orcutt Crk at W. Main	34.95757	-120.63149	42-50
C/S Coast - S. Maria	Oso Flaco Crk at Oso Flaco Lake Rd	35.01637	-120.58655	40-13
C/S Coast - S. Maria	Orcutt/Solomon Cnyn Crk at HWY 1	34.94145	-120.57329	42-48
C/S Coast - S. Maria	Main St. Ditch at HWY 166	34.95485	-120.4841	42-49
Imperial Valley	Rice Drain 3 at Wienert Rd	32.8689	-115.65085	13-69
Imperial Valley	Salton Sea at Obsidian Butte	33.17435	-115.64	13-58
Imperial Valley	Alamo River at Garst	33.19924	-115.59623	13-10
Imperial Valley	Alamo River at Rutherford Rd	33.04454	-115.48738	13-56
Imperial Valley	Holtville Main Drain at 115	32.93074	-115.40521	13-22
Imperial Valley	Verde Drain at Bonds Corner Rd	32.75549	-115.33678	13-25

Datum WGS 1984

Table 3. Department of Food and Agriculture, Center for Analytical Chemistry analytical method details.

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

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Chlorpyrifos	0.0008	0.01
Diazinon	0.0012	0.01
Dimethoate	0.0079	0.04
Malathion	0.0117	0.04
Methidathion	0.0111	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

Diacylhydrazine Insecticides in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Methoxyfenozide	0.00641	0.05
Tebufenozide	0.00573	0.05

Imidacloprid (IM) and Degradates in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Imidacloprid	0.0101	0.05
Imidacloprid Olefin	0.0443	0.200
Imidacloprid Urea	0.00947	0.05
Imidacloprid Quandine	0.0092	0.05
Imidacloprid Quandine Olefin	0.0081	0.05

Strobilurin Fungicides in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Azoxystrobin	0.0225	0.05
Kresoxim-methyl	0.0190	0.05
Pyraclastrobin	0.0207	0.05
Trifloxystrobin	0.0172	0.05

Pyrethroid Insecticides (PY) in Water

Chemical	***Method Detection Limit (µg/kg)***	***Reporting Limit (µg/L)***
Bifenthrin	0.00176	0.005
Lambda-cyhalothrin	0.00115	0.015
Permethirn (cis)	0.00352	0.015
Permethrin (trans)	0.00352	0.015
Cyfluthrin	0.0173	0.015
Cypermethrin	0.00175	0.015
Fenvalerate/esfenvalerate	0.00175	0.015

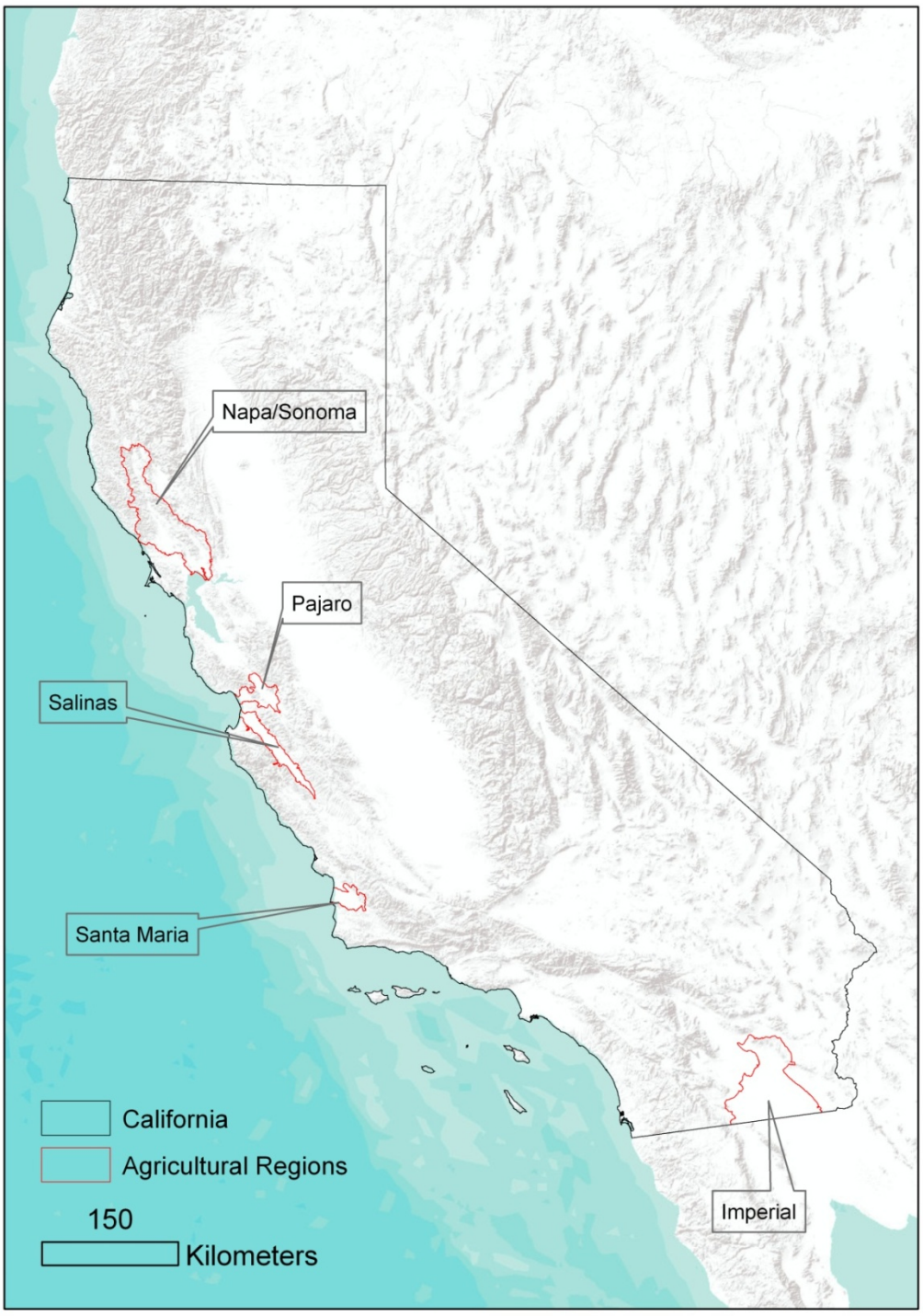

Figure 1. California agricultural monitoring regions, 2012.