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Environmental Monitoring Branch
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Study 290. Surface Water Monitoring for Pesticides in Agricultural Areas of California, 2014

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I. INTRODUCTION

Surface water monitoring for pesticides in agricultural areas of California is one of the California Department of Pesticide Regulation's (CDPR's) key environmental monitoring activities. This project was initiated in 2008 with a long term goal of collecting data to better assess potential impacts of pesticides in agricultural runoff on California aquatic environments. Project findings help guide CDPR in the development and implementation of regulatory and non-regulatory mitigation activities. In the past six years, the project has identified geographic areas with heavy pesticide uses via the Pesticide Use Report (PUR) database and selected sites adjacent to agricultural fields with high runoff potential for long term monitoring efforts. The Salinas, Santa Maria and Imperial valleys have previously been designated as high priority areas for long-term surface water monitoring due to high pesticide uses (Starner 2010, 2013). This study is a continuation of the agricultural monitoring project following the same monitoring strategies that were established in previous years in selecting monitoring sites and active ingredient (AI) candidates.

II. OBJECTIVE

The goal of the project 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 and transport of current-use pesticides under a variety of conditions for use in the development of management responses. Objectives of the project are as follows:

1) Identify runoff sampling sites in counties of high pesticide uses;
2) Annually prioritize monitoring AI candidates;
3) Measure chemical occurrences and concentrations of highly prioritized pesticides in runoff samples;
4) Characterize pesticide compositions in agricultural waterways;
5) Analyze chemistry data to evaluate potential impacts on aquatic environments.

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:	Xin Deng, PhD
Field Coordinator:	Kevin Kelley
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 Xin Deng PhD at (916) 445-2506 or by email at xdeng@cdpr.ca.gov.

IV. STUDY PLAN

According to the PUR database, over 600 pesticide AIs in a total amount of 135.6 million pounds were applied in agricultural areas of the state in 2011 (CDPR 2013). Those pesticide AIs possess a wide range of toxicity to aquatic organisms (US EPA 2013). In order to conduct the statewide monitoring effectively and better use limited resources, CDPR recently developed a pesticide Monitoring Prioritization Model (MPM) that automates the process of identifying potential monitoring candidates. The model develops a ranking of AIs based on their use amounts that were reported to the CDPR's PUR database (CDPR 2013) and their toxicity "Aquatic Life Benchmarks" that were developed by US EPA (US EPA 2013). Pesticide AIs that were selected as monitoring candidates for 2014 were identified using the MPM.

As a result of our statewide assessment using the MPM that was based on average use data from 2009-2011 and single-year use data from 2011, the top 10 statewide priority AIs were identified (Table 1). Of these, seven were selected for inclusion into this project: chlorpyrifos, malathion, permethrin, bifenthrin, pendimethalin, oxyfluorfen, and chlorothalonil. These AIs were also identified as monitoring candidates in the previous year (Starner 2013), except for bifenthrin which replaced trifluralin on the top 10 list. Analytical methods are available for all seven AIs.

Three of the top 10 AIs from the assessment were not included in the current project because analytical methods are not yet available for paraquat dichloride and ziram, and for copper, environmental concentrations would not provide meaningful information on agricultural uses of copper due to confounding non-pesticide sources. In the future, additional factors will be assessed to determine if monitoring, and therefore the development of analytical methods, is warranted for these AIs. These factors may include chemical/physical properties, environmental fate, and detailed use patterns.

For the seven selected AIs, areas with periods of intensive use in the vicinity of surface water were identified through spatial/temporal analysis of PUR data (CDPR 2013). Chlorpyrifos, malathion and permethrin uses are high (>5000 lbs. active ingredient) in the Salinas and Santa Maria valleys throughout the irrigation season as well as in the Imperial Valley in the fall (Figure 1). DPR has previously designated these three geographic areas as high priority areas for long-term surface water monitoring, largely due to the high use of these AIs (Starner 2010). This assessment supports that designation as well. For permethrin and bifenthrin analysis, the analytical method includes four additional pyrethroids: Lambda-cyhalothrin, cyfluthrin, cypermethrin and fenvalerate/esfenvalerate (Table 3).

Uses of oxyfluorfen and pendimethalin are high during the irrigation season in Salinas and Santa Maria valleys, and are high in the Imperial Valley and the Palo Verde area in Riverside County in the spring (Figure 1). Monitoring for these AIs will be conducted in these areas. The herbicide analytical method includes five additional dinitroanilines (i.e., oryzalin, ethalfluralin, trifluralin, benfluralin and prodiamine) that will be analyzed together as well.

Chlorothalonil use is high in several areas of the Central Valley, as well as in Salinas, Santa Maria, and Imperial valleys. Monitoring will include two areas of the Central Valley (Figure 1), where use is high on tomatoes, as well as in the three high priority monitoring regions. CDPR started to monitor for chlorothalonil in agricultural areas in 2013.

For each of the regions selected above for inclusion in the project, an additional region-specific assessment was conducted using the pesticide MPM. The goal of these assessments was to identify AIs that have significant aquatic toxicity and high use within a specific geographic region, but for which use was not high enough on a statewide basis to rank in the statewide analysis. The assessment was conducted using PUR data from 2009-2011 as well as the single-year data from 2011. The regional assessment for the Salinas Valley (Monterey County) resulted in the addition of diazinon, methomyl, pyraclostrobin and imidacloprid for monitoring in that area. Significant use of pendimethalin and malathion in Palo Verde concurrent with the high trifluralin use was also identified; those AIs will be included in the monitoring. Diacylhydrazine insecticides including methoxyfenozide and tebufenozide were previously detected at high frequencies in the Salinas Valley and will be included in the monitoring.

Monitoring in each area will be conducted for the appropriate AIs during the season or seasons of historically high pesticide use (CDPR 2013, Table 2). Sampling will commence in March 2014 and continue through October 2014.

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 CDPR 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 2. 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 multiple years of data to characterize patterns and trends in detection frequencies; assessment of results to determine potential additional monitoring in regions with similar pesticide use patterns.

VIII. TIMETABLE

Field Sampling:	March 2014 through October 2014
Chemical Analysis:	March 2014 through December 2014
Draft Report:	June 2015

IX. BUDGET

Analysis	Samples	Cost/sample	Cost Estimate
Organophosphate	85	600	51000
Diazinon	30	510	15300
Chlorothalonil	35	660	23100
Pyrethroids	30	960	28800
Dinitroanilines	30	960	28800
Methomyl	18	480	8640
Imidicaloprid	40	720	28800
Strobilurins	45	840	37800
Diacylhydrazines	17	720	12240
Subtotal Analysis			**234480**

Continuing QC	Samples	Cost/sample	Cost Estimate
Organophosphate	9	600	5400
Diazinon	4	510	2040
Chlorothalonil	4	660	2640
Pyrethroids	3	960	2880
Dinitroanilines	3	960	2880
Methomyl	2	480	960
Imidicaloprid	4	720	2880
Strobilurins	4	840	3360
Diacylhydrazines	2	720	1440
Subtotal QC			**24480**
Total			**258960**

X. REFERENCES

CCVRWQCB (California Central Valley Regional Water Quality Control Board) 2012. Criteria reports. Accessed January 10 2013.
http://www.swrcb.ca.gov/rwqcb5/water_issues/tmdl/central_valley_projects/central_valley_pesticides/criteria_method/index.shtml

CDPR (California Department of Pesticide Regulation) 2013. California Department of Pesticide Regulation’s Pesticide Information Portal, Pesticide Use Report (PUR) data.
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http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prioritization_report.pdf

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Starner, K. 2013. Study 282. Surface Water Monitoring for Pesticides in Agricultural Areas of California, 2013. http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study282protocol.pdf

US EPA 2013. Aquatic Life Benchmark Table. http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

Table 1. Top 10 Pesticides Identified by Monitoring Prioritization Model Based on Statewide Yearly-Average Use Data from 2009-2011

Chemical Name	Use in pound	Use score	Benchmark (µg/L)	Toxicity score	Final score
CHLORPYRIFOS	1271377.5	5	0.05	6	30
PERMETHRIN	110277.6	3	0.01	7	21
COPPER	4938598.8	5	2.05	4	20
PENDIMETHALIN	1802207.6	5	5.2	4	20
PARAQUAT DICHLORIDE	831544.0	4	0.396	5	20
OXYFLUORFEN	611999.4	4	0.29	5	20
MALATHION	500470.3	4	0.3	5	20
BIFENTHRIN	85113.5	3	0.075	6	18
CHLOROTHALONIL	844393.7	4	1.8	4	16
ZIRAM	746473.6	4	9.7	4	16

Table 2. Monitoring Plan, 2014

Region	Season	Analytical Screen	Events
Salinas	spring through fall	Organophosphate	6
		Diazinon	6
		Chlorothalonil	3
		Pyrethroids	3
		Strobilurins	3
		Dinitroanilines	2
		Methomyl	3
		Imidicaloprid	3
		Diacylhydrazines	3
Santa Maria	spring through fall	Organophosphate	3
		Chlorothalonil	1
		Pyrethroids	1
		Dinitroanilines	1
		Imidicaloprid	2
Imperial	spring	Organophosphate	1
		Chlorothalonil	1
		Dinitroanilines	1
Imperial	fall	Organophosphate	1
		Diazinon	1
		Pyrethroids	1
		Imidicaloprid	1
Palo Verde	spring	Organophosphate	1
		Dinitroanilines	1
Los Banos/SJ Delta	fall	Chlorothalonil	1

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	0.02
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

Chlorothalonil in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Chlorothalonil	0.111	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

Pyrethroid Insecticides (PY) in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***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

Imidacloprid (IMD) in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Imidacloprid	0.0101	0.05

Methomyl in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Methomyl	0.0265	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

Figure 1. California Agricultural Monitoring Regions, 2014.

IX. BUDGET (revised, Study 290)

Analysis	Samples	Cost/sample	Cost Estimate
Organophosphate	83	600	49800
Diazinon	48	510	24480
Chlorothalonil	24	660	15840
Pyrethroids	38	960	36480
Dinitroanilines	35	840	29400
Methomyl	18	480	8640
Imidicalоprid	60	720	43200
Strobilurins	29	840	24360
Diacylhydrazines	19	720	13680
Subtotal Analysis			**245880**

QC	Samples	Cost/sample	Cost Estimate
Organophosphate	8	600	4800
Diazinon	7	510	3570
Chlorothalonil	4	660	2640
Pyrethroids	4	960	3840
Dinitroanilines	3	840	2520
Methomyl	2	480	960
Imidicaloprid	6	720	4320
Imidicaloprid	3	840	2520
Diacylhydrazines	2	720	1440
Subtotal QC			**26610**
Total			**272490**

* Lab blind spiked samples are not included.