Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, California 95812

Study 282. Surface Water Monitoring for Pesticides in Agricultural Areas of California, 2013

Keith Starner
February 27, 2013

I. INTRODUCTION

As part the California Department of Pesticide Regulation's (CDPR) Surface Water Protection Program, surface water monitoring for pesticides is conducted in agricultural areas of the state. A wide variety of agricultural pesticides are applied in California throughout the year. In 2011, over 300 pesticide active ingredients (AIs) were applied in agricultural areas (CDPR 2013). Many pesticide AIs with significant use in California agriculture are toxic to aquatic organisms (US EPA 2013). Surface water monitoring data for these pesticides are needed in order to assess the potential impacts of California pesticide use on aquatic systems.

For CDPR's 2013 agricultural surface water monitoring project, potential monitoring candidates were identified using DPR's Draft Pesticide Prioritization for Surface Water Monitoring Program ("Prioritization Program"). This is a computer program recently developed by CDPR (Luo 2012) which automates the process of identifying potential monitoring candidates based on their use amounts in California and their toxicity to aquatic organisms. The program uses CDPR's Pesticide Use Reporting (PUR) data (CDPR 2013) in conjunction with US EPA Aquatic Life Benchmarks (US EPA 2013) to develop a rank of AIs. The candidates identified in this way are then further screened individually for appropriateness as monitoring candidates. The primary elements of this additional assessment include consideration of chemical-physical properties, environmental fate data, any available recent monitoring data, and existing analytical methodology, as well as the completion of a more detailed assessment of spatial and temporal use patterns.

Based on a statewide assessment using the Prioritization Program, the top 10 state-wide priority AIs were identified. Of these, seven were selected for inclusion in this project: chlorpyrifos, malathion, permethrin, trifluralin, pendimethalin, chlorothalonil, and oxyfluorfen. These seven AIs were also identified as monitoring candidates in a previous assessment (Starner 2008), and analytical methods are available for all of them.

Three of the top 10 AIs from the assessment that are not included in the current project are paraquat dichloride, copper (copper sulfate), and ziram; these AIs were not identified in the previous assessment from 2008. The analytical lab used by CDPR for sample analysis does not currently have analytical methods for these AIs. Additional factors will be assessed to determine if monitoring, and therefore the development of analytical methods, is warranted for these AIs. Factors to be considered should include any available recent monitoring results, the chemical/physical properties and environmental fate, and detailed use patterns of these AIs.

For the seven AIs, areas with periods of intensive use in the vicinity of surface water were identified through spatial/temporal analysis of PUR data (CDPR 2012). Chlorpyrifos, malathion and permethrin use is very high in the Salinas and Santa Maria Valleys throughout the irrigation season as well as in 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 analysis, the analytical method includes five additional pyrethroids (Table 2). As such, monitoring for permethrin will provide data for these other commonly used pyrethoids as well. Use of trifluralin and pendimethalin is very high in Imperial Valley, as well as in the Palo Verde area in Riverside County, in the spring (Figure 1). Monitoring for these AIs will be conducted in these areas; DPR has not recently conducted surface water monitoring in Palo Verde. Chlorothalonil use is high in several areas of the Central Valley, as well as in Salinas, Santa Maria, and Imperial Valleys. Monitoring will be included in two areas of the Central Valley (Figure 1) where use is high on tomatoes, as well as in the three high priority monitoring regions. DPR has not previously monitored for chlorothalonil in agricultural areas in any part of the state. Oxyfluorfen use is highest in California during the winter months (CDPR 2013); winter season monitoring is not included in the current study. However, oxyfluorfen use is also high during the irrigation season in Salinas and Santa Maria Valleys; some oxyfluorfen monitoring will be included in those regions.

For each of the regions selected above for inclusion in the project, an additional region-specific assessment was conducted using the Prioritization Program. 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 regional assessment for Salinas Valley (Monterey County) resulted in the addition of diazinon, methomyl 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 in this way; those AIs will be included in the monitoring there.

II. OBJECTIVE

The objective of the 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

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 for the appropriate AIs during the season or seasons of historically high pesticide use (CDPR 2013, Table 1). Sampling will commence in March 2013 and continue through October 2013.

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 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 2013 through October 2013
Chemical Analysis:	March 2013 through December 2013
Draft Report:	September 2014

IX. BUDGET

Organophosphate	85	600	$51,000
Diazinon	45	510	22950
Chlorothalonil	35	660	23100
Pyrethroids	30	960	28800
Dinitroanilines	30	960	28800
Methomyl	18	480	8640
Imidicaloprid	30	720	21600
Diacylhydrazines	17	720	12240
Subtotal Analysis			**$197,130**

Continuing QC	**Samples**	**Cost/sample**	**Cost Estimate**
Organophosphate	9	600	$5,400
Diazinon	5	510	2550
Chlorothalonil	4	660	2640
Pyrethroids	3	960	2880
Dinitroanilines	3	960	2880
Methomyl	2	480	960
Imidicaloprid	3	720	2160
Diacylhydrazines	2	720	1440
Subtotal QC			**$20,910**

Total	**$218,040**

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. http://calpip.cdpr.ca.gov/

Luo, Y. 2012. Documentation, Pesticide Prioritization for Surface Water Monitoring Program. Software documentation,, Draft December 2012.

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

Starner, K. 2008. Review of the Environmental Protection Agency Aquatic Life Benchmarks, with Monitoring Recommendations. CDPR Technical Memorandum. http://www.cdpr.ca.gov/docs/emon/pubs/analysmemos.htm?filter=surfwater

Starner, K. 2010. Long-term Pesticide Monitoring in High-Use Agricultural Areas.

http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study262protocol.pdf

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

Table 1. Monitoring Plan, 2013

Region	Season	Analytical Screen	Events
Salinas	spring through fall	Organophosphate	6
		Diazinon	6
		Chlorothalonil	3
		Pyrethroids	3
		Dinitroanilines	2
		Methomyl	3
		Imidicaloprid	2
		Diacylhydrazines	3
Santa Maria	spring through fall	Organophosphate	3
		Chlorothalonil	1
		Pyrethroids	1
		Dinitroanilines	1
		Imidicaloprid	2
Imperial	spring	Organophosphate	1
		Diazinon	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 2. 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
Pendimethalin	0.01	0.05
Oxyfluorfen	0.01	0.05

Chlorothalonil in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Chlorothalonil	0.0348	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 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

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

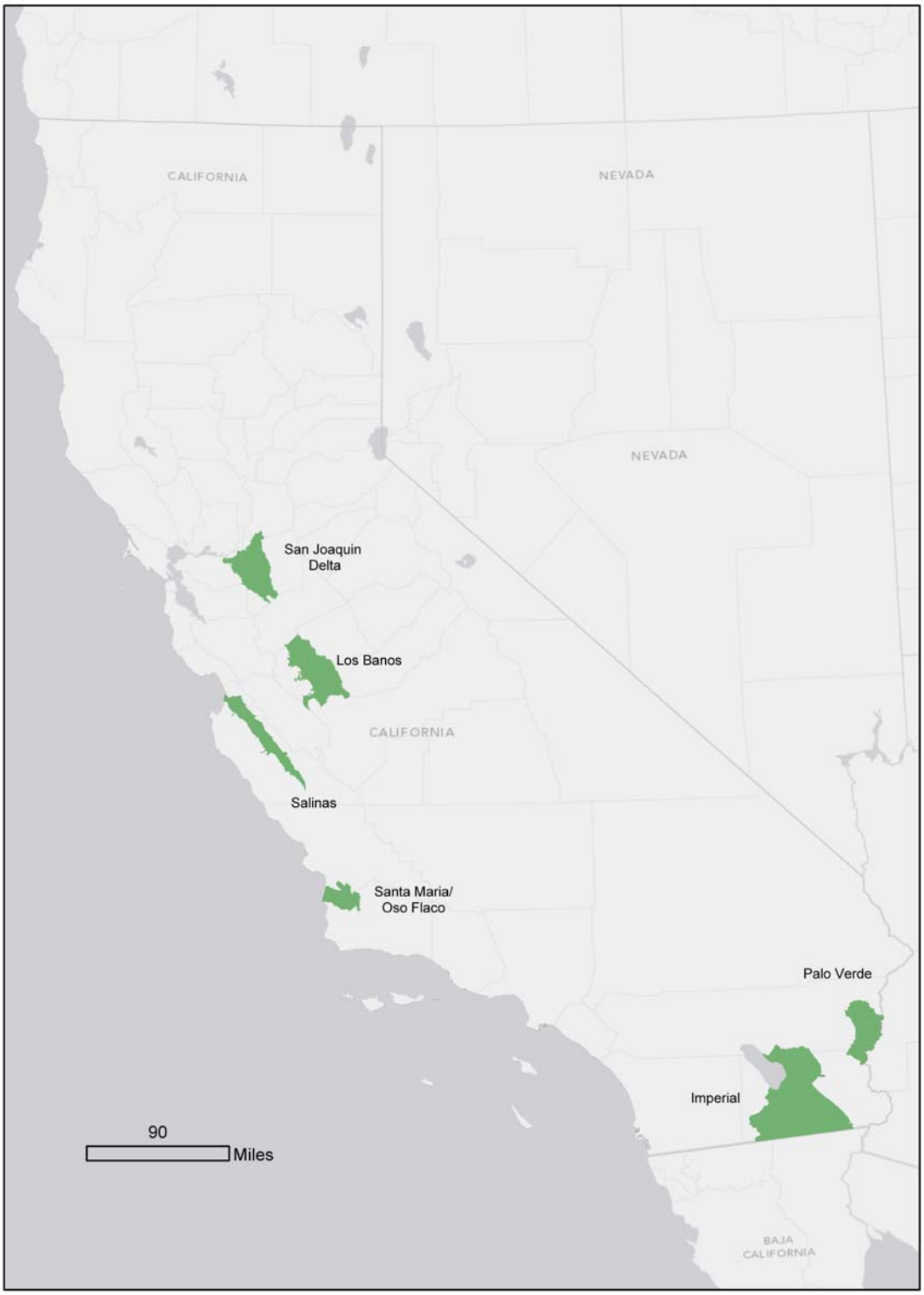

Figure 1. California agricultural monitoring regions, 2013.