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Study 262. Long-term Pesticide Monitoring in High-Use Agricultural Areas, Year Three.

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I. INTRODUCTION

In California, a wide variety of pesticides are applied throughout the year. In 2008, for example, over 300 pesticide active ingredients (AIs) were applied in agricultural areas of the state (CDPR 2010a). 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 2007a). 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 identified by Starner (2009a) as possessing relative high aquatic toxicity are widely used in the Central Coast and Imperial Valley regions (Figure 1). Agricultural pesticide use in these areas is among the highest in the state for a wide variety of pesticides, including insecticides, herbicides and fungicides. The two areas represent different climates, soil types, treated crops, and agricultural practices, factors which impact the potential for offsite movement of pesticides. Pest pressures, water availability, and crops grown can vary from year to year; as such, management practices and pesticide use patterns can also vary from year to year.

Recent monitoring results from these areas indicate that, for several of these 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, 2009b). Consequently, consistent monitoring over time is needed to understand the environmental fate of current-use pesticides under a variety of conditions and for development of management responses. As such, DPR plans to maintain a permanent surface water monitoring presence in these two areas.

Additionally, monitoring data from these two high-use areas provide insight into the potential for off-site movement of specific AIs in other agricultural regions of California. A lack of detections of a specific AI in the two regions of high use may indicate that significant off-site movement is unlikely under similar conditions in other areas with lower use; conversely, AIs that are frequently detected in these high use areas may also be moving off-site in other, lower use regions of the state. In this way, the monitoring results from these two areas will be used to develop additional targeted monitoring efforts in other areas of the state where such data do not already exist. These targeted monitoring efforts may be large in scale, or may focus on only one or two AIs with a brief period of high use in another area of the state. Such expanded targeted monitoring will broaden the understanding of the environmental fate of specific AIs.

For example, malathion has been detected in recent DPR monitoring efforts in Imperial Valley (alfalfa) and the Central Coast (lettuce) (unpublished data, DPR). Malathion is also commonly used in high amounts on alfalfa in Merced County in the spring; no targeted malathion monitoring data exist for this use in the area. Based on this, DPR will conduct targeted monitoring for malathion in the spring of 2010 in the Merced area.

Note: All pesticide use data cited are agricultural use data from DPR 2010a unless specified otherwise.

II. OBJECTIVE

The objective of this study is to provide 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.

IV. STUDY PLAN

Long-term monitoring, Central Coast and Imperial Valley

Monitoring in each geographic area will be conducted during the season or seasons of historically high pesticide use (Table 1, CDPR 2010a). Central Coast monitoring will be conducted during the irrigation season (April through September) in the Salinas/Pajaro Valleys and Santa Maria Valley. Sampling will take place approximately once per month during this period. Imperial Valley monitoring will include spring and fall monitoring.

Six to ten "primary" sites in each area will be sampled at least once at every sampling interval. Primary sites will be sampled for organophosphate and carbamate insecticides at every sampling event. Samples will also be collected for additional AIs at the primary sites as appropriate based on historical pesticide use and recent monitoring results. In addition to the primary sites, additional "secondary" sites will 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. Site selection will follow the general guidelines in Standard Operating Procedure (SOP) FSWA002.00 (Bennett 1997) where applicable. Sampling will commence in Spring 2010 and continue through October 2010.

Expanded Targeted Monitoring, Merced

Monitoring in the Merced area will be conducted in the spring, coinciding with historic use of malathion on alfalfa. Approximately six to eight sites will be sampled for organophosphate insecticides and dinitroaniline herbicides. Locations of individual sampling sites will be determined based on historical pesticide use patterns in the area. Site selection will follow the general guidelines in Standard Operating

Procedure (SOP) FSWA002.00 (Bennett 1997) where applicable. Sampling will be conducted in Spring 2010. Long-term monitoring in this area is not under consideration at this time.

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, or other sampling equipment designed to collect a sample directly into a 1-liter glass bottle. 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 2010, US EPA 2009, Marshack 2008, CDFG 1994a, 1994b, 1995, 1996a, 1996b, 1998a, 1998b, 2000); spatial analysis of data in order to identify correlations between observed pesticide concentrations and region-specific pesticide use and geographical features such as climate, soil type, cropping patterns and agricultural practices; assessment of results to determine potential additional monitoring in regions with similar pesticide use patterns.

VIII. TIMETABLE

Field Sampling:	February 2010 through October 2010
Chemical Analysis:	February 2010 through March 2011
Draft Report:	September 2011

IX. BUDGET

Sample analysis	Samples	Cost/Sample	Cost Estimate
Organophosphates	81	$600	$48600
Diazinon	64	425	27200
Carbamates	68	800	54400
Acephate/methamid.	40	800	32000
Bensulide	59	510	30090
Imidacloprid	37	500	18500
Dinitroanilines	17	800	13600
Subtotal Analysis			**$224,390**

Continuing QC	Samples	Cost/Sample	Cost Estimate
Organophosphates	8	$600	$4800
Diazinon	6	425	2550
Carbamates	7	800	5600
Acephate/methamid.	4	800	3200
Bensulide	6	510	3060
Imidacloprid	4	500	2000
Dinitroanilines	2	800	1600
Subtotal QC			**$22,810**
Total			**$247,200**

X. REFERENCES

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Table 1. Monitoring Plan, 2010.

Area	**Analytical Screen**	**Season**	**Sample events**
Merced	Organophosphates	Spring	1
Merced	Dinitroanilines	Spring	1
Central Coast	Organophosphates	Spring though Fall	6
Central Coast	Carbamates	Spring through Fall	6
Central Coast	Acephate/Methamid.	Spring through Fall	6
Central Coast	Bensulide	Spring through Fall	6
Central Coast	Imidacloprid	Spring through Fall	3
Imperial Valley	Organophosphates	Spring and Fall	2
Imperial Valley	Carbamates	Spring and Fall	2
Imperial Valley	Dinitroanilines	Spring	1
Imperial Valley	Bensulide	Fall	1
Imperial Valley	Imidacloprid	Fall	1

Note: all sampling dates are in 2010.

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)***
Aldicarb SO	0.0277	0.05
Aldicarb SO2	0.0214	0.05
Oxamyl	0.0255	0.05
Methomyl	0.0265	0.05
Mesurol SO	0.0264	0.05
3 OH-Carbofuran	0.0232	0.05
Aldicarb	0.0196	0.05
Carbofuran	0.0244	0.05
Carbaryl	0.0136	0.05
Mesurol	0.0270	0.05

Acephate/Methamidaphos (ACE) in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Acephate	0.0370	0.25
Methamidophos	0.126	0.25

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

Figure 1. Primary Agricultural Monitoring Areas, 2010