



**Department of Pesticide Regulation  
Environmental Monitoring Branch  
1001 I Street  
Sacramento, CA 95812  
February 25, 2009**

**STUDY #255: SURFACE WATER MONITORING FOR DORMANT SEASON  
USE HERBICIDES: A PRELIMINARY INVESTIGATION**

**Michael Ensminger**

**I. INTRODUCTION**

Oxyfluorfen is one of California's most heavily applied pesticides, with between 600,000 to 700,000 lb ai. applied for each of the past three years (CDPR, 2008). Oxyfluorfen is used on many crops, with main use on grapes and almonds. In addition, more than two-thirds of oxyfluorfen's agricultural use occurs during the winter rainy season (Table 1). In a recent analysis of this herbicide, Starner (2008a) has shown that it is a potential concern in surface waters due to its high use and due to its aquatic toxicity to nonvascular plants. Although the California Department of Pesticide Regulation (CDPR) has recently included oxyfluorfen in its monitoring programs, it has not been the focus of this work (Starner, 2007; Starner, 2008b).

In addition to oxyfluorfen, three dinitroaniline herbicides (oryzalin, pendimethalin, and trifluralin), one triazine herbicide (simazine), and one urea herbicide (diuron) also have high use in the winter rainy season. All of these herbicides have high acute toxicity to nonvascular plants (US EPA, 2009). Starner (2008a) has recommended that CDPR monitor these herbicides based on their high use and toxicity.

**II. OBJECTIVES**

The objectives of this study are to:

1. Collect surface water samples from ten creek and river sites in Napa, Sonoma, and Yolo Counties;
2. Analyze these water samples for the herbicides listed in Table 3 to determine their frequency of occurrence and their concentrations;
3. Compare the concentration of any detected herbicide for its potential to cause toxicity to nonvascular plants based on the US EPA aquatic life benchmarks (US EPA, 2009).

### III. PERSONNEL

CDPR Environmental Monitoring Branch staff, under the overall supervision of Kean S. Goh, Program Manager (Supervisor) I will conduct this study. Other key personnel include:

- Project Leader: Mike Ensminger
- Field Coordinator: Jennifer Kusler
- Research Scientist: Frank Spurlock
- Chemicals: California Department Food and Agriculture, Center for Analytical Chemistry (CDFA) Staff Chemists

Please direct questions regarding this study to Michael Ensminger, Environmental Scientist, at (916) 324-4186 or [mensminger@cdpr.ca.gov](mailto:mensminger@cdpr.ca.gov).

### IV. STUDY PLAN

#### **Study Sites**

CDPR will collect water samples from ten sites in Napa, Sonoma, and Yolo Counties (see Figures 1 and 2). During the winter rainy season, these counties have high use of the herbicides listed in Table 1. Because this is a preliminary study, CDPR chose these monitoring sites based on known sites in these counties. Future monitoring work with these herbicides could expand to other counties of high winter season use.

#### **Field Parameters**

In addition to collecting water samples for chemical analysis, we will take the following field parameters *in situ*: pH, dissolved oxygen, electrical conductivity, turbidity, and temperature. CDPR scientists will collect these parameters using a YSI 6920 V2-2 Multiparameter Sonde as described by Doo and Lee (2008).

#### **Quality Assurance/Quality Control**

Quality Assurance/Quality Control (QA/QC) will be conducted in accordance with approved CDPR SOP QAQC001.00 (Segawa, 1995). For field QC, 10% of the samples will be QC samples; these samples will comprise of field blanks and field duplicate samples.

## V. SAMPLING METHODS/CHEMICAL ANALYTICAL METHODS

### Sampling Methods

#### A. Water

CDPR staff will collect water samples for chemical analysis following CDPR SOP FSWA002.00 (Bennett, 1997). Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed.

### Chemical Analyses

CDPR staff will transport samples following the procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999b). A chain-of-custody record will be completed and accompany each sample. CDFA will conduct chemical analysis for the herbicides listed in Table 3. Herbicides will be reported as detected if they are found at concentrations equal to or greater than their RL (reporting limit). Concentrations of the herbicides will be reported in  $\mu\text{g L}^{-1}$  (ppb).

## VI. DATA ANALYSIS

For this study, we are interested in detections or non-detections of herbicides in surface waters. When herbicides are detected, we will analyze their potential to cause toxicity to nonvascular plants. The findings will be written in a summary report.

## VII. TIMETABLE

CDPR will collect the water samples in February and March 2009. CDPR will collect a total of 40 samples, not including QC for the study. See Table 2 for a timetable of data collection.

Table 1. Agricultural use of herbicides in California, 2007

Herbicide	2007 Agricultural Use (Acres)		
	Year Total	Rainy Season <sup>1</sup>	Percentage
Oxyfluorfen	645,235	435,552	68%
Pendimethalin	1,009,327	661,760	66%
Trifluralin	896,251	319,571	34%
Oryzalin	578,417	438,133	76%
Simazine	475,812	347,965	73%
Diuron	463,890	367,823	79%

<sup>1</sup> November, December, January, February

Table 2. Sampling sites and approximate sampling dates for study 255.

Herbicide Screen		DN <sup>1</sup>		TR <sup>2</sup>	
Approximate Sampling Dates		Feb	Mar	Feb	Mar
		16 - 17	16 - 17	16 - 17	16 - 17
County	Site	Sample Collection (X)			
Yolo	Dry Slough at CR99	X	X	X	X
	Willow Slough at CR99	X	X	X	X
	Willow Slough at CR102	X	X	X	X
Yolo	Willow Slough, S. Fork at SR 16	X	X	X	X
	Irrigation canal at CR19/SR16	X	X	X	X
	Cache Creek at Highway 113	X	X	X	X
Napa	Napa River at Yountville Rd	X	X	X	X
	Napa River at Trancas Rd	X	X	X	X
Sonoma	Sonoma Creek at Madrone Rd. and Highway 121	X	X	X	X
	Sonoma Creek near 121	X	X	X	X
QC	Field blanks, duplicate	X	X	X	X
	Blind spikes	X			X
Grand Total		13	12	12	13

<sup>1</sup>DN = dinitroaniline herbicides and the diphenylether herbicide oxyfluorfen.

<sup>2</sup>TR = photosynthetic affecting herbicides include triazines, ureas, and the phenylpyridazinone herbicide norflurazon.

Table 3. Minimum detection limits (MDL) and reporting limits (RL) for the herbicide analyses.

<b>Dinitroaniline Herbicides and Oxyfluorfen (DN) in Water</b>	<b>MDL (<math>\mu\text{g L}^{-1}</math>)</b>	<b>RL (<math>\mu\text{g L}^{-1}</math>)</b>	<b>Photosynthetic Affecting Herbicides ("Trazines" [TR])</b>	<b>MDL (<math>\mu\text{g L}^{-1}</math>)</b>	<b>RL (<math>\mu\text{g L}^{-1}</math>)</b>
Oryzalin	0.0048	0.05	Atrazine	0.02	0.05
Ethalfuralin	0.0150	0.05	Simazine	0.013	0.05
Trifluralin	0.0140	0.05	Diuron	0.022	0.05
Benfluralin	0.0120	0.05	Prometon	0.016	0.05
Prodiamine	0.0120	0.05	Bromacil	0.031	0.05
Pendimethalin	0.0120	0.05	Hexazinone	0.040	0.05
Oxyfluorfen	0.0100	0.05	Norflurazon	0.019	0.05
			DEA	0.010	0.05
			ACET	0.030	0.05
			DACT	0.016	0.05
			Propazine		0.05

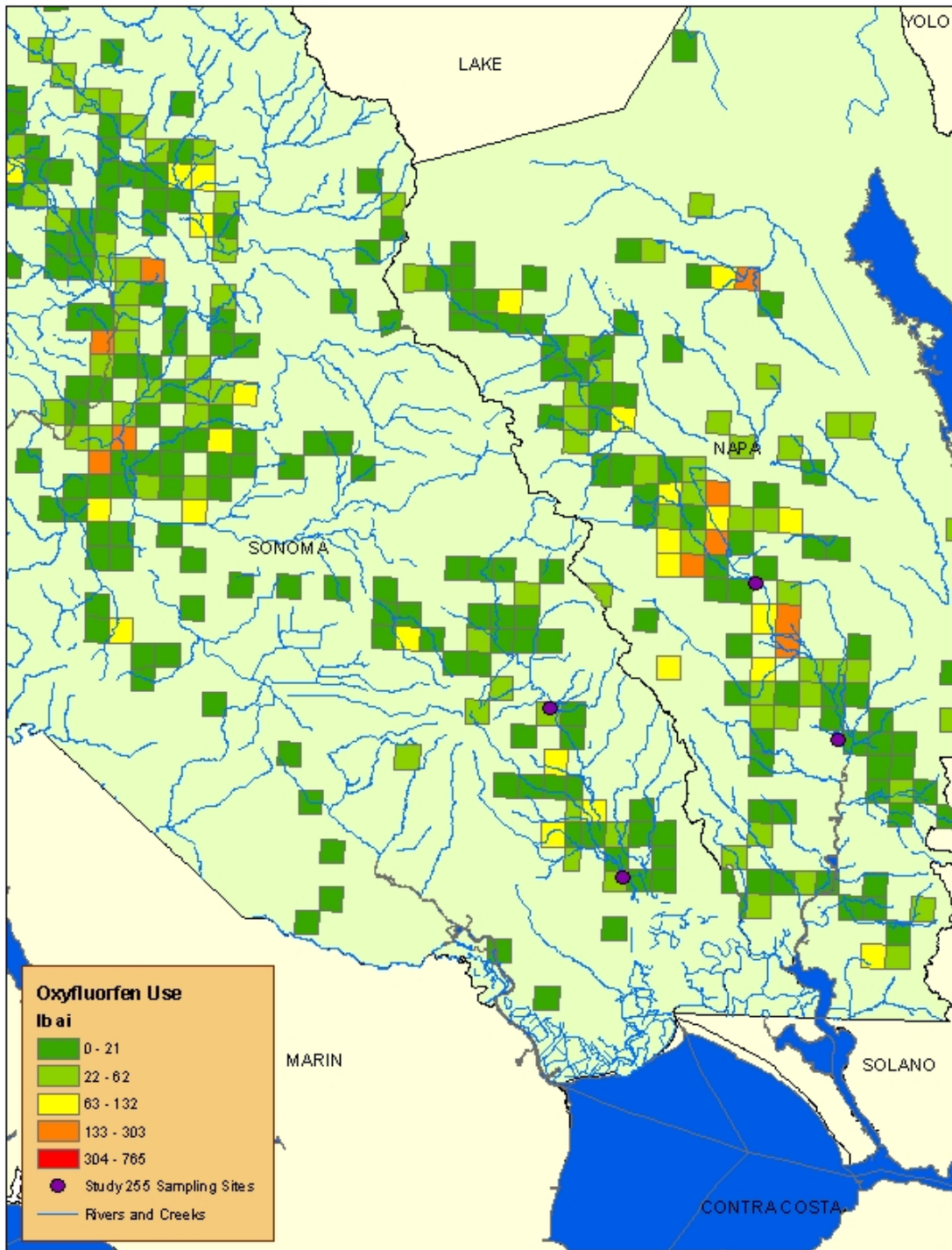


Figure 1. Oxyfluorfen use and sampling sites in Napa and Sonoma Counties. Oxyfluorfen use is during January, February, November, and December 2007.

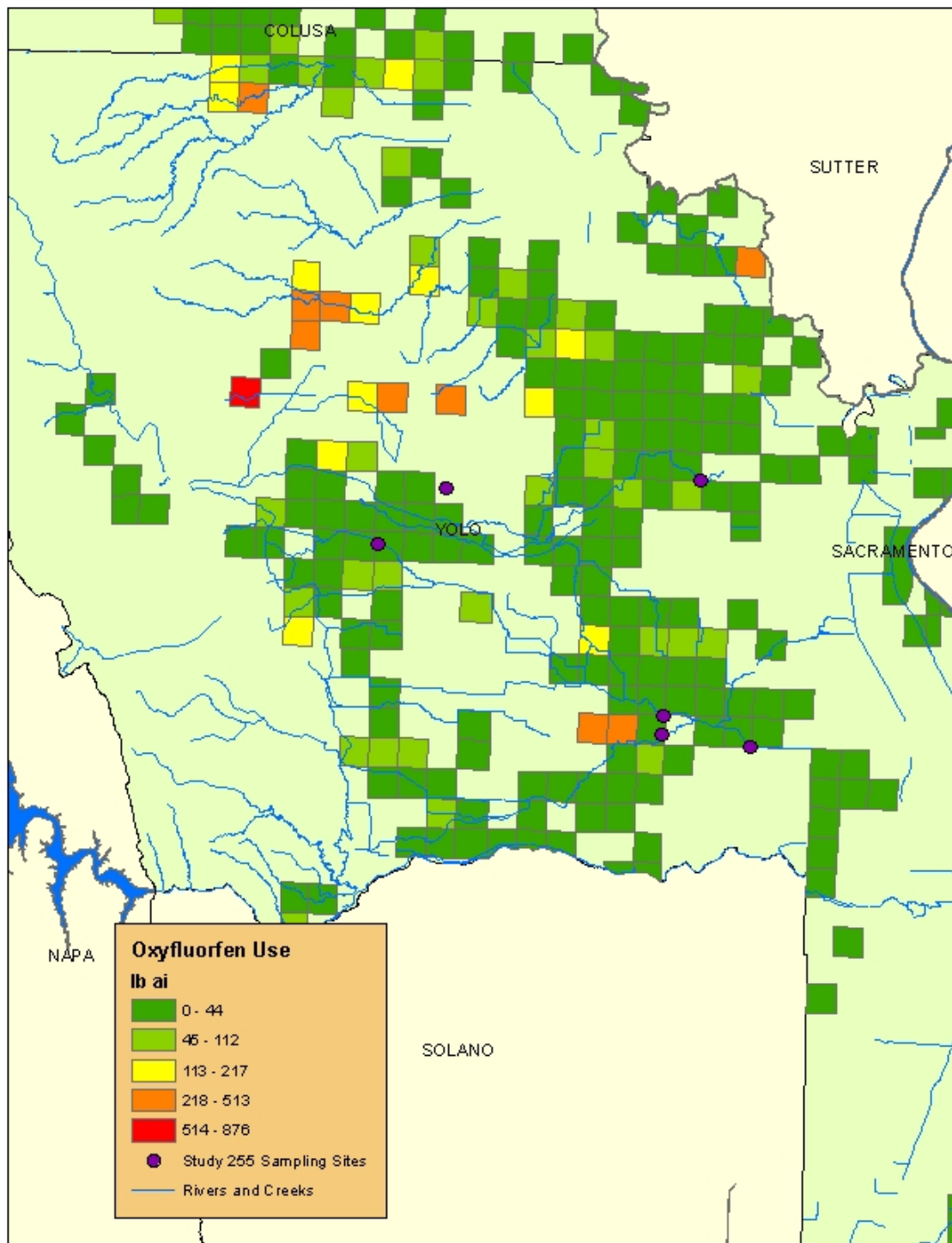


Figure 2. Oxyfluorfen use and sampling sites in Yolo County. Oxyfluorfen use is during January, February, November, and December 2007.

## VIII. LITERATURE CITED

- Bennett, K. 1997. California Department of Pesticide Regulation SOP number FSWA002.00: Conducting surface water monitoring for pesticides. Available at <http://www.cdpr.ca.gov/docs/empm/pubs/sops/fswa002.pdf> (accessed 5 February 2009).
- CDPR. 2008. California Department of Regulation. California Pesticide Information Portal (CalPIP), Pesticide Use Report (PUR) Data Available at <http://calpip.cdpr.ca.gov/cfdocs/calpip/prod/main.cfm> (accessed on 20 January 2009).
- Doo, S and H. Lee. 2008. California Department of Pesticide Regulation SOP number EQWA010.00: Calibration, field measurement, cleaning, and storage of the YSI 6920 V2-2 Multiparameter Sonde. Available at <http://www.cdpr.ca.gov/docs/empm/pubs/sops/fswa002.pdf> (accessed 20 January 2009).
- Jones, D. 1999b. California Department of Pesticide Regulation SOP number QAQC004.01: Transporting, packaging and shipping samples from the field to the warehouse or laboratory. Available at <http://www.cdpr.ca.gov/docs/empm/pubs/sops/qaqc0401.pdf> (accessed 31 October 2007).
- Segawa, R. 1995. California Department of Pesticide Regulation SOP number QAQC001.01: Chemistry Laboratory Quality Control. Available at <http://www.cdpr.ca.gov/docs/emon/pubs/sop.htm> (accessed on 11 February 2009)
- Starner, K. 2007. Study 248. Long-term pesticide monitoring in high-use agricultural areas: Central Coast and Imperial Valley. Available at <http://www.cdpr.ca.gov/docs/emon/pubs/protocol.htm> (accessed on 20 January 2009).
- Starner, K. 2008a. Review of the U.S. Environmental Protection Agency aquatic life benchmarks, with monitoring recommendations. Available at <http://www.cdpr.ca.gov/docs/emon/surfwtr/policies.htm> (accessed on 20 January 2009).
- Starner, K. 2008b. Study 252. Long-term pesticide monitoring in high-use agricultural areas: Year two, Central Coast and Imperial Valley. Available at <http://www.cdpr.ca.gov/docs/emon/pubs/protocol.htm> (accessed on 20 January 2009).
- US EPA. 2009. Aquatic life benchmarks. Available at [http://www.epa.gov/oppefed1/ecorisk\\_ders/aquatic\\_life\\_benchmark.htm](http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm) (accessed on 11 February 2009).