



Surface Water Monitoring for Dormant Season Use Herbicides in Northern California

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Abstract

Surface water studies conducted by the California Department of Pesticide Regulation (CDPR) have focused on monitoring for insecticides due to their toxicity to aquatic invertebrate organisms. However, there is new interest in herbicides that may cause toxicity to nonvascular plants and algae. Several of the herbicides with low toxicity benchmarks have high reported use during the winter months. Rain during this season could lead to greater herbicide concentrations in the water column. Therefore, a preliminary study was initiated in 2009 to determine the concentrations of various herbicides that may impact these organisms. Water from ten sites in Napa, Sonoma, and Yolo Counties were sampled and analyzed for several photosynthetic inhibitor and dinitroaniline herbicides, oxyfluorfen, and norflurazon. Preliminary results show that oryzalin and hexazinone were detected in Yolo County, diuron was detected in Napa and Yolo Counties, and simazine was detected in all three counties. Two of the diuron detections (4.08 and 4.64 $\mu\text{g L}^{-1}$) exceeded the US EPA Aquatic Life Benchmarks of 2.4 $\mu\text{g L}^{-1}$ for nonvascular plants.

Objectives

The objectives of this study were to:

1. Collect surface water samples from ten creek and river sites in Napa, Sonoma, and Yolo Counties.
2. Analyze these water samples for oxyfluorfen, norflurazon, and dinitroaniline and photosynthetic inhibitor herbicides to determine their frequency of occurrence and 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).



Figure 2. Sampling site in Yolo County.

Table 1. Agricultural use of herbicides in California, 2007.

Herbicide	2007 Agricultural Use (acres)		
	Year Total ¹	Rainy Season ²	Percentage
Bromacil	24,939	18,729	75%
Diuron	463,890	367,823	79%
Hexazinone	74,986	60,147	80%
Oryzalin	578,417	438,133	76%
Oxyfluorfen	645,235	435,552	68%
Pendimethalin	1,009,327	661,760	66%
Simazine	475,812	347,965	73%
Trifluralin	896,251	319,571	34%

¹ CDPR, 2009.

² January, February, November, December

Table 2. Highest concentration of herbicide detected in the water samples compared to EPA's aquatic benchmarks.

Analyte	MDL ($\mu\text{g L}^{-1}$)	RL ($\mu\text{g L}^{-1}$)	Highest Detection ($\mu\text{g L}^{-1}$)	US EPA Aquatic Life Benchmark for Nonvascular Plants ($\mu\text{g L}^{-1}$)
Bromacil	0.031	0.05	0.163	6.80
Diuron	0.022	0.05	4.64	2.4
Hexazinone	0.04	0.05	1.35	7.0
Oryzalin	0.0048	0.05	0.129	42.0
Simazine	0.013	0.05	0.828	36.0

Materials and Methods

Study sites

Ten monitoring sites were selected in three counties of California: Napa, Sonoma, and Yolo (Figures 1 and 2). The sites included rivers and creeks (Figure 2). Sampling was performed during the rainy season due to the high historical herbicide use during this period (Table 1) and due to the potential for rain runoff. A total of 44 samples were collected from the 10 sites during February and March 2009. Of these 44 samples, four were designated for quality control in the form of field blanks and field duplicates.

Surface water samples were collected from the middle of the water body directly into 1-L glass amber bottles via the grab method (Figure 3). The bottles were then sealed and transported on wet ice to CDPR's West Sacramento facilities where they were refrigerated at 4°C until extracted for chemical analysis. *In situ* measurements of pH, dissolved oxygen, electrical conductivity, turbidity, and temperature were also taken at each site using a YSI 6920 V2-2 Multiparameter Sonde.

Chemical Analysis

The California Department of Food and Agriculture's Center for Analytical Chemistry (CDFA) analyzed the surface water samples for the following herbicides and herbicide degradates: oxyfluorfen, norflurazon, oryzalin, ethalfuralin, trifluralin, benfluralin, proflumicarb, pendimethalin, atrazine, simazine, diuron, prometon, bromacil, hexazinone, prometryn, metribuzin, DEA, ACET, and DACT. The reporting limits (RL) for all herbicides are 0.05 $\mu\text{g L}^{-1}$. Detections above the RL were reported in $\mu\text{g L}^{-1}$; detections below the RL but above the method detection limit were reported as trace detections. Trace detections were not quantified.



Figure 1. Counties sampled in the study.



Figure 3. Sampling site in Napa County.

References:

CDPR, 2009. California Department of Regulation. California Pesticide Information Portal (CalPIP). Pesticide Use Report (PUR) Data Available at <http://calpip.cdpr.ca.gov/cdprdocs/calpip/prod/main.cfm> (accessed on 20 January 2009).

US EPA, 2009. Aquatic Life Benchmarks. Available at http://www.epa.gov/oppfead1/ecorisk_ders/aquatic_life_benchmark.htm (accessed 11 February 2009).

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Results

Preliminary results from 15 water samples indicate that of the 19 herbicides and degradates screened, five were detected: bromacil, diuron, hexazinone, oryzalin, and simazine.

Bromacil was detected in two of seven samples from Yolo County. Bromacil was not detected in either Napa or Sonoma Counties.

Diuron was detected in five out of seven samples from Yolo County. Of these five detections, three were quantifiable while the other two were trace detections. Two of these detections exceeded the US EPA Aquatic Life Benchmarks for nonvascular plants (Table 2). Diuron was detected in both samples from Napa County. Diuron was not detected in any samples from Sonoma County.

Hexazinone was detected in five out of seven samples from Yolo County. Hexazinone was not detected in either Napa or Sonoma Counties.

Oryzalin was detected in five out of seven samples from Yolo County. Three of these detections were quantifiable, while the other two were trace detections. Results from chemical analyses of the Napa and Sonoma samples are pending.

Simazine was detected in three out of seven samples from Yolo County. Two of the detections were quantifiable, while the other was a trace detection. There were quantifiable detections in both samples from Napa County and in all four samples from Sonoma County.