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Environmental Monitoring Branch
Surface Water Protection Program
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Surface Water Monitoring for Dormant Season Use Herbicides in Northern California

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Introduction

Historically, surface water monitoring conducted by the California Department of Pesticide Regulation (CDPR) has focused on insecticides given their toxicity to aquatic invertebrates. More recently CDPR is interested in monitoring herbicides that may be toxic to non-vascular plants based on Starner's (2008) recommendations. Several herbicides with low toxicity benchmarks have high use during the rainy season, which can contribute to herbicide runoff and may produce high concentrations in surface water. In 2008, over 18 million pounds of herbicides were applied in California with at least one third of the applications during the months of November through February. Specifically, 65% of the total pounds of oxyfluorfen active ingredient (a.i.) that was applied occurred during the rainy season. Due to the high dormant season use of herbicides, in 2009 a study was conducted to monitor the concentrations of herbicides in surface water. Three counties with traditionally high herbicide use were selected for monitoring to compare the effects of storm and baseflow events on herbicide concentrations and frequencies.

Table 1. Agricultural use (acres) of herbicides in California, 2008.

	2008 Agricultural Use (acres)		
Herbicide	Year Total[1]	Rainy Season[2]	Percentage[3]
Bromacil	21,471	14,862	69%
Diuron	512,682	230,257	45%
Hexazinone	129,204	106,727	83%
Oryzalin	266,061	182,861	69%
Oxyfluorfen	1,550,619	746,325	48%
Pendimethalin	745,960	464,798	62%
Simazine	319,257	224,505	70%
Trifluralin	548,378	126,255	23%

1. CDPR, 2009.
2. November, December, January, February.
3. Percentage applied during rainy season.

Table 2. Agricultural use of herbicides (pounds of a.i.) in California, 2008.

	2008 Agricultural Use (pounds of a.i.)		
Herbicide	Year Total[1]	Rainy Season[2]	Percentage[3]
Bromacil	70,013	53,718	77%
Diuron	733,237	578,769	79%
Hexazinone	110,722	70,522	64%
Oryzalin	592,972	413,049	70%
Oxyfluorfen	683,485	441,108	65%
Pendimethalin	1,454,999	1,042,416	72%
Simazine	436,933	327,884	75%
Trifluralin	662,740	196,144	30%

Objectives

The objectives of this study were to:

1. Collect surface water samples from ten agricultural creek and river sites in Napa, Sonoma, and Yolo Counties – a region characteristic of the state's top producing crops.
2. Analyze these water samples for norflurazon, oxyfluorfen, and several 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).

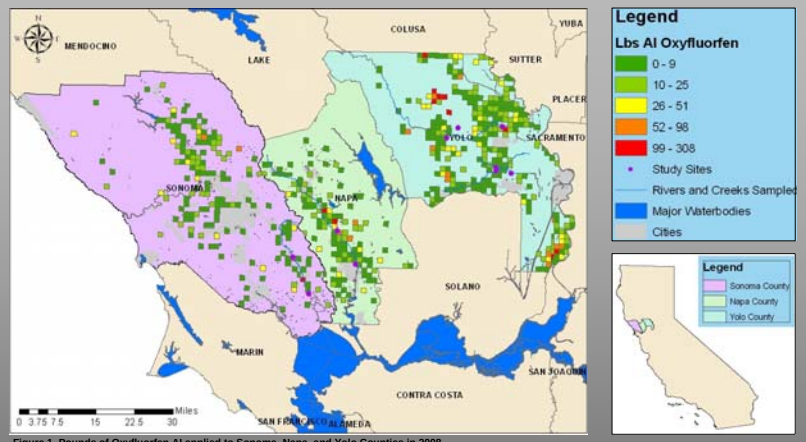

Figure 1. Pounds of Oxyfluorfen AI applied to Sonoma, Napa, and Yolo Counties in 2008.

Materials & Methods

Study Sites

- Ten river and creek sites were sampled in Napa, Sonoma, and Yolo Counties.
- 50 surface water samples taken during storm and baseflow events were collected from sites during February and March 2009.

Chemical Analysis

- California Department of Food and Agriculture (CDFA) analyzed oxyfluorfen, norflurazon, oryzalin, ethalfluralin, trifluralin, benfluralin, prodiamine, pendimethalin, atrazine, simazine, diuron, prometon, bromacil, hexazinone, prometryn, metribuzin, DEA, ACET, and DACT.
- Reporting limits (RL) for all herbicides were 0.05 ppb. Detections below the RL but above the method detection limit (MDL) were reported as trace detections, which were not quantified. All trace detections were assigned as 0.025 ppb for statistical analysis.

Statistical Analysis

- Concentrations during storm, four days after storm, and baseflow events at ten sites were pooled and compared using the paired non-parametric directional Wilcoxon signed-rank test.

Results & Discussion

- Of the 19 herbicides analyzed, eight were detected which included: bromacil, diuron, hexazinone, oryzalin, oxyfluorfen, pendimethalin, simazine, and trifluralin. The 11 herbicides not detected were: ACET, atrazine, benfluralin, DACT, DEA, ethalfluralin, metribuzin, norflurazon, prodiamine, prometon, and prometryn. The MDLs for herbicides not detected ranged from 0.01 to 0.03 ppb.
- The highest detected concentrations of each analyte occurred during the storm event in February at two sites in Yolo County and at one site in Sonoma County.
- Bromacil, diuron, hexazinone, oryzalin, oxyfluorfen, pendimethalin, simazine, and trifluralin were detected at significantly higher concentrations during the storm than baseflow events in Yolo County and one site in Sonoma County (Wilcoxon Signed-Rank test, $p < 0.025$) [Fig. 2]. Detection frequencies were also significantly higher during the storm than baseflow events (Wilcoxon Signed-Rank test, $p \leq 0.01$) [Fig. 3].
- In Napa and Sonoma Counties, diuron, oryzalin, and simazine were also detected at significantly higher concentrations four days after the storm than baseflow events (Wilcoxon Signed-Rank test, $p < 0.005$) [Fig. 5].
- Two of the diuron detections (4.64 ppb and 4.08 ppb) and one of the oxyfluorfen detections (1.139 ppb) from the storm event exceeded US EPA Aquatic Life Benchmarks of 2.4 ppb and 0.29 ppb for acute non-vascular plants, respectively [Fig. 6,7].
- Overall, detection frequencies and concentrations were consistently higher during the storm and four days after the storm than during the baseflow events.

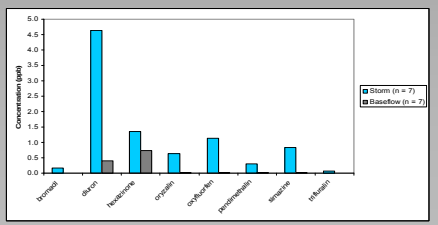

Figure 2. Highest concentration detected (ppb) during storm vs. non-storm events in Yolo County and one site in Sonoma County.

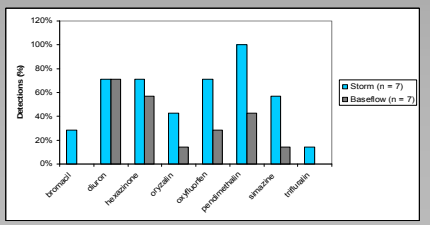

Figure 3. Detection frequency during storm vs. baseflow events in Yolo County and one site in Sonoma County.

Figure 4. Cache Creek at Highway 113 at Yolo County study site. Photo by M. Ensminger.

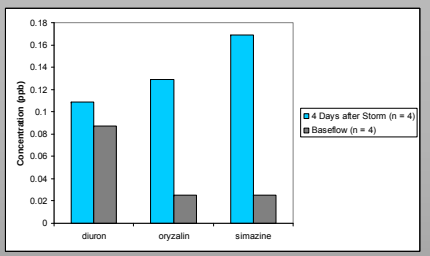

Figure 5. Highest concentration detected (ppb) four days after storm vs. non-storm events in Napa and Sonoma Counties.

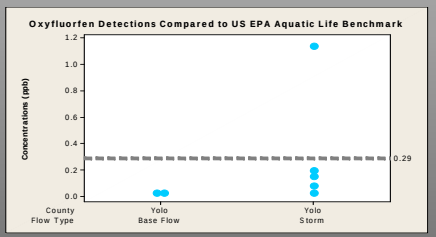

Figure 6. Oxyfluorfen detections (ppb) compared to US EPA Aquatic Life Benchmark.

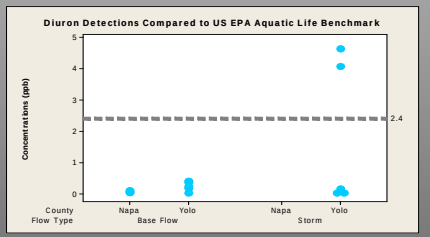

Figure 7. Diuron detections (ppb) compared to US EPA Aquatic Life Benchmark.

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Acknowledgements

Many people have generously given their time and talents to help this study succeed. We would like to thank Sheryl Gill for her overall support of this study and swift and succinct review of the poster. We would like to thank Sue Peoples for sample coordination and organization between DPR and the CDFA, and we would like to thank Jesse Ybarra for his help in maintaining DPR's West Sacramento's facility. Furthermore, we would like to thank the staff at DPR, Environmental Monitoring Branch for assisting in field sampling. Finally, we extend gratitude to the staff at CDFA for sample analysis.

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