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Simazine, Diuron, and Atrazine Detections in California Surface Waters

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Abstract

In 2007, 35 surface water samples were collected from 28 sites in three agricultural regions within California and analyzed for selected herbicides using a reporting limit (RL) of 0.05 μg L^{-1}. In Napa and Sonoma counties, monitoring coincided with the late winter high-use season for simazine. Simazine was detected in all seven of those samples following a rainstorm. Additional detections in these samples included diuron (two detections) and prometon (one detection). No simazine was detected above the RL in samples collected during an earlier dry period in the same area (14 samples); two of these samples had trace amounts of simazine. Diuron was detected in five of these samples. In Imperial County, monitoring was conducted to coincide with the high-use season for atrazine, which was detected in four of ten samples; DEA, a degradate of atrazine, was detected at trace levels in an additional sample. Diuron was also detected in one sample collected in Imperial County. Furthermore, diuron was detected in three of four early spring samples in Monterey County. Maximum detected concentrations are compared to aquatic toxicity benchmarks; mass loadings for herbicides detected during the single storm event are also presented.

Introduction

A wide variety of herbicides are applied annually in high amounts throughout California. In 2006, 65 herbicide active ingredients were each applied in amounts over 1,000 kg active ingredient; this amounted to about 8.8 million kg herbicides applied (CA DPR 2007a). For many of these herbicides, recent surface water monitoring data from areas of high use are lacking (CA DPR 2007b); such data are needed in order to assess their potential impacts on aquatic systems.

Simazine and atrazine, both triazine herbicides used to control broadleaf weeds and annual grasses, are toxic to non-target aquatic plants (US EPA 2007). Simazine is used in several agricultural regions of California and is applied to wine grapes in the Sonoma/Napa area during California's wet season; almost half of California's atrazine use occurs in the Imperial Valley. No recent triazine surface water monitoring data are available for these regions of high use. In 2006, DPR initiated a monitoring study designed to begin assessing pesticide contamination of surface waters in high-use regions of the state (Starner 2006). As part of that study, surface water samples were collected from Napa, Sonoma, and Imperial Counties in early 2007 and analyzed for a suite of seven herbicide active ingredients. In addition, water samples were collected from Monterey County during a period of relatively low herbicide use in that area.

Materials and Methods

Twenty-eight monitoring sites were chosen in three regions of California: Napa/Sonoma, Imperial, and Monterey Counties (Figure 1). Sites included main stem rivers, tributary creeks, agricultural drains, and an inland saline lake. From the 28 sites, a total of 35 samples were collected in January, February, or March 2007.

In two regions of California, sampling was timed to coincide with historic periods of high triazine herbicide use; simazine in Napa/Sonoma Counties, and atrazine in Imperial County. In the third region, Monterey County, samples were collected in early spring. For one sampling interval in Napa/Sonoma, storm run-off samples were collected during a winter storm. All other sampling occurred during dry weather.

Surface water samples were collected as close as possible to the center channel by using an extendable pole, collecting the water sample directly into a 1 L amber bottle. After collecting the samples, bottles were sealed with Teflon®-lined lids and transported on wet ice or refrigerated at 4°C until extracted for chemical analysis. At each site, dissolved oxygen, pH, specific conductance and water temperature were measured *in situ*.

The California Department of Food and Agriculture's Center for Analytical Chemistry (CDFA) analyzed the surface water samples for the following herbicides: atrazine, simazine, diuron, prometon, bromacil, hexazinone, and norflurazon. Reporting limits (RL) for all herbicides are 0.05 μg L^{-1}. Detections above the RL were reported in μg L^{-1}; detections below the RL but above the method detection limit were reported as trace detections. Trace detections were not quantified.

Figure 1. The three agricultural regions monitored during the study.

Table 1. Summary of 2007 herbicide monitoring results.

Region	Date	Number of Samples	Detections (trace detections[2]) Simazine	Atrazine	Diuron	Other
Napa/Sonoma	Jan 2007	14	0 (2)	0	2 (3)	none
Napa/Sonoma	Feb 2007[1]	7	7	0	2	prometon: 1
Imperial	Mar 2007	10	0	2 (2)	1	DEA: 0 (1)
Monterey	Mar 2007	4	0	0	2 (1)	none

[1] Storm samples
[2] First number is the number of detections (> RL); the number in parentheses, when present, is the number of trace detections (< RL).

Results and Discussion

Several herbicides were detected in the water samples from the three regions (Table 1). Simazine was detected only in the Napa/Sonoma region; all storm samples had detections above the RL (Figure 2). Samples collected during dry weather in Napa/Sonoma had two trace detections of simazine. Atrazine was detected only in Imperial County; two samples had detections above the RL and two additional samples had trace detections (Figure 3). Overall, 40% of samples collected in Imperial County had atrazine detections. An additional sample from Imperial County had a trace detection of deethyl-atrazine (DEA), a degradate of atrazine. Diuron was detected above the RL in all three regions. The overall detection frequency of diuron, including trace detections, was over 30%; this is especially significant considering that diuron use is relatively low in these regions at the times sampled.

The detected concentrations of simazine, atrazine and diuron were compared to US EPA Aquatic Life Benchmarks (US EPA 2007). No exceedances of these benchmarks occurred (Table 2). However, triazine herbicides, as well as diuron, have been shown to potentiate the effects of organophosphate (OP) insecticides (Banks et al. 2005, Lydy and Austin 2004). As such, concentrations of these herbicides that are not themselves toxic to aquatic organisms can increase the toxicity of OP insecticides that are present in the aquatic system. OP insecticides were co-detected with diuron in two samples from Monterey County and one sample from Imperial County. Additionally, both atrazine and simazine are suspected endocrine disruptors and the US EPA has recommended additional monitoring for these compounds (U.S. EPA 2003a, 2003b, 2006). For diuron, monitoring results available elsewhere indicate that, in over 1200 samples collected throughout California between 2000 and 2005, the diuron benchmark of 2.4 μg L^{-1} was exceeded in about 5% of samples (CA DPR 2007b).

The mass loading of herbicides during storm samples can also be substantial, as shown in Table 3. Mass loading calculations for simazine, diuron, and prometon indicate that large amounts of these herbicides can enter water bodies during storm events. Perhaps the most interesting data are for atrazine in the Salton Sea. The Salton Sea contains ca. 9.25 trillion L of water (Salton Sea Authority 2007); it represents a large reservoir for potential dilution of incoming water. While the number of samples were limited, atrazine concentrations in the Salton Sea were greater than those in the primary input waters (Alamo and New Rivers; Figure 3). In addition, atrazine was detected in the Salton Sea ca. 42 km from the primary agricultural drainage inflows. Because the Salton Sea is a sensitive aquatic habitat, further sampling is warranted to better define the temporal and spatial extent of atrazine concentrations, evaluate those concentrations relative to aquatic toxicology benchmarks, and investigate the mass budgets of atrazine and other herbicides in the Salton Sea.

Figure 2. Herbicides detected (concentrations in μg L^{-1}) during storm sampling in Napa and Sonoma Counties.

Figure 3. Herbicides detected (concentrations in μg L^{-1} or trace detections) in Imperial County. Water samples taken where no herbicides were detected are marked with the symbol♦).

Conclusions

The results from this study indicate that atrazine, simazine, and diuron are contaminants in surface water. Based on these results, additional monitoring for these herbicides is warranted. Monitoring for other herbicides with low aquatic toxicity benchmarks and high use, especially those with high use during California's wet season, is also recommended. Herbicides that fit this profile include oxyfluorfen and several of the dinitroaniline herbicides (trifluralin, pendamethalin, and oryzalin). Where indicated, simultaneous monitoring for OP insecticides should also be considered.

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

Herbicide	Detection (μg L^{-1})[1]	Aquatic benchmark (μg L^{-1})[2]
Atrazine	0.083	18
Diuron	0.237	2.4
Prometon	0.092	--
Simazine	1.94	36

[1] Highest concentration of atrazine, diuron, prometon, or simazine detected in water samples.
[2] Lowest EPA aquatic benchmark.

Table 3. Mass loading of creeks and rivers from detected herbicides using flow data from USGS gauging stations.

Water Body (flow rate[1], L sec^{-1})	Herbicide detected (μg L^{-1})	Mass loading (mg sec^{-1})	Mass loading (g day^{-1})
Napa River (14,385)	diuron (0.095)	1.4	118
Napa River (14,385)	simazine (0.556)	8.0	691
Russian River (291,664)	diuron (0.077)	22.5	1,940
Russian River (291,664)	simazine (0.842)	245.6	21,218
Russian River (235,879)	simazine (0.096)	22.6	1,957
Mark West Creek (42,192)	simazine (1.94)	81.9	7,072
Mark West Creek(42,192)	prometon (0.092)	3.9	335
Sonoma Creek (15,065)	simazine (0.227)	3.4	296

[1] Flow data from USGS 2007, for sampling dates.

Acknowledgments

Many people have generously given their time and talents to help this study succeed. We would like to thank Kean S. Goh for his overall support of this study and to Frank C. Spurlock and Marshall Lee for their swift and succinct review of the poster. We would like to thank Carissa Ganapathy for sample coordination and organization between DPR and CDFA and we would like to thank Jessie 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 Steven Siegel, Jane White, Jean Hsu, and the staff at CDFA for sample analysis.

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