Simazine, Diuron, and Atrazine Detections in California Surface Waters

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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. For many of these herbicides, recent surface water monitoring data from areas of high use are lacking; 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. 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. As part of that study, surface water samples were collected from Napa, Sonoma, Monterey, and Imperial Counties in early 2007 and analyzed for a suite of seven herbicide active ingredients.

Materials And Methods

Twenty-eight monitoring sites were chosen in three regions of California: Napa/Sonoma, Imperial, and Monterey Counties. 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. 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 but were not quantified.

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. Samples collected during dry weather in Napa/Sonoma had two trace detections of simazine. Atrazine was detected only in Imperial County; two samples were detectioned above the RL and two additional samples were trace 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 did not exceed the US EPA Aquatic Life Benchmarks. However, triazine herbicides, as well as diuron, have been shown to potentiate the effects of organophosphate (OP) insecticides. 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. 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 $\mu g\ L^{-1}$ was exceeded in about 5% of samples.

The mass loading of herbicides during storm samples can also be substantial, as shown in Table 2. 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; 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). 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.

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 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).

Table 2. Mass loading of water bodies from detected herbicides using flow data from USGS gauging stations.

Water Body (flow rate, L sec^{-1})	Herbicide detected ($\mu g\ L^{-1}$)	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

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