Analysis of Herbicide Detections and Use From 1996-2006

CA Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program

1001 I Street, Sacramento, CA 95812

Rick Bergin, Steve Doo, Sheryl Gill, Frank Spurlock

For more information, contact Rick Bergin at rbergin@cdpr.ca.gov or 916-324-0827

Abstract

Herbicide contamination of California surface water is a problem that needs further scrutiny. This paper assesses herbicide sampling data from 41 studies in the California Department of Pesticide Regulation's (CDPR) Surface Water Database. The data were collected from 1996 to 2006. Herbicides with high detection rates (≥ 5%) were chosen for further investigation of their use patterns during the same time interval. Pesticide use data from CDPR's Pesticide Use Reporting (PUR) Database were analyzed to evaluate the relationship between herbicide use and herbicide detections in surface water runoff. The time of year and application site are two use variables that lead to herbicide runoff in surface water. Generally, herbicides applied during times and at sites with high runoff potential (rainy season, rights of way, and intensively irrigated crops like rice and corn) are more likely to enter surface water and be detected at higher frequencies.

Introduction

From 1996 to 2006, over 1.2 billion lbs of herbicide were used in California (CDPR 2008a). Herbicides are used in many applications, including crops such as corn, alfalfa, rice, wheat, citrus, and almonds (1 billion lbs A.I.). Herbicides are also used in many non-agricultural settings such as landscaping, structural pest control, and rights of way (~135 million lbs A.I.). Fifteen herbicides were selected due to their increased frequency in CDPR's Surface Water database. The selected herbicides are used in the following manner (UC IPM 2008):

2,4-D: 2,4-D functions as a systemic herbicide and is used to control many types of broadleaf weeds.

Atrazine: Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds. It is also used as a nonselective herbicide on non-cropped industrial lands and on fallow lands.

Bromacil: Bromacil is an herbicide used for brush control on non-cropland areas. It is sprayed or spread dry on the soil surface just before, or during, a period of active weed growth.

Diuron: Diuron is a substituted urea herbicide used to control a wide variety of annual and perennial broadleaf and grassy weeds, as well as mosses.

EPTC: EPTC is a selective thiocarbamate herbicide used for control of annual grassy weeds, perennial weeds, and some broadleaf weeds. It is usually applied as a preemergent and is usually incorporated into the soil immediately after application either mechanically or by overhead irrigation.

Metolachlor: Metolachlor is usually applied to crops before plants emerge from the soil. It is used to control certain broadleaf and annual grassy weeds.

Molinate: It is toxic to germinating grassy weeds in rice.

Norflurazon: Norflurazon is registered for use as a selective preemergent herbicide to control germinating annual grasses and broadleaf weeds.

Oryzalin: Oryzalin is a selective pre-emergence surface-applied herbicide used for control of annual grasses and broadleaf weeds.

Pendimethalin: Pendimethalin is a selective herbicide used to control most annual grasses and certain broadleaf weeds. It is used both in preemergence and early postemergence applications.

Prometon: A nonselective herbicide which can be applied before or following weed emergence. It controls most annual and many perennial broadleaf weeds and grasses, generally for a full season or longer.

Simazine: It is used to control broad-leaved weeds and annual grasses.

Thiobencarb: Can be applied pre-flood directly to the soil, or post-flood, post-emergence to drained rice fields to control annual weeds.

Triclopyr: Triclopyr is a selective systemic herbicide used for control of woody and broadleaf plants.

Trifluralin: Trifluralin is a selective, preemergence herbicide used to control many annual grasses and broadleaf weeds.

Methodology

The herbicide detection and use data collected for this analysis comes from CDPR's Surface Water and PUR databases, respectively. The Surface Water Database was examined for all herbicide detections from 1996 to 2006; compounds with a detection frequency greater than or equal to 5% were selected for further study (Table 1). For the fifteen selected herbicides, pesticide use reporting data was gathered from 1996 to 2006. Each herbicide was examined for use patterns: when it was applied, where the application took place, and how much active ingredient (A.I.) was used. The crops with the highest herbicide applications were investigated for their aggregate application on a monthly basis over the eleven-year data period (Table 2).

The Surface Water Database contains information from 41 different studies, with reporting limits ranging from 0.0005 ppb to 5.0 ppb (CDPR 2008b). In order to standardize and make comparisons amongst the data, the limit of quantification (LOQ) for this study was set to 0.015 ppb. Every concentration less than the LOQ was considered a non-detect (ND) in all subsequent calculations.

It should be noted that not every study sampled California evenly during the entire year; most studies were designed to maximize the likelihood of detecting herbicides. However, this analysis aims to relate pesticide use to detection frequency: do certain herbicides runoff the field and into the surrounding rivers and streams?

Acknowledgements

We would like to thank Marshall Lee for his timely review of this poster. Also, we would like to thank Keith Starner for his help extracting data from CDPR's databases

Table 1. Detections of Selected Herbicides and Their Concentrations in Surface Water

Chemical	Number of Samples	Percent of Samples with Detections	**Median** (Range) of Concentrations [a]
Diuron	1523	40.3	**0.25** (0.015-160)
Metolachlor	1598	29.8	**0.07** (0.016-3.88)
Triclopyr	297	29.6	**0.78** (0.025-14.5)
Simazine	3303	29.2	**0.07** (0.015-42.7)
2,4-D	239	26.8	**0.15** (0.02-4.42)
Molinate	2296	20.2	**1.60** (0.015-44.09)
Norflurazon	552	13.8	**0.10** (0.024-1.49)
EPTC	1721	13.7	**0.06** (0.015-13.45)
Trifluralin	1983	12.0	**0.05** (0.015-1.74)
Thiobencarb	2762	11.8	**1.00** (0.015-150)
Pendimethalin	2003	10.4	**0.05** (0.015-3.5)
Bromacil	1056	7.0	**0.10** (0.019-68)
Oryzalin	372	5.6	**0.62** (0.05-110)
Prometon	2778	5.5	**0.05** (0.05-0.7)
Atrazine	3099	5.0	**0.04** (0.015-3.18)

a. Detections are in ppb (µg/L).

Table 2. Use Data for Selected Herbicides with a Detection Frequency ≥ 5%.

Chemical	Crop [a]	Lbs A.I. [b]	Application Month [c]
Molinate	Rice	8,413,971	May-Jun
Thiobencarb	Rice	7,369,252	May-Jun
Diuron	Rights of Way	6,298,529	Nov-Mar
Trifluralin	Alfalfa	5,478,669	Jan-May
Simazine	Grape	2,850,176	Nov-Mar
Pendimethalin	Cotton	1,948,710	Nov-Apr
EPTC	Alfalfa	1,495,634	Mar-Jul
Oryzalin	Almond	1,443,510	Nov-Feb
2,4-D	Wheat	1,320,839	Jan-Mar
Triclopyr	Rice	545,370	Jun-Jul
Norflurazon	Almond	509,688	Nov-Mar
Metolachlor	Corn	470,489	Apr-Jun
Bromacil	Rights of Way	280,546	Nov-Mar
Atrazine	Corn	178,141	May-Jun
Prometon	Landscape Maintenance	96	Jan-Jun

a. Highest use crop.

b. Total use from 1996-2006.

c. Period in which the majority of the herbicide was applied.

Table 3. Highest Concentrations (ppb) of Selected Herbicides Compared to EPA's Aquatic Benchmarks.

Chemical	Detection Conc. [a]	Aquatic Benchmark [b]	Detections > Benchmark
Diuron	160	2.4	53
Metolachlor	3.88	780	0
Triclopyr	14.5	100	0
Simazine	42.7	36	4
2,4-D	4.42	299.2	0
Molinate	44.09	105	0
Norflurazon	1.49	13	0
EPTC	13.45	1,360	0
Trifluralin	1.74	1.14	3
Thiobencarb	150	1	167
Pendimethalin	3.5	5.4	0
Bromacil	68	6.8	2
Oryzalin	110	15.4	3
Prometon	0.7	NA	NA
Atrazine	3.18	18	0

a. Highest detected concentration.

b. Lowest EPA Aquatic Benchmark.

Results and Discussion

Forty-eight herbicide compounds were detected from 1996 to 2006. Of those 48, fifteen had detection frequencies greater or equal to 5%. For every chemical, the time of their greatest detection frequency coincided with application dates of heaviest use. In other words, herbicide detections were the greatest when herbicide applications were also the greatest. Two major factors dictate when detections are present in surface water: season and crop type.

Season

The majority of the herbicides examined (9/15 or 60%) is most intensively applied during the winter, from November to March (Table 2). These herbicides include diuron, trifluralin, simazine, pendimethalin, oryzalin, 2,4-D, norflurazon, bromacil, and prometon. All of these herbicides are applied as a preemergent application on bare soil (usually) during the rainy season in California. It appears that herbicide applications during the winter rainy season lead to a higher frequency of herbicide detections in surface water. The majority of these detections occur in January and February (Fig. 1), the period of time where precipitation and herbicide application are the greatest (Fig. 2). Even though the herbicide is applied in significant amounts throughout the year, the majority of the detections take place during the rainy months.

Crop Type

The remaining herbicides (6/15 or 40%) are mainly applied during the summer months but on water-intensive crops such as rice, corn, and alfalfa (Table 2). These herbicides include molinate, thiobencarb, triclopyr, EPTC, metolachlor, and atrazine. The detection frequency for these herbicides depends on crop irrigation regimes. Like season-driven herbicide detections, the application time of the herbicide is closely related to when herbicides are detected. However, rainfall is not responsible for runoff in this situation; crop irrigation regimes are the driving force behind the detection of these herbicides. Therefore, crops with a high amount of irrigation tail-water runoff are more than likely the source for high herbicide detections in rivers and streams. Figures 3 and 4 show molinate detections have increased frequency during the peak of molinate applications, namely in May and June. This relationship only works with crops that create runoff, such as rice in this case. If there is no runoff or the runoff is mitigated, then surface contamination is less of a concern.

Water Quality

The detected concentrations of the fifteen selected herbicides were compared to US EPA Aquatic Life Benchmarks (US EPA 2008). Herbicides that exceeded the benchmarks, in ascending order of exceedances, are bromacil, oryzalin, trifluralin, simazine, diuron, and thiobencarb (Table 3). For some herbicides, the concentrations are high enough to warrant environmental health concerns. Thiobencarb, especially, should be monitored for future discharges as a large portion of detections (52%) exceeded US EPA's aquatic life benchmark for chronic invertebrate toxicity.

Season-Driven Detections

Figure 1. Diuron Detections by Month

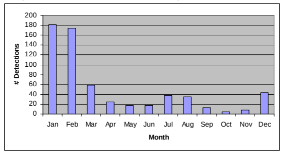
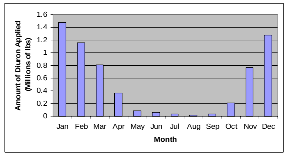


Figure 2. Diuron Application on Rights of Way



Crop-Driven Detections

Figure 3. Molinate Detections by Month

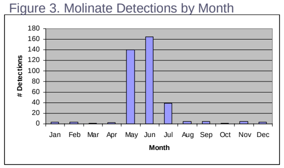
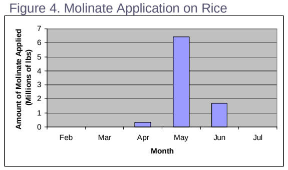


Figure 4. Molinate Application on Rice



References:

CA DPR 2008a. California Department of Pesticide Regulation, California pesticide information portal, pesticide use report (PUR) [Online]. Available at http://calpip.cdpr.ca.gov/cfdocs/calpip/prod/main.cfm (accessed on March 2008).

CA DPR 2008b. California Department of Pesticide Regulation, California surface water database [Online]. Available at http://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm (accessed on March 2008).

UC IPM 2008. University of California Integrated Pest Management Program, UC IPM Pest Management Guidelines [Online]. Available at http://ipm.ucdavis.edu/PMG/crops-agriculture.html (accessed on April 2008).

US EPA 2008. Technical overview of ecological risk assessment Aquatic Life Benchmark Table [Online]. Available at http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm (accessed on April 2008).