Analysis of Herbicide Detections and Use from 1996 – 2007

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Beginning in 1990, California has required full reporting of all agriculture use pesticides. Agriculture use in California is broadly defined, Non-production agriculture uses as landscape maintenance, structural pest control, and rights-of-way applications are included in this definition of agriculture use. The agricultural use data is stored in the Department of Pesticide Regulation (DPR) Pesticide Use Reporting (PUR) database and verified data is ava ilable for public use (CDPR, 2009a). In addition, DPR maintains a surface water database through its Environmental Monitoring Branch. This database has voluntary submissions; DPR actively collects all surface water monitoring data from any organization that conducts pesticide monitoring studies in California surface waters. Like the PUR database, the surface water database also contains data since 1990. Currently the surface water database contains data from over 9,500 samples taken in 54 studies (CDPR 2009b).

Using both the PUR and surface water databases, frequency of herbicide use and frequency of herbicide detections in surface waters were determined. For herbicide use, greater than 15 million pounds of herbicides are applied annually. Twenty-four herbicides have had at least 100,000 pounds active ingredient (lb a.i.) applied at least in one year in the past twelve years between 1996 and 2007 (Table 1). Although nearly 100 herbicides are used in California, these 24 herbicides account for greater than 90% of all herbicide use in California (CDPR 2009a).

Glyphosate is the most frequently used herbicide in California, and accounts about 40% of all herbicide applications (CDPR, 2009a). Glyphosate use has increased steadily since 1996, from over 4 million lb a.i. in 1996 to over 7 million lb a.i. in 2007. However other herbicides have had higher percentage of increases during this twelve year period; these include propanil, pendimethalin, metolachlor, and bensulide. Glufosinate use has increased from no use in 1996 to 131,634 lb a.i. in 2007. Three other herbicides also have increased use during this time period: paraquat, oryzalin, and oxyfluorfen.

As the above mentioned herbicides have had their use increase, other herbicides have had decreased use. The most dramatic decrease in use has been molinate, which has declined from 1.4 million lb a.i. to 75,241 lb a.i.; 2008 data also shows further decline. Several other herbicides had their use cut in half or greater; these include thiobencarb, DCPA, EPTC, prometryn, and

norflurazon. MCPA and hexazinone use decreases were slightly less than half. Diuron, trifluralin, simazine, acrolein, and 2,4-D also had less use over this twelve year period (Table 1).

As previously mentioned, the DPR surface water database houses data from greater than 9,500 environmental samples. In this analysis, 83 herbicides were monitored and 46 herbicides were detected between 1997 and 2006. The most frequently detected herbicides in the surface water database are simazine and diuron, with 1,110 and 698 detections, respectively. Simazine and diuron also have the highest detection rate of any of the monitored herbicides, with a 30% and 40.4%, respectively, detection rate. Metolachlor has the third highest number of detections (510); it also has the third highest detection rate (28.9%). Nine other herbicides have had between 100 and 500 detections, and 18 herbicides had between 10 and 100 detections (Table 2). Sixteen additional herbicides have had less than 10 but at least one detection; 37 other herbicides have been monitored but not detected (data not shown).

The rice herbicides molinate and thiobencarb had 431 and 302 detections, respectively. The use of these herbicides has been decreasing. Propanil use in rice has been increasing; however this herbicide is less frequently detected in surface waters. Propanil has only been detected 68 times. Although it has had less monitoring, its detection rate (4.3%) is much less than either molinate or thiobencarb (17.4% and 10%, respectively). These herbicides are mainly detected during the rice growing season, May through August.

Generally, herbicides have been detected with their agricultural use. For many herbicides, like diuron, simazine, and pendimethalin, most detections occur in the rainy season (December through April), which is also their high use period. However, these herbicides also have numerous detections during the irrigation season (approximately April through August) when their use is less. With other herbicides, as EPTC and metolachlor, which are generally applied during the growing (irrigation) season, most detections occur during this time period. Trifluralin has a slightly different detection sequence; most trifluralin detections occur in April through August whereas use in manly January through June. However, both trifluralin and metolachlor have a high detection peak in February. Thus, both rain and irrigation tend to move herbicides into surface waters.

Environmental scientists are interested in herbicides in surface waters because of their potential to harm aquatic life. Phytoplankton are the bottom level of the food chain; reduced growth of these organisms may have an effect on organisms higher up on the food chain, and may be one of the causes of pelagic organism decline (Sommer *et al.*, 2007). However, more work is needed to determine the effect of herbicides on phytoplankton (Edmunds *et al.*, 1999). The US EPA has listed aquatic benchmarks for many herbicides; if herbicides are known to exist in surface waters above the EPA benchmarks, there is a concern that these herbicides may cause toxicity to aquatic life (US EPA, 2009). In this analysis, eight herbicides were detected at

concentrations above their EPA aquatic benchmarks. Of these eight herbicides, thiobencarb, diuron, and metolachor had the most detections above their respective benchmarks.
The herbicides that have been detected above their EPA aquatic benchmarks are shown below:

Herbicide	Benchmark (ppb)	Detections > Benchmark
Thiobencarb	1.0	142
Diuron	2.4	63
Metolachlor	1.0	19
Simazine	36	5
Oryzalin	15.4	4
Oxyfluorfen	0.29	3
Bromacil	6.8	2
Atrazine	1.0	1

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Table 1. Herbicides that have had 100,000 pounds a.i. (active ingredient) of use in California in at least one year from 1996 through 2007.

Herbicide	1996 Use	2007 Use	Increase or Decrease from 1996 to 2007	Lowest use[1]	Highest Use[1]	12 Year Average Use
Glyphosate	4,181,967.7	7,236,786.5	173%	4,089,690.0	7,777,941.4	5,605,715.2
Diuron	1,265,426.4	859,909.0	68%	859,909.0	1,504,731.0	1,213,017.9
Propanil	89,366.8	1,801,607.1	2016%	89,366.8	1,801,607.1	1,131,424.5
Trifluralin	1,143,694.9	898,976.0	79%	898,976.0	1,261,482.0	1,088,361.4
Paraquat	891,165.4	966,583.0	108%	752,605.0	1,144,220.0	950,050.5
Molinate	1,356,257.6	75,241.0	6%	75,241.0	1,356,257.6	698,025.0
Simazine	839,208.9	538,627.0	64%	538,627.0	839,208.9	685,667.3
Thiobencarb	618,411.8	289,046.0	47%	289,046.0	1,007,249.0	634,709.5
Oryzalin	568,940.9	656,439.0	115%	110,714.0	912,715.0	571,946.5
2,4-D[2]	669,063.7	442,318.9	66%	442,318.9	669,063.7	523,763.2
Pendimethalin	429,945.8	1,124,396.0	262%	312,561.0	1,124,396.0	519,688.1
Oxyfluorfen	429,904.0	644,523.0	150%	347,589.0	712,370.0	506,508.7
EPTC	703,996.4	152,707.0	22%	108,209.0	703,996.4	312,163.5
Metolachlor[3]	186,092.7	352,193.0	189%	186,092.7	392,880.6	310,457.8
Acrolein	322,578.4	201,112.0	62%	201,112.0	341,245.0	270,972.8
DCPA[4]	522,861.0	205,377.0	39%	133,627.7	522,861.0	250,604.2
MCPA	363,534.0	186,988.0	51%	170,579.6	363,534.0	233,688.3
Bensulide	94,586.9	258,164.0	273%	94,586.9	284,533.0	209,163.6
Prometryn	162,673.0	69,525.5	43%	69,525.5	307,634.0	183,337.9
Norflurazon	196,141.9	77,615.0	40%	77,615.0	286,214.0	181,880.7
Triclopyr	153,740.8	131,037.7	85%	102,099.1	177,330.6	150,195.2
Hexazinone	137,536.1	81,170.2	59%	81,170.2	137,536.1	107,756.5
Pronamide[5]	108,929.0	114,400.9	105%	101,267	120,804	109,659
Glufosinate	0	131,634.0	--	0	131,634.0	24,201.9

[1]Lowest and highest use during the 12 years from 1996 to 2007.

[2]All formulations and salts of 2,4-D.

[3]Includes both metolachlor and s-metolachlor.

[4]DCPA is the WSSA approved name for chlorthal-dimethyl.

[5]Pronamide is the WSSA approved name for propyzamide

Table 2. Monitoring data from the Surface Water Database (1997 – 2006) of herbicides with 10 or more detections.

Herbicide	Number of Detections	Number of Samples Collected	Percentage of Detections
Simazine	1110	3695	30.0%
Diuron	698	1727	40.4%
Metolachlor	510	1765	28.9%
Molinate	431	2474	17.4%
Thiobencarb	302	3014	10.0%
Trifluralin	261	2159	12.1%
Pendimethalin	249	2162	11.5%
EPTC	219	1822	12.0%
Cyanazine	157	2563	6.1%
Prometon	149	3165	4.7%
Atrazine	144	3433	4.2%
Triclopyr	100	370	27.0%
Bromacil	89	1228	7.2%
Norflurazon	87	701	12.4%
2,4-D	72	305	23.6%
Propanil	68	1572	4.3%
Metribuzin	56	2253	2.5%
Napropamide	50	1367	3.7%
Prometryn	40	1509	2.7%
Tebuthiuron	37	1712	2.2%
DCPA	33	1851	1.8%
MCPA	32	270	11.9%
Oryzalin	27	431	6.3%
Pebulate	27	1365	2.0%
Ethalfluralin	21	1366	1.5%
Bentazon	17	251	6.8%
Hexazinone	16	670	2.4%
Glyphosate	14	456	3.1%
Pronamide	13	1516	0.9%
Oxyfluorfen	10	156	6.4%