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Detections of Pyrethroid Insecticides in Surface Waters from Urban Areas of California, 1993-2010.

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Abstract

We analyzed the presence of pyrethroid insecticides in California's surface waters from urban areas. Monitoring data were obtained from various sources including government agencies and university researchers. In total, 8,834 water and 2,010 sediment samples were collected between 1993 and 2010. Samples were taken at locations of storm drain outfall, receiving water body and effluence of water treatment plants. Bifenthrin was the most frequently detected with detection rates of 85.2% and 73.1% in sediment and water, respectively. Bifenthrin was also detected at the maximum concentrations of 1,211 ppb in sediment and 6,121 ppt in water, much higher than the maximum concentrations of other pyrethroids. The maximum concentrations in water samples were higher in storm drain samples than those from receiving water or water treatment plant. However, this difference was not significant in sediment samples. Detected water concentrations were compared with the U.S.EPA acute benchmarks for fish and aquatic invertebrates. Over 8% water samples of bifenthrin and cyfluthrin exceeded the acute benchmarks for fish and over 12% water samples of cyfluthrin and permethrin exceeded those for aquatic invertebrates. Future research will be devoted to investigate the toxicity of sediment samples when data on total organic matter contents becomes available.

Introduction

The widespread detections of pyrethroid insecticides in California's waterways have resulted in its re-evaluation by the California Department Pesticide Regulation (Sanders, 2005). Many monitoring studies have been conducted to collect water and sediment samples to determine the presence of pyrethroid insecticides in urban waters. Pyrethroids were often detected with concentrations toxic to aquatic organism (Weston et al., 2005, 2010, Holmes et al, 2008). To evaluate the impacts of their presence on aquatic ecosystems, it is essential to identify the detection frequencies and the magnitudes of the detected concentrations. Hence, we compiled all the monitoring data in California that are currently available to obtain an overall view on the presence of pyrethroid insecticides in California's surface waters within urban areas.

Data sources

During the past 17 years, many monitoring studies on pyrethroids have been conducted at a wide range of geographical areas. Samples were taken at urban areas across California from Orange

County in the south to Sacramento County in the north. A total of 10,844 samples were obtained between 1993 and 2010, of which 2,010 were sediment samples and 8,834 were water samples. In general, samples were taken from three types of locations: storm drain outfall, receiving water body and effluence of water treatment plant. Nine pyrethroid insecticides have been monitored including bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, permethrin and resmethrin (Table 1). Data for chemicals with different isomers were combined. For example, data on cis-permethrin and trans-permethrin were combined as a group and listed as permethrin.

Monitoring data were obtained from sources including state and federal agencies as well as university researchers. Below is a detailed list of all the sources:

a) DPR Surface Water Monitoring Database (1,072 records)
   Pyrethroid urban monitoring data in the database are from the following sources:
   - USGS NAWQA bimonthly sampling during 1996-1998.
   - USGS report 98-4017. Samples were taken in 1994 and 1995.
   - Department of Pesticide Regulation Red Imported Fire Ant Surface Water Monitoring Program. 1999-2002. Orange Co., CA.
   - California State Water Resources Control Board - Division of Water Quality; Aquatic Toxicity in the Pajaro River Watershed. Samples were taken in December 1994 and January 1995.
   - USGS NAWQA data; water years 2005-2010.
   - Weston, DP, Holmes, RW, You J, Lydy MJ. 2005. Aquatic toxicity due to residential use of pyrethroid insecticides. ES&T 39:9778-9784.

b) Surface Water Ambient Monitoring Program (SWAMP database) (929 records)
   - Data was downloaded via California Environmental Data Exchange Network (CEDEN) (http://ceden.org/index.shtml).
   - Water and sediment records from year 2005 to 2008 were included. SWAMP data before 2005 was included in DPR's Surface Water Monitoring Database as listed in a).

c) Published journal papers (1,073 records)
   - Amweg EL, Weston DP, You J, Lydy MJ. 2006. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. ES&T 40: 1700–1706.
   - Weston DP, Amweg EL, Mekebri A, Ogle RS, Lydy MJ. 2006. Aquatic effects of aerial spraying for mosquito control over an urban area. ES&T 40:5817-22.
   - Holmes RW, Anderson BS, Phillips BM, Hunt JW, Crane DB, Mekebri A, Connor V. 2008. Statewide investigation of the role of pyrethroid pesticides in sediment toxicity in California's urban waterways. ES&T 42: 7003–7009.
   - Weston DP, Holmes RW, Lydy MJ, 2009. Residential runoff as a source of pyrethroid pesticides to urban creeks. Environmental Pollution. 157: 287-294.
   - Weston DP, Lydy MJ, 2010.Urban and agricultural sources of Pyrethroid insecticides to the Sacramento-San Joaquin Delta of California. ES&T 44: 1833-1840

d) Un-published monitoring studies (7,770 records)
   - DPR Study 265. Budd, R. 2010. Urban Pesticide Monitoring in Southern California.
   - DPR Study 264. Ensminger, M. 2010. Urban Pesticide Monitoring in Northern California.

- Ongoing monitoring study on urban drains in Northern and Southern California. Data obtained from Jay Gan at UC Riverside

Results

Water samples

Pyrethroids were detected in about 30% of the 8.834 water samples (Table 1). Permethrin was the most heavily monitored with 2,071 samples, twice as much as bifenthrin samples. The rest of the group-III pyrethroids have relatively less samples (845 - 974). There were 141 samples for resmethrin, but it was not detected in any of the samples. Among the nine chemicals, bifenthrin was the most frequently detected with the highest concentration of 6,121 ppt. Other pyrethroids with both high detection rates and maximum concentrations include cyfluthrin, permethrin and cypermethrin. Cypermethrin, lambda-cyhalothrin and deltamethrin were less frequently detected with lower maximum concentrations. Compared to other pyrethroids, esfenvalerate and fenpropathrin were of less detection frequencies and lower concentrations.

The majority of water samples were taken at storm drain outfalls with a total of 7,470 samples comparing to 1,212 from receiving water and 152 from water treatment plant (Table 2). Water samples taken from different locations show differences in detection frequencies and maximum concentrations. For all the pyrethroids, detection rates at storm drain sites were much higher than those from receiving water and water treatment plant. Almost all the maximum concentrations were from storm drain samples.

Sediment samples

Pyrethroids were detected in about 46% of the 2,010 sediment samples (Table 3). Permethrin was the most heavily monitored pyrethroids with 353 sediment samples. About 250 samples were taken for each of the other pyrethroids except for fenpropathrin (110 samples) and resmethrin (51 samples). Bifenthrin again was the most frequently detected with a detection rate of 85.2% followed by permethrin (68.8%), cyfluthrin (55%) and lambda-cyhalothrin (42%). All the pyrethroids were detected in more than 30% of the samples except for esfenvalerate, fenpropathrin and resmethrin.

The maximum concentrations of these chemicals ranged from 8.9 ppb for resmethrin to 1,211 ppb for bifenthrin (Table 3). Not only was bifenthrin the most frequently detected, but also the one with the highest maximum concentration. Other pyrethroids with both high detection rates and maximum concentrations include cyfluthrin, cypermethrin and permethrin. Lambda-cyhalothrin and deltamethrin were also frequently detected but with much lower maximum concentrations. Compared to other pyrethroids, esfenvalerate, fenpropathrin and resmethrin were of less detection frequencies and much lower concentrations.

A total of 1,283 sediment samples were taken from receiving water bodies while 727 were taken at storm drain outfalls (Table 4). Bifenthrin was detected more frequently in receiving water samples than in storm drain samples. However, detection rates for other pyrethroids are slightly higher in storm drain samples than receiving water samples with the exception of fenpropathrin and resmethrin, which have only one or two samples in each location type. Almost all of the maximum concentrations were from samples taken at storm drain outfalls.

Toxicity

Detected concentrations in water samples were compared with the benchmark values for aquatic invertebrate and fish acute toxicity established by the U.S. EPA (Fig 1). The exceeding rate was calculated as the percentage of samples with concentrations higher than the benchmarks. Bifenthrin samples showed a high exceeding rate for fish (11.2%) but a low rate of 0.7% for aquatic invertebrates. In general, pyrethroids are more toxic to aquatic invertebrates than fish. The low exceeding rate of bifenthrin for aquatic invertebrates is due to the high benchmark value of 800 ppt, which is much higher than those for fish (75 ppt) and the LC50s/EC50s measured in the literature (Anderson et al., 2006, Weston and Jackson, 2009, Wheelock et al., 2004). EPA's acute invertebrate benchmark was calculated as 0.5 times the lowest 48- or 96-hour EC_{50} or LC_{50} in a standardized test (usually with midge, scud, or daphnids). According to Wheelock et al. (2004), the 48-hour EC50 of bifenthrin for *Ceriodaphinia dubia* was 142 ppt. If this value was used instead, the benchmark equivalence of bifenthrin would have been 71 ppt for acute invertebrates, resulting in the exceeding rate of bifenthrin to be 11.7% for acute invertebrates.

Cyfluthrin samples had high exceeding rates of 8.3% and 17.7% for fish and invertebrates, respectively. Permethrin and lambda-cyhalothrin samples showed low exceeding rates for fish but high rates for invertebrates. Samples of cypermethrin, deltamethrin and esfenvalerate showed relatively low exceeding rates for both fish and invertebrates.

Similar comparison for the sediment concentrations was not conducted because the data for total organic matter content (TOC) in the samples were currently unavailable. Future efforts will be devoted to collect TOC data so that the dry weight concentrations can be normalized to TOC and compared to toxicity endpoints to infer the toxicity of the samples.

Conclusions

Pyrethroid insecticides have been frequently detected in water and sediments of urban waters in California. The most frequently detected pyrethroids were bifenthrin followed by permethrin and cyfluthrin. Bifenthrin and cyfluthrin were detected with the highest concentrations in both water and sediment. Over 8% water samples of bifenthrin and cyfluthrin exceeded the acute benchmarks for fish and over 12% water samples of cyfluthrin and permethrin exceeded those for aquatic invertebrates. Comparisons of sediment concentrations with toxicity values were not conducted due to lack of TOC data.

References

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Table 1: Detections of pyrethroid insecticides in waters of California's urban areas

Analyte Name	Detections	Total samples	Detection rate	Concentration (ppt)	
				Min	Max
Bifenthrin	786	1,075	73.1%	0.4	6,121.4
Cyfluthrin	468	974	48.0%	0.1	692.6
Cypermethrin	241	974	24.7%	0.5	369.2
Deltamethrin	163	880	18.5%	0.2	395.7
Esfenvalerate	62	900	6.9%	0.1	45.7
Fenpropathrin	7	845	0.8%	1.8	22.6
Lambda-cyhalothrin	202	974	20.7%	0.1	280.4
Permethrin	758	2,071	36.6%	0.1	1,084.2
Resmethrin	0	141	0.0%	NA	NA
Total	2,687	8,834	30.4%	0.1	6121.4

Table 2: Detections of pyrethroid insecticides in waters of California's urban areas (grouped by types of sampling sites)

Analyte Name	Receiving Water				Storm Drain				Water Treatment Plant Effluence			
	Detection rate*		Concentration (ppt)		Detection rate*		Concentration (ppt)		Detection rate		Concentration (ppt)	
			Min	Max			Min	Max			Min	Max
Bifenthrin	23.3%	(55/236)	5.3	2,300.0	88.2%	(724/821)	0.4	6,121.4	38.9%	(7/18)	1.4	6.3
Cyfluthrin	0.7%	(1/135)	17.0	17.0	56.8%	(466/821)	0.1	692.6	5.6%	(1/18)	1.7	1.7
Cypermethrin	0.7%	(1/135)	18.0	18.0	29.1%	(239/821)	0.5	369.2	5.6%	(1/18)	17.0	17.0
Deltamethrin	0.0%	(0/40)	--	--	19.6%	(161/822)	0.2	395.7	11.1%	(2/18)	2.7	2.7
Esfenvalerate	0.0%	(0/39)	--	--	7.2%	(61/843)	0.1	45.7	5.6%	(1/18)	3.7	3.7
Fenpropathrin	0.0%	(0/36)	--	--	0.9%	(7/791)	1.8	22.6	0.0%	(0/18)	--	--
Lambda-cyhalothrin	0.7%	(1/135)	4.0	4.0	24.1%	(198/821)	0.1	280.4	16.7%	(3/18)	2.8	5.5
Permethrin	0.5%	(2/423)	16.1	23.9	46.2%	(749/1622)	0.1	1,084.2	26.9%	(7/26)	7.0	17.2

* Numbers in parentheses are numbers of detections / total numbers of samples.

Table 3: Detections of pyrethroid insecticides in **sediments** of California's urban waters

Analyte Name	Detections	Total samples	Detection rate	Concentration (ppb)	
				Min	Max
Bifenthrin	213	250	85.2%	1.0	1,211.0
Cyfluthrin	137	249	55.0%	1.1	992.5
Cypermethrin	103	249	41.4%	0.6	940.0
Deltamethrin	88	247	35.6%	1.1	78.0
Esfenvalerate	29	246	11.8%	1.0	17.0
Fenpropathrin	1	110	0.9%	14.7	14.7
Lambda-cyhalothrin	107	255	42.0%	1.0	67.0
Permethrin	243	353	68.8%	1.0	701.0
Resmethrin	3	51	5.9%	3.6	8.9
Total	924	2,010	46.0%	0.6	1,211.0

Table 4: Detections of pyrethroid insecticides in **sediments** of California's urban waters (grouped by types of sampling sites)

Analyte Name	Receiving Water				Storm Drain			
	Detection rate*		Concentration (ppb)		Detection rate*		Concentration(ppb)	
			Min	Max			Min	Max
Bifenthrin	87.9%	(145/165)	1.0	437.0	80.0%	(68/85)	1.6	1,211.0
Cyfluthrin	48.8%	(80/164)	1.1	992.5	67.1%	(57/85)	1.2	471.0
Cypermethrin	39.0%	(64/164)	0.6	295.8	45.9%	(39/85)	1.5	940.0
Deltamethrin	28.2%	(46/163)	1.1	59.1	50.0%	(42/84)	1.1	78.0
Esfenvalerate	10.4%	(17/164)	1.1	6.9	14.6%	(12/82)	1.0	17.0
Fenpropathrin	1.6%	(1/62)	14.7	14.7	0.0%	(0/48)	--	--
Lambda- cyhalothrin	40.7%	(68/167)	1.1	24.2	44.3%	(39/88)	1.0	67.0
Permethrin	63.3%	(140/221)	1.0	335.0	78.0%	(103/132)	1.1	701.0
Resmethrin	7.7%	(1/13)	5.7	5.7	5.3%	(2/38)	3.6	8.9

* Numbers in parentheses are numbers of detections / total numbers of samples.

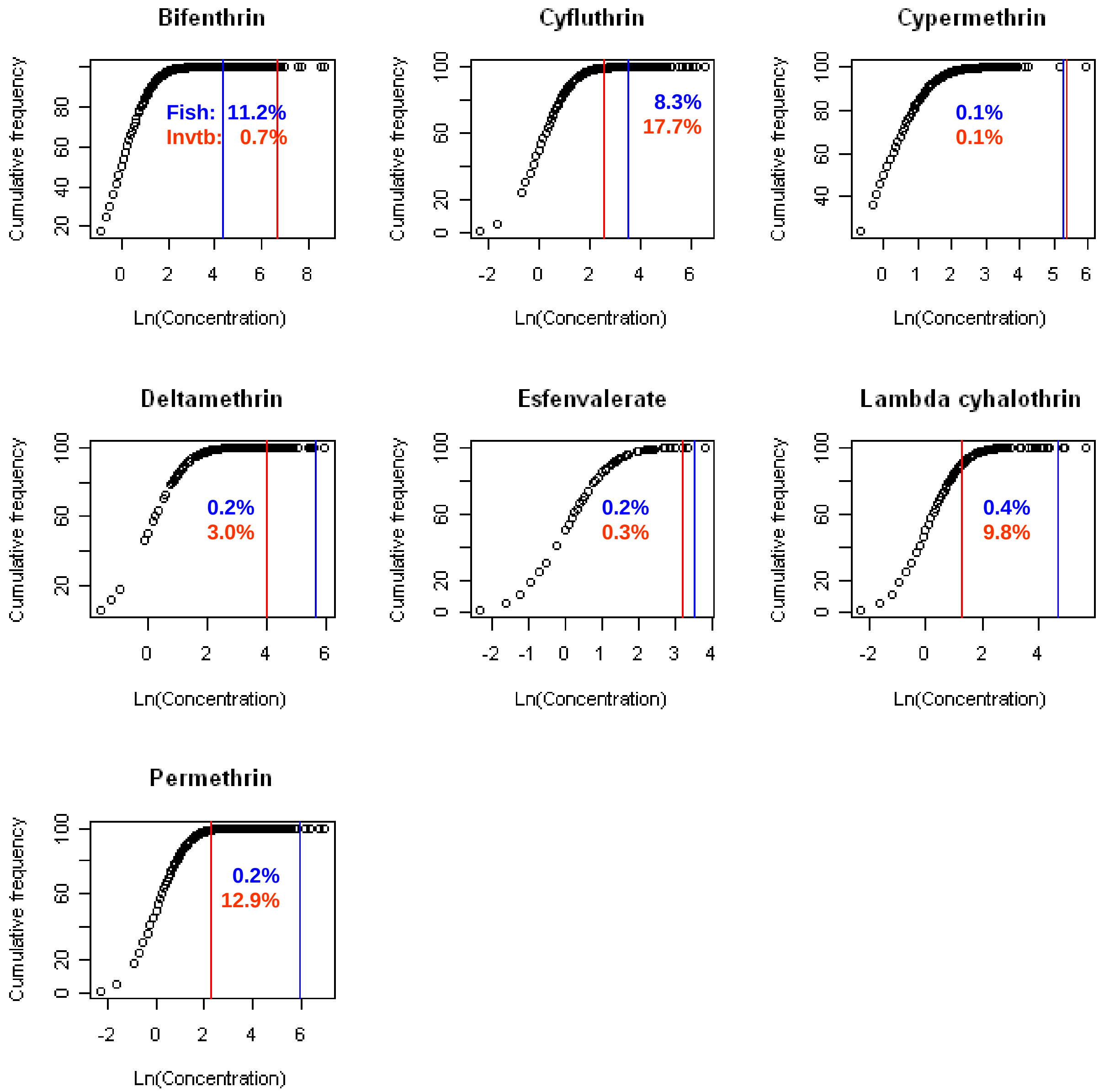

Fig. 1. Cumulative frequency distribution of pyrethroid concentrations in water samples compared with USEPA acute benchmarks for aquatic invertebrates (red line) and fish (blue line). The percentage numbers are the percentage of samples with concentrations higher than the benchmarks (exceeding rate). The benchmark values of bifenthrin (fish: 75 ppt; invertebrates: 800 ppt), cyfluthrin (fish:34 ppt; invertebrates: 12.5 ppt), cypermethrin (fish:195 ppt; invertebrates: 210 ppt), deltamethrin (fish:290 ppt; invertebrates: 55 ppt), esfenvalerate (fish:35 ppt; invertebrates: 25ppt), lambda-cyhalothrin (fish:105 ppt; invertebrates: 3.5 ppt) and permethrin (fish:395 ppt, invertebrates: 10 ppt) were obtained from the U.S.EPA OPP website with the last update on September 16, 2010: http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm#benchmarks