Pyrethroid Concentrations in Surface Water and Bed Sediment in High Agricultural Use Regions of California.

Keith Starner and K. Kelley

California Department of Pesticide Regulation
Sacramento, CA 95812

Monterey County, California

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Keith Starner* and K. Kelley, California Dept. of Pesticide Regulation, Environmental Monitoring Branch, Sacramento, CA

*Contact: kstarner@cdpr.ca.gov, 916/324-4167

ABSTRACT

Over 50 surface water and bed sediment samples were collected from four agricultural regions within the state of California and analyzed for a suite of pyrethroid insecticides. Total organic carbon (TOC) was determined for sediment samples from each sampling site, and a toxicity unit (TU) analysis was completed in order to identify sediment concentrations that could potentially result in toxicity to *H. azteca*. Overall, 30% of samples had detectable pyrethroids in either water or sediment, and 13% of sediment samples had > 1 TU.

INTRODUCTION

Pyrethroid insecticides are applied to a variety of crops in California throughout the year. In 2003, over 127,000 kilograms of pyrethroid active ingredients were applied to agricultural fields throughout the state. Six of the primary pyrethroids used in California agriculture, in order of decreasing amount applied in 2003, are permethrin, esfenvalerate, lambda-cyhalothrin, cyfluthrin, bifenthrin and cypermethrin (DPR 2005). Due to the aquatic toxicity of the pyrethroids, offsite movement of these compounds into surface water is of concern. Recent monitoring studies conducted in agricultural areas of California have shown pyrethroid contamination of both surface water and stream bed sediment (Kelley and Starner, 2004; Weston *et al*., 2004; Gill and Spurlock, 2004; Bacey *et al*., 2003; Walters, *et al*.; 2002). Considering their high and increasing use, information regarding the environmental fate and transport of these compounds is increasingly important. In 2004, the California Department of Pesticide Regulation (DPR) initiated a monitoring study designed to begin assessing the extent of pyrethroid contamination of the aquatic environment in high-use regions of the state (Starner, 2004).

MATERIALS AND METHODS

Four regions of high agricultural pyrethroid-use (Salinas River, Sacramento Valley/Feather River, Northern San Joaquin Valley (NSJV), and Imperial Valley) (Figure 1) were sampled three times each over a 12-month period. Bed sediment and whole water samples were analyzed for the six primary pyrethroid insecticides. Method detection limits (MDL) and reporting limits (RL) are presented in Table 1.

Representative sediment samples from each sampling location were analyzed for total organic carbon (TOC). Based on measured pyrethroid concentrations, TOC content, and pyrethroid toxicity data for *Hyallela azteca* (Amweg *et al*. 2005) an estimation of toxicity of the sediment samples was also completed. *H. azteca* toxicity data are presented in Table 2.

RESULTS AND DISCUSSION

Pyrethroid insecticides were detected in three of the four regions, with an overall detection frequency of 30% (Table 3). Detection frequency was highest in the Salinas River region (60%), and was > 25% in Imperial and NSJV. No pyrethroids were detected in the Feather River region.

For all regions, most detections were in bed sediment; there were relatively few detections in whole water samples (Tables 4 and 5). There were no detections of cypermethrin or cyfluthrin in any of the four regions.

A toxicity unit (TU) analysis was completed in order to identify sediment concentrations that could potentially result in toxicity to *H. azteca*. TU was calculated by dividing the organic carbon normalized concentration of the detected pyrethroid by its associated LC50 value. Trace detections were not included in the TU analysis. Pyrethroid toxicity was assumed to be additive; when multiple pyrethroid active ingredients were detected in a single sediment sample, their individual TUs were added together. A summary of the results of the TU analysis are shown in Table 6.

Overall, 13% of sediment samples had > 1 pyrethroid TU, indicating that those sediments would be expected to be acutely toxic to *H. azteca*. In both the Salinas and Imperial regions, 20% of sediment samples had > 1 TU.

Amweg *et al.* showed that significant pyrethroid toxicity occurs at about 0.5 TU; the 1 TU benchmark used here is then a relatively conservative one. Additionally, the sediment analytical method utilized in this study was of inadequate sensitivity to detect all toxicologically significant concentrations. Indeed, the trace concentrations of esfenvalerate, lambda-cyhalothrin, and bifenthrin (Table 5) would have each added an additional 1 TU to each of the samples in which they occurred if assumed to be equal to the respective method detection limits. A more sensitive analytical method has been developed and will be utilized in future pyrethroid monitoring efforts.

CONCLUSIONS

The results of the monitoring study indicate that pyrethroid insecticides are present in surface water bed sediments in various agricultural regions throughout California at concentrations that could be expected to cause toxicity.

DPR has subsequently initiated a follow up monitoring project, utilizing more sensitive analytical methods, designed to further assess pyrethroid contamination throughout the state of California.

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Disclaimer

The mention of commercial products, their source, or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such product.

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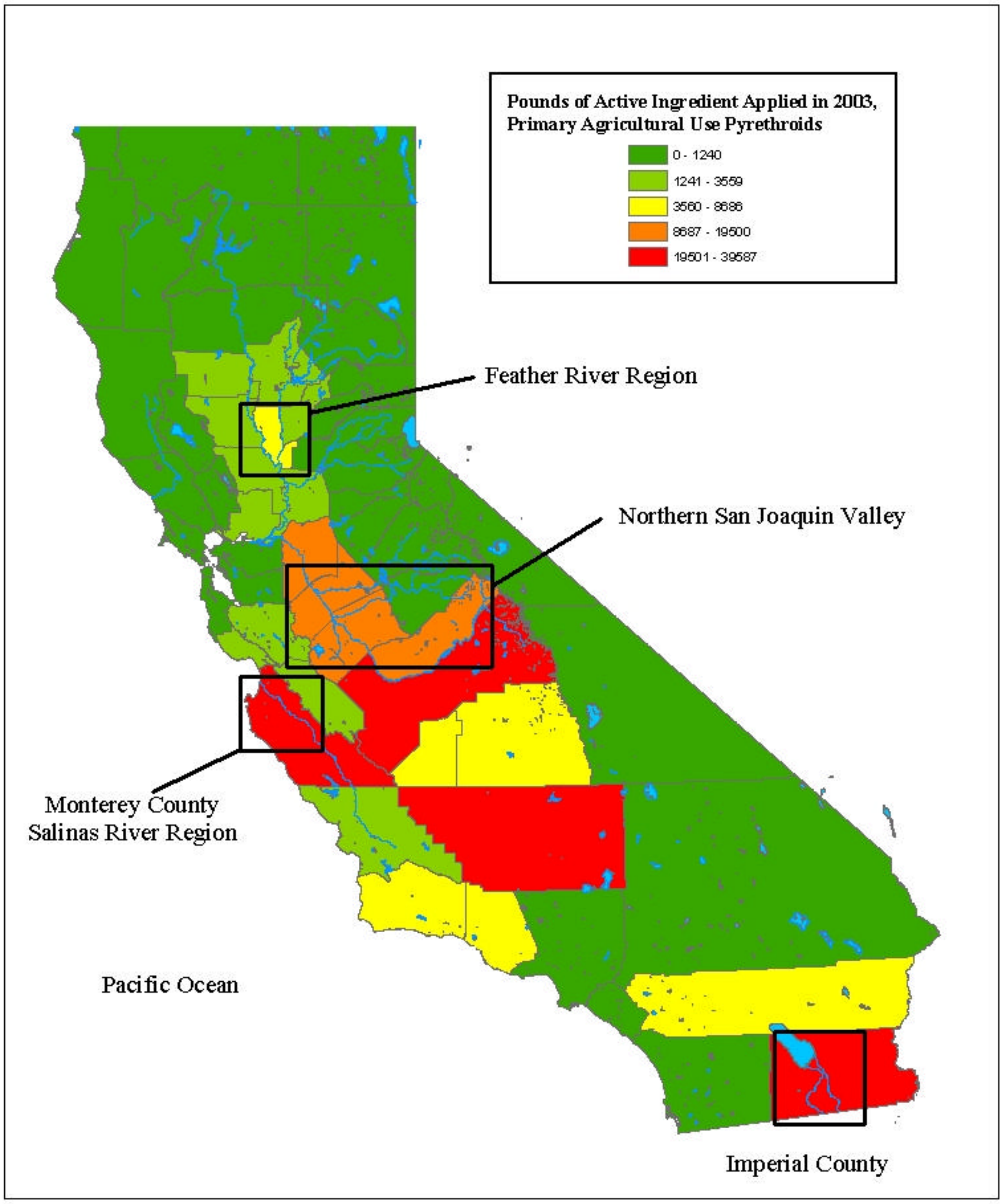

Figure 1. Agricultural Pyrethroid Use in California, 2003. The four study areas are indicated.

Table 1: Analytical method details

Pyrethroid Pesticides in Surface Water by GC/MSD		
Compound	**Method Detection Limit (ug/L)**	**Reporting Limit (ug/L)**
Bifenthrin	0.00216	0.005
Cyfluthrin	0.0555	0.08
Cypermethrin	0.0566	0.08
Esfenvalerate	0.0225	0.05
Lambda-cyhalothrin	0.00776	0.02
Permethrin	0.0169	0.05
Pyrethroid Pesticides in Sediment by GC/EC, confirmation by GC/MSD		
Compound	**Method Detection Limit (ug/g)**	**Reporting Limit (ug/g)**
Bifenthrin	0.007	0.01
Cyfluthrin	0.008	0.01
Cypermethrin	0.008	0.01
Esfenvalerate	0.008	0.01
Lambda-cyhalothrin	0.009	0.01
Permethrin	0.006	0.01

Table 2. Pyrethroid sediment median lethal concentrations (LC50).

Compound	**Ave. 10 day LC50 (ug/g OC), *H. azteca***
lambda-cyhalothrin	0.45
bifenthrin	0.52
cyfluthrin	1.08
esfenvalerate	1.54
permethrin	10.83

Source: Amweg *et al*. 2005

Table 3. Summary of pyrethroid detections, water and sediment samples

Region	No. Sampling Sites	No. Samples (each, water and sed.)	No. Samples with Detections*	Overall Detection Frequency (%)	AIs detected
Imperial	5	15	4	27	lambda cyhalothrin, esfenvalerate, permethrin
Salinas	5	15	9	60	permethrin, esfenvalerate, bifenthrin
NSJV	4	11	3	27	lambda cyhalothrin
Feather	4	12	0	0	none
Overall	18	53	16	30	lambda cyhalothrin, esfenvalerate, permethrin, bifenthrin

* detection of at least one AI in either water or sediment

Table 4. Range of whole water detection concentrations (ug/L)

Region	Esfenvalerate	Lambda-cyhalothrin	Permethrin	Bifenthrin
Imperial	no detections	no detections	trace	no detections
NSJV	no detections	0.11 - 0.14	no detections	no detections
Salinas	no detections	no detections	trace - 0.08	trace
Feather	no detections	no detections	no detections	no detections
Total no. detections	0	1	3	1

A trace detection is defined as a residue concentration between the RL and the MDL that is determined by the analytical chemist to be likely due to the analyte of interest.

Table 5. Range of sediment detection concentrations (ug/g dry sediment)

Region	esfenvalerate	lambda-cyhalothrin	permethrin	bifenthrin
Imperial	trace - 0.02	0.04 - 0.31	trace	no detections
NSJV	no detections	trace - 0.02	no detections	trace
Salinas	0.03 - 0.06	no detections	trace - 0.13	trace
Feather	no detections	no detections	no detections	no detections
Total no. detections	4	5	8	2

Table 6. Estimation of sediment toxicity

Region	No. Sampling Sites	Total Samples	No. of sediment samples with est. toxicity > 1 TU*	Percent Samples with est. toxicity > 1 TU	Primary source of toxicity
Imperial	5	15	3	20	lambda-cyhalothrin
Salinas	5	15	3	20	esfenvalerate
NSJV	4	11	1	9	lambda-cyhalothrin
Feather	4	12	0	0	none
Overall	18	53	7	13	

* TU = Toxicity Unit