Pyrethroid Insecticides in California Surface Waters and Bed Sediments: Concentrations and Estimated Toxicities.

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Monterey County, California Photo: K. Starner

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ABSTRACT

Over 100 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 (PYs). 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 *Hyallela azteca*. Overall, 60% of samples had detectable pyrethroids in either water or sediment, and 30% of sediment samples had > 1 TU.

INTRODUCTION

Pyrethroid insecticides are applied to a variety of crops in California throughout the year. In 2004, over 285,000 pounds (ca. 130,000 kilograms) of pyrethroid active ingredients were applied to agricultural fields throughout the state. 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 (Anderson *et al.* 2006; Kelley and Starner, 2004; Weston *et al*., 2004; Gill and Spurlock, 2004; Bacey *et al*., 2003). Considering their high and increasing use, information regarding the environmental fate and transport of these compounds is increasingly important. Beginning in 2004, the California Department of Pesticide Regulation (DPR) initiated monitoring studies designed to begin assessing the extent of pyrethroid contamination of the aquatic environment in high-use regions of the state (Starner, 2004; Starner, 2005).

MATERIALS AND METHODS

Four regions of high agricultural pyrethroid-use (Salinas River/Monterey, Sacramento Valley/Feather River, Northern San Joaquin Valley (NSJV), and Imperial Valley) (Figure 1) were sampled a minimum of three times each over a 24-month period. Bed sediment and whole water samples were analyzed for pyrethroid insecticides. Method reporting limits (RL) are presented in Table 1. During the first half (Phase A) of the 24-month study, each region was sampled three times and all samples analyzed using analytical Method A (Table 1). In the second half of the study (Phase B), an improved analytical

method with additional analytes and lower reporting limits (Method B) was adopted for all sample analysis. In Phase B, samples were collected primarily from the Salinas region, with a few additional samples from the Imperial region, and all were analyzed utilizing Method B.

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 *H. 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

Pyrethroids were detected in three of the four regions, with an overall detection frequency of 61% (Table 3). Detection frequency was highest in the Salinas River region (85%), and was ca. 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 deltamethrin or resmethrin in any of the four regions. Many sediment samples, especially in samples from the Salinas region, had detections of multiple pyrethroid active ingredients.

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. At the time of this analysis, sediment toxicity data for fenpropathrin were not available. As such, detections of fenpropathrin 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, 30% of sediment samples had > 1 pyrethroid TU (Table 6), indicating that those sediments would be expected to be acutely toxic to *H. azteca*. Amweg *et al.* (2005) showed that significant pyrethroid toxicity occurs in sediment at about 0.5 TU; the 1 TU benchmark used here is then a relatively conservative one. Approximately 45% of all sediment samples had > 0.5 TU.

The highest frequency of detection (85%) and exceedance of the 1 TU benchmark (42%) both occurred in the Salinas region (Tables 3 and 6). Even considering only the earlier (Phase A) data, utilizing the less sensitive analytical method A (Table 1), the Salinas samples still contained detectable concentrations of pyrethroids 60% of the time (Table 3). The higher detection frequency in Salinas samples is likely due at least partially to the higher organic carbon content of the bed sediments in that region relative to that of the

other regions studies (Table 7). Due to the hydrophobic nature of the pyrethroids, accumulation in sediment organic carbon is expected.

Additional factors that may contribute to the observed differences in pyrethroid concentrations for the four regions include the length of the pyrethroid use season, the amount of pyrethroid use in each region, and the agricultural/irrigation practices for the crops treated (Table 7).

CONCLUSIONS

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

On August 31, 2006, DPR placed products containing pyrethroids into reevaluation (DPR, 2006b). Reevaluation is a process DPR uses when it determines that currently registered pesticides may cause unreasonable adverse effects to people or the environment. Specific factors that may initiate reevaluation include hazards to workers, the general public, or fish and wildlife. Regulations allow DPR to require any data it deems necessary to assure that products under reevaluation can be used without endangering public health or the environment. This reevaluation is based on recent monitoring surveys and toxicity studies revealing the widespread presence of pyrethroids in the sediment of both agricultural and urban dominated California waterways at levels toxic to *H. azteca*. For more information, access the DPR web site below: http://www.cdpr.ca.gov/docs/registration/reevaluation/chemicals/pyrethroids.htm

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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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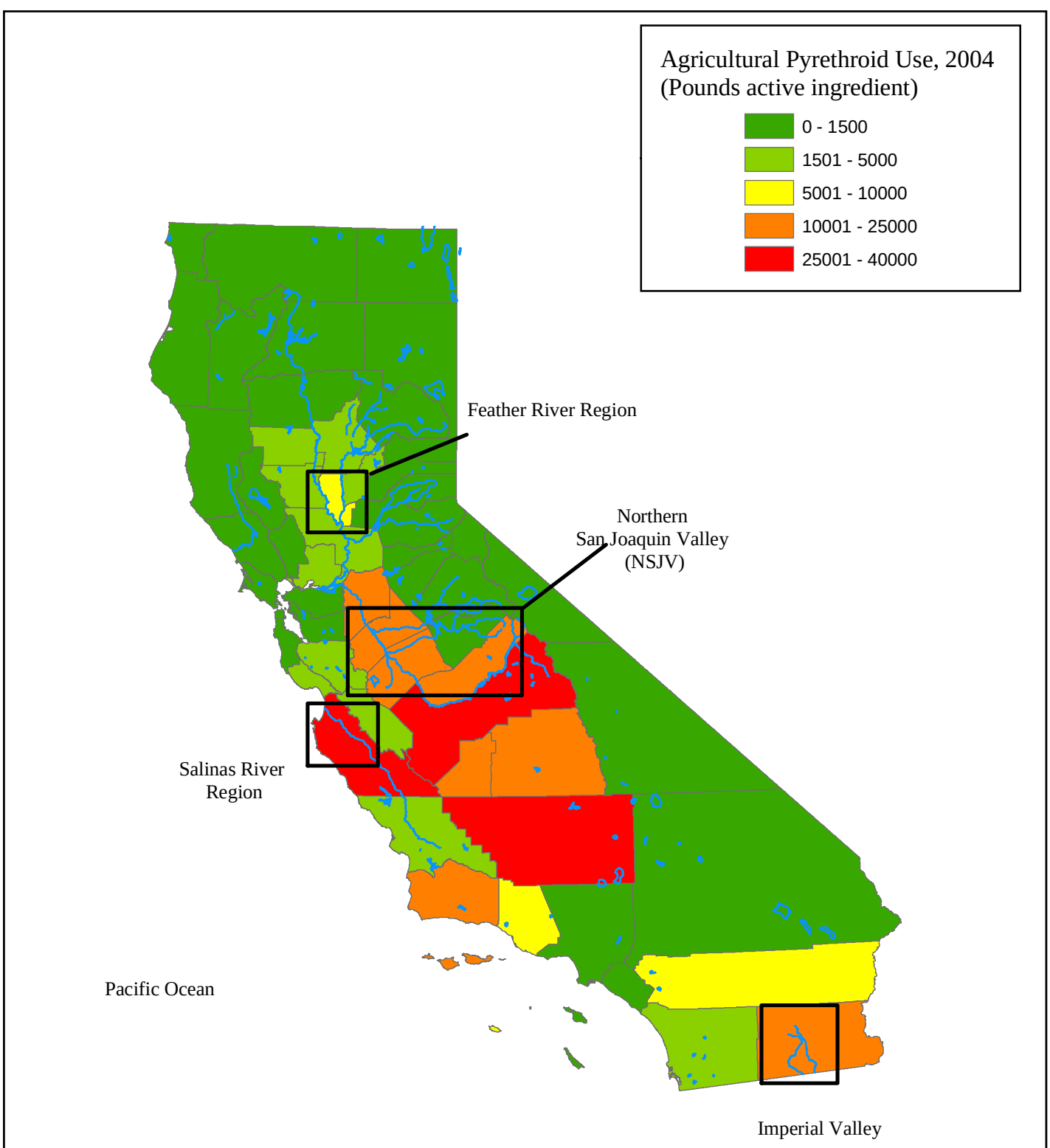

Figure 1. Agricultural Pyrethroid Use in California, 2004.
The four study areas are indicated.

Table 1: Analytical method details

Pyrethroid Pesticides in Surface Water by GC/MSD		
Compound	**Method A Reporting Limit (ug/L)**	**Method B Reporting Limit (ug/L)**
Bifenthrin	0.005	0.005
Cyfluthrin	0.08	0.015
Cypermethrin	0.08	0.015
Deltamethrin	Not included	0.015
Esfenvalerate	0.05	0.015
Fenpropathrin	Not included	0.015
Lambda-cyhalothrin	0.02	0.015
Permethrin	0.05	0.015
Resmethrin	Not included	0.015
Pyrethroid Pesticides in Sediment by GC/EC, confirmation by GC/MSD		
Compound	**Method A Reporting Limit (ug/g)**	**Method B Reporting Limit (ug/g)**
Bifenthrin	0.01	0.0010
Cyfluthrin	0.01	0.0010
Cypermethrin	0.01	0.0010
Deltamethrin	Not included	0.0010
Esfenvalerate	0.01	0.0010
Fenpropathrin	Not included	0.0010
Lambda-cyhalothrin	0.01	0.0010
Permethrin	0.01	0.0010
Resmethrin	Not included	0.0015

Method A was utilized for the first portion of the 24-month study. Approximately mid-way through the study, an improved analytical method (Method B) was adopted for sample analysis. This method included additional analytes and lower reporting limits.

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
cypermethrin	0.38

Source: Amweg *et al.* 2005, Maund *et al.* 2002.

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	6 (5)	21 (15)	5 (4)	24 (27)	lambda cyhalothrin, esfenvalerate, permethrin
Salinas	14 (5)	76 (15)	65 (9)	85 (60)	permethrin, esfenvalerate, bifenthrin, fenpropathrin, lambda
NSJV	4	11	3	27	lambda cyhalothrin
Feather	4	12	0	0	none
Overall	28	120	73	61	

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

For Imperial and Salinas, the value in parentheses is Phase A only data (see text).

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

Region	Esfenvalerate	Lambda-cyhalothrin	Permethrin	Bifenthrin	Cypermethrin
Imperial	no detections	0.0274	trace	no detections	no detections
Salinas	trace	no detections	trace - 0.08	trace	0.055
NSJV	no detections	0.11 - 0.14	no detections	no detections	no detections
Feather	no detections	no detections	no detections	no detections	no detections
Total no. detections	3	3	5	1	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	cypermethrin	fenpropathrin
Imperial	trace - 0.02	0.04 - 0.31	trace	no detections	no detections	no detections
Salinas	0.002 - 0.06	0.0018 - 0.1441	0.00167 - 0.1441	0.0013 - 0.0790	0.0020 - 0.0118	0.0017 - 0.0094
NSJV	no detections	trace - 0.02	no detections	trace	no detections	no detections
Feather	no detections	no detections	no detections	no detections	no detections	no detections
Total detections	51	29	60	46	8	28

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 est. toxicity
Imperial	6 (5)	21 (15)	4 (3)	19 (20)	lambda-cyhalothrin
Salinas	14 (5)	76 (15)	32 (3)	42 (20)	esfenvalerate, bifenthrin
NSJV	4	11	1	9	lambda-cyhalothrin
Feather	4	12	0	0	none
Overall	28	120	37	31	

TU = Toxicity Unit
For Imperial and Salinas, the value in parentheses is Phase A only data (see text).

Table 7. Summary of region characteristics.

Region	Bed sediment % TOC	PY use per unit area	Primary PY use season(s)	Primary crops
Imperial	< 1.0	34	March/October	alfalfa/lettuce
Salinas	2 to 3.5	113	April through September	lettuce, spinach
NSJV	< 1.0	10	May through August	almonds, pistachios
Feather River	0.5 to 1.5	20	May through August	peaches

PY use per unit area: Pounds of active ingredients per square mile in the primary use regions. Not an application rate. Source: DPR 2006.