SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 29, No. 4, pp. 813–823, 2010

Printed in the USA
DOI: 10.1002/etc.106

PYRETHROID INSECTICIDE CONCENTRATIONS AND TOXICITY IN STREAMBED SEDIMENTS AND LOADS IN SURFACE WATERS OF THE SAN JOAQUIN VALLEY, CALIFORNIA, USA

JOSEPH L. DOMAGALSKI,*† DONALD P. WESTON,‡ MINGHUA ZHANG,§ and MICHELLE HLADIK†

†U.S. Geological Survey, 6000 J Street, Placer Hall, Sacramento, California 95819

‡Department of Integrative Biology, University of California, 3060 Valley Life Sciences Building, Berkeley, California 94720-3140, USA

§Department of Land, Air and Water Resources, University of California, One Shields Avenue, Davis, California 95616, USA

(*Submitted* 22 *August* 2009; *Returned for Revision* 2 *October* 2009; *Accepted* 11 *November* 2009)

Abstract—Pyrethroid insecticide use in California, USA, is growing, and there is a need to understand the fate of these compounds in the environment. Concentrations and toxicity were assessed in streambed sediment of the San Joaquin Valley of California, one of the most productive agricultural regions of the United States. Concentrations were also measured in the suspended sediment associated with irrigation or storm-water runoff, and mass loads during storms were calculated. Western valley streambed sediments were frequently toxic to the amphipod, *Hyalella azteca,* with most of the toxicity attributable to bifenthrin and cyhalothrin. Up to 100% mortality was observed in some locations with concentrations of some pyrethroids up to 20 ng/g. The western San Joaquin Valley streams are mostly small watersheds with clay soils, and sediment-laden irrigation runoff transports pyrethroid insecticides throughout the growing season. In contrast, eastern tributaries and the San Joaquin River had low bed sediment concentrations (<1 ng/g) and little or no toxicity because of the preponderance of sandy soils and sediments. Bifenthrin, cyhalothrin, and permethrin were the most frequently detected pyrethroids in irrigation and storm water runoff. Esfenvalerate, fenpropathrin, and resmethrin were also detected. All sampled streams contributed to the insecticide load of the San Joaquin River during storms, but some compounds detected in the smaller creeks were not detected in the San Joaquin River. The two smallest streams, Ingram and Hospital Creeks, which had high sediment toxicity during the irrigation season, accounted for less than 5% of the total discharge of the San Joaquin River during storm conditions, and as a result their contribution to the pyrethroid mass load of the larger river was minimal. Environ. Toxicol. Chem. 2010;29:813–823. © 2010 SETAC

Keywords—Pyrethroids Sediment toxicity *Hyalella azteca* Storm runoff Agriculture

INTRODUCTION

Pyrethroid insecticides are in current use in California, USA, agriculture on a variety of crops and for other pest control purposes, such as structural treatment and landscape maintenance. Sales of pyrethroid insecticides have been increasing in California because of regulatory restrictions on other insecticides, primarily organophosphate insecticides. Total statewide sales of pyrethroid insecticides in 2007 were 293,074 kg (http://cdpr.ca.gov/docs/pur/purmain.htm). Applications of pyrethroid insecticides may occur at any time of the year; pyrethroids may be used in the summer growing season or applied to dormant orchards in the winter to control pests that may affect the trees during the subsequent flowering in the spring. Commonly used pyrethroid insecticides in California are permethrin, esfenvalerate, fenpropathrin, λ-cyhalothrin, cyfluthrin, bifenthrin, and cypermethrin.

There is concern about the toxicity of these compounds to aquatic organisms as a result of runoff from agricultural fields and other sources [1]. Because the pyrethroids have generally high organic carbon partitioning coefficients ($\log K_{OC} > 5$), offsite movement is attributed mainly to the erosive runoff of soil from agricultural fields and other sources [2]. Transport of the suspended sediments and their incorporation into the bed sediments of nearby surface water bodies can adversely affect aquatic life, particularly benthic invertebrates. Although the presence of pyrethroid compounds and associated toxicity in California agricultural and urban streams has been documented [3–8], questions remain about how the compounds are transported (irrigation runoff or storm water runoff), how long the compounds persist in the environment under various conditions, and how much of the applied compounds, relative to use, may be transported in runoff. Pyrethroid insecticides tend to have soil half-lives that range from weeks to months [9]. Less is known about their persistence once transported to aquatic sediments.

The objectives of this study were to determine whether measured levels of pyrethroid insecticides in the bed sediments of the streams are toxic to benthic organisms, to determine the effects of watershed characteristics (irrigation, storm-water runoff, and soil/sediment types) on the occurrence and transport of pyrethroids, and to determine which streams contribute most to downstream loads. Bed sediments were sampled in representative streams of the San Joaquin Valley, California, at the beginning, middle, and end of the irrigation season, and the amounts transported in these streams were assessed during winter storms. Streams were selected on the basis of access and having a stream-gauging station that recorded daily discharge. Agriculture in the San Joaquin Valley is dependent on irrigation water, because essentially no rainfall occurs during the April through October growing season. Pyrethroid use on crops within the San Joaquin Valley increased from 16,221 kg

* To whom correspondence may be addressed (joed@usgs.gov).

Published online 8 January 2010 in Wiley InterScience (www.interscience.wiley.com).

in 2001 to 35,770 kg in 2006 (California Department of Pesticide Regulation, 2008, unpublished data). Major crops on which pyrethroids are used include almond, pistachio, lettuce, corn, alfalfa, cotton, and tomatoes. Because of differences in soil drainage characteristics, runoff of excess irrigation water occurs in some agricultural watersheds and can dominate stream flow, whereas in other portions of the Valley, very little runoff occurs during the irrigation season. The chosen streams were selected in order to compare and contrast this range of conditions. The majority of rainfall occurs in the San Joaquin Valley during November through March. Accordingly, samples of stream and river water were collected during winter rainfall, suspended sediment was recovered, and pyrethroid insecticides were measured in the solids. In the present paper, streambed sediment concentrations and toxicity and the concentrations and loads of pyrethroid insecticides in storm water runoff are discussed.

MATERIALS AND METHODS

Description of study area

The area of the drainage basin of the perennial San Joaquin River is 19,024 km^2. Of this total, 11,134 km^2 is within the Sierra Nevada, 5,812 km^2 is within the San Joaquin Valley, and 2,078 km^2 is within the Coast Ranges. The study area is defined as the portion of the San Joaquin Valley downstream of Mud and Salt Sloughs (Fig. 1). Approximately two-thirds of the streamflow of the San Joaquin River near the mouth of the basin originates from the three large east-side tributaries (Merced, Tuolumne, and Stanislaus Rivers). The San Joaquin Valley has a mix of agricultural and urban land uses, whereas the Sierra Nevada and Coast Ranges are mostly forest, grassland, or natural vegetation. Agricultural land use within the valley consists of fruit and nut orchards, row crops, and livestock. Irrigation is required because of a lack of rainfall in the growing season. The annual precipitation near the mouth of the basin is approximately 38 cm/y, and most of the rainfall occurs in the winter months [10]. Crops are typically irrigated from March through September. The western San Joaquin Valley has a slightly longer history of agriculture, dating to the early 1900s, whereas the eastern San Joaquin valley agriculture dates to the 1920s [11]. Soil types tend to be different between the eastern and the western San Joaquin Valley. Soils of the east tend to be coarse or sandy and are derived partially from weathering of granitic rock of the Sierra Nevada [10]. In contrast, soils of the western valley are derived from erosion of the Coast Ranges and tend to be finer grained, with higher clay content. These differences are reflected in the bed sediment of the steams, with the streams of the western valley having a much higher clay, or fine-grained, composition relative to the sandy bed material of the eastern valley (Table 1).

In 2006, the top three pyrethroid insecticides used in the study area agriculturally were permethrin, cyfluthrin, and cypermethrin. Bifenthrin also had high use, but its use for structural pest control purposes exceeded the use for agriculture. Approximately 80% of the bifenthrin use in the San Joaquin Valley was

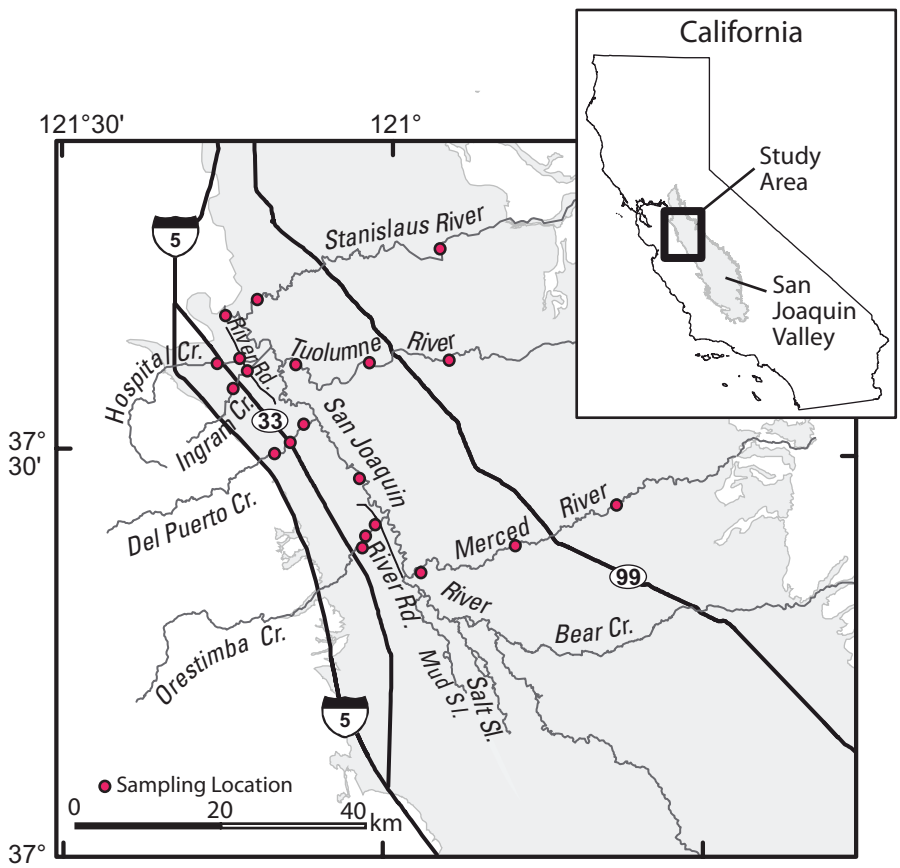

Fig. 1. Map of the study area and sampling sites within the San Joaquin Valley, California, USA. [Color figure can be seen in the online version of this article, available at www.interscience.wiley.com.]

Table 1. Percentage of silt and clay and size fractions of bed sediment analyzed for sediment toxicity and chemistry within the San Joaquin Valley (California, USA)

Sample ID	Date	% >250 μm	% 63–250 μm	% Silt/clay
Del Puerto Creek (1)	4/27/07	13.8	52.5	33.7
Del Puerto Creek (1)	7/24/07	4.9	51.3	43.9
Del Puerto Creek (1)	9/27/07	16.1	42.1	41.8
Del Puerto Creek (2)	4/27/07	14.0	31.0	55.0
Del Puerto Creek (2)	7/24/07	11.6	30.0	58.4
Del Puerto Creek (2)	9/27/07	7.9	41.5	50.6
Del Puerto Creek (3)	4/27/07	4.2	49.7	46.2
Del Puerto Creek (3)	7/24/07	0.9	27.5	71.6
Del Puerto Creek (3)	9/27/07	5.6	32.0	62.5
Hospital Creek (1)	4/27/07	1.3	43.3	55.4
Hospital Creek (1)	7/24/07	7.9	45.7	46.3
Hospital Creek (1)	9/27/07	17.1	41.9	41.0
Hospital Creek (2)	4/27/07	2.5	26.9	70.5
Hospital Creek (2)	7/24/07	7.6	38.1	54.2
Hospital Creek (2)	9/27/07	5.4	37.2	57.4
Ingram Creek (1)	4/27/07	13.0	24.7	62.3
Ingram Creek (1)	7/24/07	0.4	13.5	86.2
Ingram Creek (1)	9/27/07	4.6	24.5	70.9
Ingram Creek (1)	4/27/07	1.0	25.3	73.7
Ingram Creek (2)	7/24/07	22.1	36.0	41.9
Ingram Creek (2)	9/27/07	0.3	10.3	89.4
Orestimba Creek (1)	4/27/07	5.1	8.8	86.1
Orestimba Creek (1)	7/24/07	0.7	2.8	96.4
Orestimba Creek (1)	9/27/07	18.8	26.0	55.2
Orestimba Creek (2)	4/27/07	3.7	34.0	62.2
Orestimba Creek (2)	7/24/07	27.1	18.0	54.9
Orestimba Creek (2)	9/27/07	30.3	23.0	46.7
Orestimba Creek (3)	4/27/07	36.5	20.6	42.9
Orestimba Creek (3)	7/24/07	18.9	27.8	53.3
Orestimba Creek (3)	9/27/07	29.4	20.0	50.6
Merced River (1)	6/3/07	31.5	44.6	23.9
Merced River (1)	7/26/07	38.6	51.4	10.0
Merced River (1)	10/12/07	17.1	55.6	27.3
Merced River (2)	6/3/07	25.9	66.4	7.7
Merced River (2)	7/26/07	46.1	38.0	15.9
Merced River (2)	10/12/07	67.9	29.0	3.1
Merced River (3)	6/3/07	27.3	63.7	9.0
Merced River (3)	7/26/07	52.5	41.5	6.0
Merced River (3)	10/12/07	75.9	18.7	5.4
Stanislaus River (1)	7/26/07	44.0	41.6	14.3
Stanislaus River (1)	10/12/07	32.9	61.2	5.9
Stanislaus River (2)	6/3/07	11.7	67.7	20.6
Stanislaus River (2)	7/26/07	61.0	29.7	9.3
Stanislaus River (2)	10/12/07	73.7	23.2	3.1
Tuolumne River (1)	6/3/07	31.5	52.9	15.6
Tuolumne River (1)	7/26/07	46.5	36.5	17.0
Tuolumne River (1)	10/12/07	68.9	23.9	7.2
Tuolumne River (2)	6/3/07	19.2	61.5	19.2
Tuolumne River (2)	7/26/07	23.3	64.6	12.1
Tuolumne River (2)	10/12/07	33.5	58.4	8.2
Tuolumne River (3)	6/3/07	18.5	59.5	22.0
Tuolumne River (3)	7/26/07	42.9	46.1	11.0
Tuolumne River (3)	10/12/07	77.0	18.4	4.6
San Joaquin River (1)	6/3/07	1.8	58.4	39.8
San Joaquin River (1)	7/26/07	1.7	52.3	46.0
San Joaquin River (1)	10/12/07	1.6	49.5	48.9
San Joaquin River (2)	6/3/07	11.4	62.4	26.2
San Joaquin River (2)	7/24/07	3.5	68.1	28.4
San Joaquin River (2)	9/27/07	13.6	71.0	15.4

Percentage silt/clay is less than 63 μm; 63–250 μm would be considered fine and very fine sands; >250 μm and would be medium sands or larger. Individual stream sites are listed in order of upstream to downstream.

for structural pest control. Permethrin was the most highly used of the agricultural pyrethroid insecticides, and the two crops with the greatest permethrin use were almonds and pistachios. Permethrin is also used extensively for structural pest control. In the San Joaquin Valley, during 2007, a total of 18,691 kg of permethrin was used, and approximately half was used for structural pest control (PAN Pesticides Database-California Pesticide Use; http://www.pesticideinfo.org/). Other pyrethroid insecticides that have high use for structural pest control include cyfluthrin (more than half of all applications), and cypermethrin (more than half of all applications). Two compounds that have mostly agricultural uses include esfenvalerate and fenpropathrin.

Site selection

During the irrigation season, streambed samples were collected from eight streams or rivers. In general, the intent was to place three sites on each tributary of the San Joaquin River when access permitted, with the most upstream site situated soon after the tributary entered agricultural lands, the most downstream site near the confluence with the San Joaquin River, and the third site midway between the other two sites. For some streams, only two sites were sampled because of difficulty in obtaining access to the stream. Four of the streams (Ingram, Hospital, Del Puerto, and Orestimba Creeks) were situated within the western San Joaquin Valley (Fig. 1). Two sites were chosen on the San Joaquin River, one near the central portion of the basin and one at its downstream boundary. Three rounds of bed sediment collection were conducted during the irrigation season of 2007: in late spring (April 27 and June 3), midsummer (July 24 and 26), and early autumn (September 27 and October 12). All sites were sampled during each sampling round, except during the first round of sediment collection when the Stanislaus River was omitted because of high flow hindering access.

Streambed sediment sampling

Samples of streambed sediment were collected by wading along an approximate 100-m reach and collecting samples of sediment in depositional zones. Care was taken to sample the upper 1 to 2 cm of sediment in order to ensure that recently deposited material was sampled. The streambed sediment was collected in clean glass jars using stainless-steel scoops. Samples were kept cold after collection and homogenized at the laboratory by hand mixing. Sample splits were then taken for toxicological or chemical analysis. One field duplicate was collected each sampling round. Thus, in total 62 bed sediment samples were collected for chemical analysis and toxicity testing over the course of the study.

Collection of whole water samples

Whole water samples were collected at a subset of the stream and river sites during two winter storms and once during the irrigation season for the purpose of isolating suspended sediment for pyrethroid insecticide analysis, and to measure total suspended sediment concentration. Sampling sites for winter storms were chosen at downstream locations on tributary sites adjacent to stream-gauging stations so that mass loads of suspended sediment and associated pyrethroid insecticides could be quantified. Two sites were chosen for sampling on the San Joaquin River, the midbasin site and at the mouth of the basin. During the irrigation season, whole water samples were collected only from the four western tributaries because there was little suspended sediment in the eastern tributaries. Large volumes of water (up to or exceeding 100 L) were

collected in order to obtain a sufficient amount of suspended sediment for chemical analysis. The water was collected with either a peristaltic or other pump. Sampling was restricted to approximately the upper two-thirds of depth in order to minimize any possibility of disturbing the bed sediment. The water samples were processed with a Westfalia continuous-flow centrifuge [12]. After centrifugation, the concentrated sediment slurry was further dewatered by centrifuging for 20 min at 10,000 rpm using a high-speed refrigerated centrifuge (Sorvall RC-5B centrifuge; Dupont).

Analytical methods

Pyrethroid insecticides analyzed, mean recovery from sediment, relative standard deviation, and detection limits are shown in Table 2. Detailed methodology for the extraction of pyrethroid insecticides from suspended sediments is given by Smalling and Kuivila [13], based on methods described by Smalling et al. [14] and LeBlanc et al. [12].

Whole water samples were analyzed for suspended-sediment concentration at the U.S. Geological Survey Sediment Laboratory in Marina, California. Details of the analytical method can be found elsewhere [15]. All suspended sediments were analyzed for organic carbon content using a PerkinElmer CHNS/O analyzer. Before analysis, sediments were dried to a constant weight at 110°C for 3 h. Sediments were combusted at 925°C in silver boats after being exposed to concentrated hydrochloric acid (HCl) fumes in a desiccator for 24 h to remove inorganic carbon. Acetanilide was used for instrument calibration of elemental carbon.

Matrix spikes, matrix spike replicates, laboratory replicates, field duplicates, method blanks, and surrogate recoveries were also processed for quality-control purposes. Matrix spikes were analyzed with 200 ng of each pyrethroid spiked into eight sediment samples (four of these sediment samples also had a matrix spike replicate). Matrix spike recoveries ranged from 70 to 130% for all of the insecticides analyzed. Eight samples were split in the laboratory and analyzed as replicates. There were three field-collected duplicate samples. The differences between replicates/duplicates were less than 25% for all insecticides detected above the method detection level (MDL). No pyrethroids were detected in any of the seven blank samples (sodium sulfate was used as the blank matrix). Recovery of the sediment surrogates was used to monitor the efficiency of each extraction. The average percentage recoveries of the surrogates, ^{13}C-labeled dichlorodiphenyldichloroethylene (*p,p′*-DDE) and *cis*-permethrin, were 82 ± 6% and 99 ± 6%, respectively. Sediment MDLs were validated in a previous study [13].

Table 2. Pyrethroid insecticides analyzed, method detection limits (MDL), mean recovery, and relative standard deviation (SD)

Pyrethroid insecticide	MDL (ng/g dry sediment)	Mean recovery (%)	Relative SD (%)
Allethrin	1.5	82.2	7.4
Bifenthrin	2.2	97.4	7.6
Cyfluthrin	2.0	82.3	6.3
λ-Cyhalothrin	2.4	89.9	9.1
Cypermethrin	2.6	86.6	7.8
Deltamethrin	2.5	82.3	9.0
Esfenvalerate	2.1	82.5	7.6
Fenpropathrin	2.1	90.3	6.2
τ-Fluvalinate	2.6	99.3	9.4
Permethrin (*cis* and *trans*)	1.0	92.9	2.8
Resmethrin	1.9	88.5	5.7
Sumithrin	1.3	101	3.3
Tetramethrin	1.4	82.8	4.3

Sediment toxicity method

Sediment toxicity tests were conducted by using the amphipod *Hyalella azteca* in 10-d exposures, with survival as the endpoint, following standard protocols [16]. Briefly, 75 ml of sediment was placed in 400-ml beakers with 250 ml overlying water, prepared by addition of salts to deionized water to achieve a moderately hard solution. *Hyalella azteca*, 7 to14 d in age, were added to eight replicate beakers per sample and held for 10 d at 23°C, with a 16:8-h light:dark photo cycle and daily addition of 1 ml yeast/cerophyll/trout food to each beaker. Five hundred milliliters of water was added to each beaker daily, with the overflow exiting through a screened hole. After the 10-d exposure, surviving amphipods were recovered on a 425-μm screen and counted. All testing was initiated within a two-week holding time. Statistical testing of field samples relative to the control (a blend of sediments from two reservoirs that had been confirmed to have no detectable pyrethroids at a concentration less than 1 ng/g) was done by *t* test using ToxCalc (Tidepool Scientific Software).

Calculation of toxic units (TU) is one approach to expressing sediment toxicity that adjusts for differences in toxicity among the various analytes. Toxic units relate sediment insecticide concentrations on an organic carbon (OC) basis to the 10-d median lethal concentration (LC50) of the sediment. Toxic units were calculated as TU = Actual sediment concentration of the analyte on an OC basis divided by *Hyalella azteca* sediment 10-d LC50 on an OC basis. *Hyalella azteca* 10-d LC50 values were obtained from the literature [1,17,18].

RESULTS AND DISCUSSION

Streambed sediment concentrations

Nine of the thirteen pyrethroid insecticides analyzed were detected in the bed sediments (Table 3). Not detected were allethrin, deltamethrin, sumithrin, and tetramethrin. Some compounds were only infrequently detected, such as cyfluthrin, cypermethrin, esfenvalerate, fenpropathrin, τ-fluvalinate, and resmethrin. Bifenthrin, cyhalothrin, and permethrin were frequently detected, particularly in the western tributaries. All three of these pyrethroids are widely used in both agriculture and nonagricultural applications within the San Joaquin Valley. Use of bifenthrin and permethrin in structural pest control and landscape maintenance exceeds agricultural use by approximately 3 to 1. Structural use and landscape maintenance use of λ-cyhalothrin is slightly less than its agricultural use (http://cdpr.ca.gov/docs/pur/purmain.htm). It is likely that, at least in the western tributaries where these compounds were most often detected, those agricultural sources dominate, because the population density is relatively low compared with the eastern San Joaquin Valley.

Pyrethroids were detected in 97% of the samples from the western-side tributaries (the sole exception being one sample from Orestimba Creek), with concentrations ranging from 1 to 20 ng/g for at least one analyte in most of the samples. Although

Table 3. Concentration of pyrethroid insecticides in bed sediments at all sampling locations, total toxic units (TU), percent organic carbon (OC), and percent survival from samples collected in the San Joaquin Valley (California, USA).

Site	Total TUs	% OC	% Survival (±SD)	Concentrations in ng/g								
				Bifenthrin	Cyfluthrin	Cyhalothrin	Cypermethrin	Esfenvalerate	Fenpropathrin	τ-Fluvalinate	Permethrin	Resmethrin
MDL, ng/g[a]				2.2	2.0	2.4	2.6	2.1	2.1	2.6	1.0	1.9
LC50, ng/g at 1% organic carbon				5.2	10.8	4.5	3.8	15.4	22.0	NA[b]	108	NA
Del Puerto Creek(1)	0.3	0.6	38 ± 21	ND[c]	ND	ND	ND	2.9	ND	ND	ND	ND
Del Puerto Creek (1)	0.1	0.4	69 ± 11	(0.2)	ND	ND	ND	ND	ND	ND	ND	ND
Del Puerto Creek (1)	0.03	1.8	91 ± 11	(0.3)	ND	ND	ND	ND	ND	ND	ND	ND
Del Puerto Creek (2)	0.2	1.8	71 ± 14	(0.9)	ND	(0.6)	ND	ND	ND	ND	ND	ND
Del Puerto Creek (2)	0.1	2.4	88 ± 18	(0.7)	ND	ND	ND	ND	ND	ND	ND	ND
Del Puerto Creek (2)	0.3	1.0	93 ± 9	(1.4)	ND	ND	ND	ND	ND	ND	1.0	ND
Del Puerto Creek (3)	0.9	1.1	0 ± 0	3.6	ND	(1.3)	ND	ND	ND	ND	ND	ND
Del Puerto Creek (3)	0.6	1.2	3 ± 5	2.4	ND	(1.2)	ND	(0.3)	ND	ND	1.2	ND
Del Puerto Creek (3)	0.6	1.4	44 ± 12	3.3	ND	(1.1)	ND	ND	ND	ND	(0.9)	ND
Hospital Creek (1)	4.0	0.8	0 ± 0	15.8	ND	(0.7)	ND	ND	ND	ND	3.2	ND
Hospital Creek (1)	2.7	0.8	0 ± 0	11.4	ND	ND	ND	ND	ND	ND	(0.7)	ND
Hospital Creek (1)	0.7	0.8	6 ± 7	2.2	ND	(0.6)	ND	ND	ND	ND	ND	ND
Hospital Creek (2)	2.6	0.7	0 ± 0	8.6	ND	(0.7)	ND	ND	ND	ND	4.1	ND
Hospital Creek (2)	2.0	0.6	3 ± 5	3.4	2.1	ND	(1.4)	ND	ND	ND	ND	ND
Hospital Creek (2)	0.7	0.6	59 ± 19	2.1	ND	ND	ND	ND	ND	ND	ND	ND
Ingram Creek (1)	0.4	0.8	74 ± 16	ND	ND	(1.3)	ND	ND	2.6	ND	ND	ND
Ingram Creek (1)	4.4	1.0	0 ± 0	ND	ND	19.8	ND	ND	(0.3)	ND	ND	(1.3)
Ingram Creek (1)	2.7	0.8	10 ± 14	(0.3)	2.9	8.1	ND	(0.5)	ND	ND	ND	ND
Ingram Creek (2)	0.9	0.9	8 ± 7	(0.8)	ND	2.4	ND	ND	ND	(1.3)	14.5	ND
Ingram Creek (2)	1.2	0.9	1 ± 4	(0.4)	ND	4.5	ND	ND	ND	(1.3)	(1.0)	ND
Ingram Creek (2)	5.8	1.1	0 ± 0	7.5	6.9	12.6	5.7	ND	ND	ND	(1.7)	ND
Orestimba Creek (1)	0.3	1.9	90 ± 8	(0.4)	ND	(2.3)	ND	ND	ND	ND	ND	ND
Orestimba Creek (1)	0.1	1.7	53 ± 26	(0.2)	ND	(0.3)	ND	ND	ND	ND	ND	ND
Orestimba Creek (1)	0.4	2.4	89 ± 11	2.4	ND	(2.0)	ND	ND	ND	ND	ND	ND
Orestimba Creek (2)	0.2	1.2	86 ± 11	(0.4)	ND	(0.7)	ND	ND	ND	ND	(0.6)	ND
Orestimba Creek (2)	0.1	1.4	88 ± 10	(0.3)	ND	(0.2)	ND	(0.3)	ND	ND	(0.6)	ND
Orestimba Creek (2)	0.4	0.9	94 ± 5	(0.7)	ND	(0.9)	ND	(0.4)	ND	ND	(0.9)	ND
Orestimba Creek (3)	0.02	0.9	98 ± 5	(0.1)	ND	ND	ND	ND	ND	ND	ND	ND
Orestimba Creek (3)	0.3	1.1	83 ± 15	(0.2)	2.2	ND	(0.5)	ND	ND	ND	(0.5)	ND
Orestimba Creek (3)	0.01	1.2	96 ± 5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus River (1)	0.04	0.3	91 ± 14	ND	ND	ND	ND	(0.2)	ND	ND	ND	ND
Stanislaus River (1)	0.01	0.6	91 ± 12	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus River (2)	0.1	0.9	94 ± 11	(0.4)	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus River (2)	0.1	0.3	96 ± 5	(0.2)	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus River (2)	0.01	0.5	93 ± 10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tuolumne River (1)	0.01	0.9	96 ± 5	ND	ND	ND	ND	ND	ND	ND	(0.5)	ND
Tuolumne River (1)	0.03	1.3	95 ± 5	(0.1)	ND	ND	ND	(0.3)	ND	ND	(0.3)	ND
Tuolumne River (1)	0.01	0.4	94 ± 7	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tuolumne River (2)	0.1	1.0	94 ± 8	(0.7)	ND	ND	ND	ND	ND	ND	ND	ND
Tuolumne River (2)	0.01	0.6	98 ± 5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tuolumne River (2)	0.01	0.3	96 ± 7	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tuolumne River (3)	0.1	1.0	98 ± 5	(0.3)	ND	ND	ND	ND	ND	ND	ND	(0.6)
Tuolumne River (3)	0.1	0.6	96 ± 5	(0.3)	ND	ND	ND	ND	ND	ND	ND	ND
Tuolumne River (3)	0.01	0.4	94 ± 7	ND	ND	ND	ND	ND	ND	ND	ND	ND
Merced River (1)	0.01	2.2	85 ± 15	ND	ND	ND	ND	ND	ND	ND	ND	ND

(*Continued*)

Table 3. (*Continued*)

Site	Total TUs	% OC	% Survival (±SD)	Concentrations in ng/g							
				Bifenthrin	Cyfluthrin	Cyhalothrin	Cypermethrin	Esfenvalerate	Fenpropathrin	τ-Fluvalinate	Permethrin	Resmethrin
Merced River (1)	0.01	3.6	93 ± 7	(0.2)	ND	ND	ND	ND	ND	ND	ND	ND
Merced River (1)	0.1	2.2	93 ± 7	(0.4)	ND	(0.8)	ND	ND	ND	ND	ND	ND
Merced River (2)	0.01	0.4	96 ± 5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Merced River (2)	0.01	1.3	93 ± 7	(0.1)	ND	ND	ND	ND	ND	ND	ND	ND
Merced River (2)	0.2	0.3	98 ± 5	ND	ND	ND	ND	(0.7)	ND	ND	ND	ND
Merced River (3)	0.01	0.4	96 ± 7	ND	ND	ND	ND	ND	ND	ND	ND	ND
Merced River (3)	0.1	0.4	91 ± 6	(0.1)	ND	ND	ND	ND	ND	ND	ND	ND
Merced River (3)	0.5	0.2	93 ± 12	(0.5)	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin River (1)	0.01	1.0	90 ± 11	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin River (1)	0.01	1.1	91 ± 8	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin River (1)	0.01	0.9	91 ± 14	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin River (2)	0.01	0.7	94 ± 9	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin River (2)	0.1	0.6	95 ± 11	(0.2)	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin River (2)	0.01	0.4	99 ± 4	ND	ND	ND	ND	ND	ND	ND	ND	ND

Concentrations and other data are displayed by site location and in the order of beginning, middle and end of irrigation season for each site. Site location are ordered in upstream to downstream order. Concentrations that were detectable but below the nominal reporting limit are shown in parentheses. As a reference point, *Hyalella azteca* 10-d sediment LC50 values are shown, assuming 1% organic carbon (LC50 values from [1, 17, 18]).

[a] Method detection limit.

[b] Not available.

[c] Not detected.

Hospital and Ingram Creeks are in close proximity to one another, different compounds tended to be detected at higher concentrations at those two sites. Bifenthrin was detected at the highest concentrations in Hospital Creek and at lower concentrations at Ingram Creek, except for the last sampling (end of the irrigation season), possibly a result of different cropping patterns with different types of pest control strategies. Some tributaries, such as Del Puerto Creek, showed a pattern of higher bed sediment concentrations of pyrethroid insecticides at downstream locations, whereas others, such as Orestimba Creek, had no discernible spatial or temporal pattern. Pyrethroid insecticides were detected at the beginning of the irrigation season in the western tributaries, and those detections may have been the result of recent applications or residues from the previous growing season.

Pyrethroid insecticides were detected in only 48% of the eastside samples and never exceeded 1 ng/g. The highest concentration found on the eastside, 0.7 ng/g bifenthrin in the Tuolumne River, was approximately one-seventh the *H. azteca* LC50. San Joaquin River sediments rarely had measurable pyrethroid concentrations; with only trace levels of bifenthrin on one occasion. Their absence from river sediments may be attributable to the difficulty of finding depositional zones of fine-grained sediments, because the river bottom is generally sandy. The amounts of silt and clay found in the western streams, eastern streams, and the two San Joaquin River sites are shown in Figure 2. Because of the higher discharge of the San Joaquin River, fine-grained sediments are more likely to be transported to more downstream locations.

Pyrethroid insecticide concentrations or occurrence in streambed sediments were highly variable, especially at the western creek sites during the irrigation or growing season (Table 3). Changes in concentration might be attributable to either the transport of recently applied compounds from different locations or the resuspension and deposition from previous applications. Although the sampling strategy was to integrate a collection over a 100-m reach, the variability of pesticide concentrations in the stream sediments may be very high and responsible for these apparent temporal differences.

Suspended sediment pyrethroid concentrations, irrigation season

Suspended sediment samples were collected once during the irrigation season (Table 4). Samples were collected only at the most downstream location of the western-side tributaries, insofar as the eastern tributaries and the San Joaquin River had low suspended sediment concentrations during the irrigation season, and it was not feasible to collect samples at those sites. The compounds detected in the suspended sediments generally matched those detected in the bed sediment, although there were some differences. For example, at Del Puerto Creek, four compounds (bifenthrin, cyhalothrin, esfenvalerate, and permethrin) were detected in the bed sediments. Among those four, only bifenthrin and cyhalothrin were detected in the suspended sediments and at lower concentrations relative to the bed sediment concentrations in the same waterway. Four compounds were detected in Hospital Creek streambed sediments (bifenthrin, cyfluthrin, cypermethrin, and permethrin). However, only two were detected in the suspended sediments (bifenthrin and permethrin). Bifenthrin concentrations in Hospital Creek were similar in both the streambed and the sus-

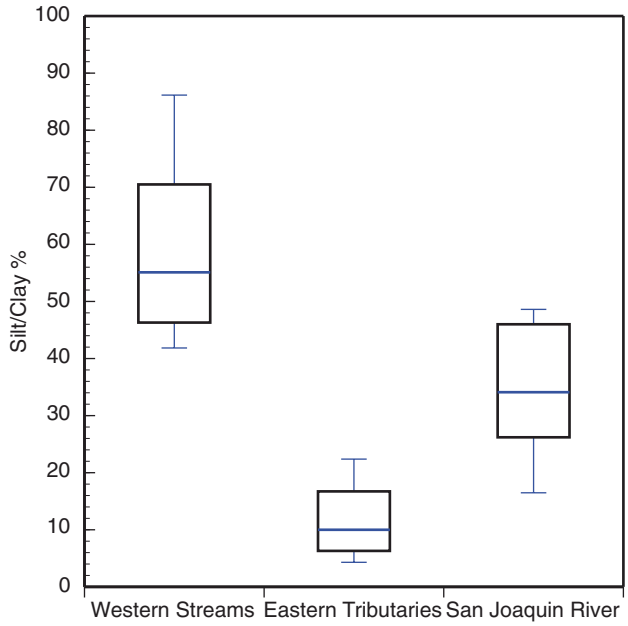

Fig. 2. Percentages of silt and clay in the western streams, eastern tributaries, and two San Joaquin River sites. Samples were collected at various locations within the San Joaquin Valley, California, USA. Boxes show 10th to 90th percentiles. Median is shown within the box. The 25th and 75th percentiles form the bottom and top of each box. [Color figure can be seen in the online version of this article, available at www.interscience.wiley.com.]

pended sediment. Five compounds were detected in the streambed sediments of Ingram Creek (bifenthrin, cyhalothrin, fenpropathrin, τ-fluvalinate, and permethrin). Only two compounds, cyhalothrin and esfenvalerate, were detected in the suspended sediment, and, of those two, esfenvalerate was not detected in the streambed sediment. Cyhalothrin had a higher concentration than any of the other pyrethroids in both the streambed and the suspended sediments of Ingram Creek. Finally, at Orestimba Creek, six compounds were detected in at least one streambed sampling location (bifenthrin, cyfluthrin, cyhalothrin, cypermethrin, esfenvalerate, and permethrin). Only two compounds were detected in the suspended sediment (bifenthrin and permethrin). In general, the compounds detected at the highest concentrations in streambed sediment tended to be the highest detected in suspended sediment, with bifenthrin predominating in Del Puerto and Hospital Creeks and cyhalothrin predominating in Ingram Creek. Differences in the types of compounds detected in either the bed or the suspended sediment may be attributable to bed sediments acting as an integrator of applications throughout the year, whereas the suspended sediments may be more reflective of recent applications coupled with irrigation runoff.

Suspended sediment pyrethroid concentrations, storm samples

Concentrations of pyrethroid insecticides in suspended sediments were determined during two storms (Table 5). In general, suspended-sediment samples collected during winter rains showed compounds and concentrations similar to those of the bed sediments and irrigation season suspended sediments as described above. However, there were some noteworthy differences. First, most of the higher concentrations of permethrin observed in this study were present in the winter collections of suspended sediment. In addition, in most of the streams that contained permethrin in the suspended sediment (Del Puerto, Stanislaus, San Joaquin), it had not been present in the bed sediments during the previous summer. One of the uses of permethrin is as a dormant spray insecticide, and detections in the storm samples may be attributable to that use. However, permethrin also has high use for structural pest control, and runoff originating near buildings may be another source. Second, suspended sediment in the San Joaquin River and eastern tributaries (Stanislaus, Tuolumne) during the winter frequently contained bifenthrin and esfenvalerate, even though these compounds were detected infrequently in the bed sediments during the previous summer and at lower concentrations. The prevalence of these insecticides in the suspended material, but not bed sediments, suggests that they are largely being transported to more downstream locations without significant deposition in the sandy sediments predominating in the eastern tributaries. The presence of 51 ng/g bifenthrin in Stanislaus River suspended sediment was by far the highest concentration observed in this study, and, given the compound's hydrophobicity, is likely to be in part related to the high organic carbon content of the suspended sediment (nearly 7%). Third, resmethrin was found in suspended sediment from Orestimba Creek at a concentration of 18.7 ng/g, 14 times higher than any bed-sediment sample. Resmethrin has no agricultural use; it is used primarily for mosquito control, with lesser amounts used for structural pest

Table 4. Concentrations of pyrethroid insecticides in suspended sediments collected during the irrigation season and percentage organic carbon (OC)

		Concentrations in ng/g								
Site	% OC	Bifenthrin	Cyfluthrin	Cyhalothrin	Cypermethrin	Esfenvalerate	Fenpropathrin	τ-Fluvalinate	Permethrin	Resmethrin
LC50, (ng/g at 1% OC)	—	5.2	10.8	4.5	3.8	15.4	22.0	NA[a]	108.3	NA
LC50, (ng/g at 2% OC)	—	10.4	21.6	9.0	7.2	30.8	44.0	NA	216.6	NA
Del Puerto Creek (3)	2.5	(0.7)	ND[b]	(0.7)	ND	ND	ND	ND	ND	ND
Hospital Creek (2)	1.2	9.6	ND	ND	ND	ND	ND	ND	(0.4)	ND
Ingram Creek (2)	1.1	ND	ND	11.1	ND	5.1	ND	ND	ND	ND
Orestimba Creek (3)	1.6	(0.3)	ND	ND	ND	ND	ND	ND	1.1	ND

The samples were collected from sites in the San Joaquin Valley (California, USA). Concentrations that were detectable but below the nominal reporting limit are shown in parentheses. Samples were collected at the most downstream sampling point. Most compounds listed in Table 2 that were not detected in these samples are not listed. As a reference point, *Hyalella azteca* 10-d sediment median lethal concentration values (LC50) are shown for sediment organic concentrations of 1 and 2% OC (LC50 values from other studies [1,17,18]).

[a] Not available.

[b] Not detected.

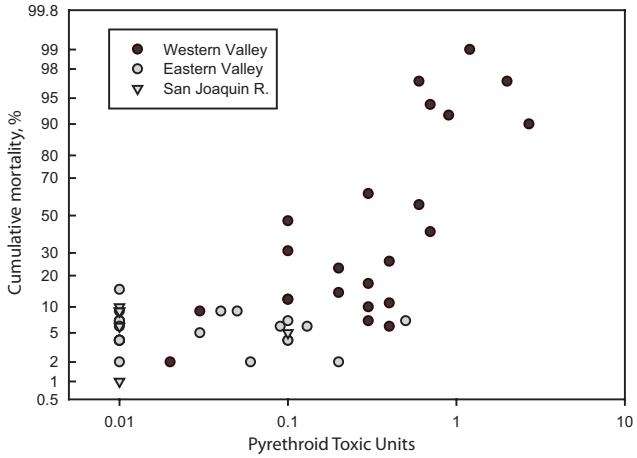

Fig. 3. Toxic units (TU) and mortality of *Hyalella azteca* exposed to all bed-sediment samples collected (California, USA). When pyrethroids were undetectable, the station is plotted at 0.01 TU.

control. However, the agency responsible for mosquito control in the study region reports no use of resmethrin in the Orestimba Creek watershed (Jerry Davis, Turlock Mosquito Abatement District, personal communication). Therefore, the source of resmethrin was not determined.

Toxicity testing: Bed sediments

Toxicity tests were conducted on all bed-sediment samples collected throughout the irrigation season. Control survival was acceptable, with an average value of 94% across all tests. The lowest control value observed was 85%, which exceeded the minimal permissible threshold for test validity of 80%. Twenty-five of the 62 field samples (40%) had survival rates that were significantly less than their controls.

Sediments from the eastside tributaries were generally less toxic to *H. azteca* than sediments from the west side (Fig. 3 and Table 3). With one minor exception, there was no sediment toxicity observed in any eastern tributary, with mean survival ranging between 88 and 99%. The sole exception was a Merced River field duplicate sample from the beginning of the irrigation season that had mean survival of 83%. This value was statistically different from its accompanying control, but the duplicate sample taken at the same location and time had 88% survival and was not significantly toxic. In contrast, eight of the 10 sampling sites from the western tributaries had acutely toxic bed sediments at least once during the study. Ingram and Hospital Creeks were by far the most toxic, with all samples tested from both of these creeks exhibiting acute toxicity every time they were tested. The highest survival rates were 59 and 74% for Hospital and Ingram Creeks, respectively. All other samples from Ingram and Hospital Creeks showed survival rates of $<10\%$, and often zero. Among the nine sediments tested from Del Puerto Creek, six showed acute toxicity, with *H. azteca* survival ranging from 0 to 71%.

In Orestimba Creek, four of the nine total samples had survival significantly less than the control, but in most cases the level of toxicity was minimal ($>80\%$ survival). There was only one Orestimba sample (most upstream site, middle of the irrigation season) that was clearly more toxic, with only 53% survival.

Toxic units were calculated for each detected compound at all sites. Many of the western samples contained more than one pyrethroid, so, assuming additivity of pyrethroid toxicity, TUs for each compound were summed to produce a total pyrethroid TU value for each of the 62 sediment samples. The TU approach can be used to help infer the cause for toxicity [1,5]. If pyrethroids were the sole agents responsible for the toxicity, then 50% survival of *H. azteca* would be expected at 1 TU

Table 5. Pyrethroid insecticide concentrations and organic carbon (OC) concentrations, for suspended sediments collected during two storms

	Suspended sediment concn. (mg/L)	% OC	Bifenthrin	Cyhalothrin	Esfenvalerate	Fenpropathrin	Permethrin	Resmethrin
LC50, (ng/g at 1% OC)	—	—	5.2	4.5	15.4	22.0	108	NA[a]
LC50, (ng/g at 2% OC)	—	—	10.4	9.0	30.8	44.0	217	NA
Storm date: 01/04/08 to 01/05/08								
Del Puerto Creek (3)	1,900	2.0	5.8	2.9	(1.5)	ND[b]	9.4	ND
Hospital Creek (2)	9,010	1.2	9.9	(1.2)	(0.8)	(1.2)	ND	ND
Ingram Creek (2)	5,500	1.3	(0.8)	4.9	ND	2.3	ND	ND
Orestimba Creek (3)	341	2.0	(0.2)	ND	1.4	ND	ND	18.7
Stanislaus River (2)	16	6.8	51.0	ND	ND	ND	15.9	ND
San Joaquin River (1)	87	2.5	(1.9)	ND	ND	ND	4.6	ND
San Joaquin River (2)	112	2.4	3.3	ND	ND	ND	5.5	ND
Storm date: 01/25/08 to 01/27/08								
Del Puerto Creek (3)	5,57	2.1	(0.2)	ND	ND	ND	ND	ND
Hospital Creek (2)	571	1.7	5.7	(0.8)	(0.7)	ND	ND	ND
Ingram Creek (2)	1,110	1.4	(0.5)	(1.2)	(0.3)	ND	ND	ND
Merced River (3)	740	2.1	(0.3)	ND	(0.5)	ND	ND	ND
Orestimba Creek (3)	259	1.8	(0.5)	(0.2)	(0.3)	ND	2.6	ND
Stanislaus River (2)	41	6.4	3.4	ND	1.4	ND	5.3	ND
Toulumne River (3)	103	2.9	2.9	ND	ND	ND	ND	ND
San Joaquin River (1)	511	2.1	(0.4)	ND	(0.2)	ND	1.2	ND
San Joaquin River (2)	334	1.9	(0.4)	ND	(0.4)	ND	1.3	ND

The samples were collected from sites in the San Joaquin Valley (California, USA). Concentrations that were detectable but below the nominal reporting limit are shown in parentheses. Compounds listed in Table 1 that were not detected in these samples are not listed. Samples were collected at the most downstream sampling location for all but the San Joaquin River, where samples were collected at an upstream (San Joaquin River 1) and a downstream site (San Joaquin River 2). As a reference point, *Hyalella azteca* 10-d sediment median lethal concentration values (LC50) are shown for sediment OC concentrations of 1 and 2% OC (LC50 values from other studies [1,17,18]).

[a] Not available.

[b] Not detected.

(actual concentration equivalent to literature-derived LC50). The onset of toxicity should occur at slightly less than 1 TU (empirically often ~0.5 TU), and complete mortality should occur at slightly over 1 TU. The data from the sampling sites closely approximate the theoretical relationship (Fig. 3), suggesting that pyrethroids are responsible for much of the *H. azteca* response observed in the toxicity tests. When less than 0.5 TU of pyrethroids was present (pyrethroid concentrations below those expected to cause toxicity), the vast majority of sites showed mortality rates within the range acceptable for control sediments (0–20%). Mortality rates rapidly climbed at approximately 0.5 TU, and there was near complete mortality at all sites with >1 TU pyrethroids. There were only four samples with appreciable deviation from the expected relationship (the sites in Fig. 3 with >20% mortality and less than 0.5 TU), suggesting that another toxicant may be playing a role in the mortality at these sites, but, in all other cases when mortality was observed, there were sufficient pyrethroids in the sediments to account for that mortality. In some cases, mortality may have been greater than expected when TUs approached 0.5, because pyrethroid insecticides might be more bioavailable in some of the western-side sediments, or, alternatively, preferential degradation of the less toxic enantiomers may occur. In the latter case, environmental residues would be more toxic than those used to develop the LC50.

The specific pyrethroids likely to be responsible for toxicity at each site are those with the highest TU values in any given sample. In Hospital Creek, there was near-complete mortality in most samples, and bifenthrin was likely responsible for the toxicity in most cases. Cyhalothrin-related toxicity was unique to Ingram Creek, and acutely toxic concentrations of that compound were pervasive throughout Ingram Creek during the summer. In the upper reaches of Del Puerto Creek, where mortality rates were relatively low (compared with downstream reaches), there were no pyrethroids present in high enough concentration to explain that mortality. However, in the lower sections of Del Puerto Creek, bifenthrin was likely the primary toxicant.

Beyond consideration of pyrethroid toxic units, several other lines of evidence indicate that toxicity in the western-side creeks is commonplace [4,19] and that pyrethroids are typically responsible for much of it. First, a thorough study of Del Puerto Creek [20] approximately 1 y before the present study determined that bifenthrin at toxic concentrations was widespread in the downstream reaches of the creek (samples collected near the downstream site of this study). A variety of toxicity-identification evaluation tools employed in that study, including temperature manipulation, esterase addition, and PBO addition, all indicated that a pyrethroid was the agent most likely responsible for the *H. azteca* toxicity. Also, a Hospital Creek sample from the present study (most upstream Hospital Creek site, collected in the middle of the irrigation season) was tested with an esterase enzyme designed to cleave the ester bond in pyrethroids, reducing their toxicity [21]. Without the esterase, the LC50 was 36% in Hospital Creek sediment (95% confidence interval 29–44%). With the esterase in the overlying water, toxicity of the sediment was reduced by slightly less than half, with an LC50 of 61% (95% confidence interval 52–73%) [22]. This toxicity-identification evaluation manipulation indicates that an ester-containing compound, consistent with a pyrethroid pesticide, was responsible for most of the observed toxicity. Finally, other investigators have studied toxicity at a nearby canal (Westley Wasteway, a constructed watercourse located between Del Puerto Creek and Ingram Creek). Toxicity-identification evaluation manipulations with sediment from this site led to the conclusion that pyrethroids were likely responsible for the observed toxicity [23].

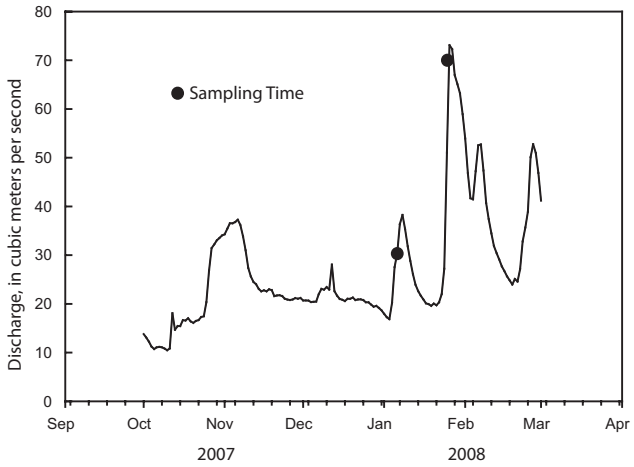

Fig. 4. Discharge of the San Joaquin River at the most upstream location (Patterson, California, USA) and hydrograph positions when suspended sediment samples were collected.

Given that pyrethroids appear to be responsible for the toxicity seen in the western-side creeks, temperature becomes an important variable to consider. Pyrethroids are known to become more toxic as sediment temperature decreases. The laboratory toxicity testing is conducted at a temperature of 23°C, as standardized by U.S. Environmental Protection Agency testing protocols, yet a temperature of 18°C doubles the toxicity of pyrethroids, and it is tripled at 13°C [18]. During April sampling, the temperature of the bed sediments in the westside creeks ranged from 17 to 32°C. It ranged from 24 to 29°C in July and from 18 to 24°C during September sampling. Because the sampling for this project was conducted in the warmer months of the year, there was not a large discrepancy between the test temperature of 23°C and the in situ temperatures, so the toxicity measured in the laboratory was a reasonable approximation of the in situ toxicity of those sediments. However, in the winter months, when temperatures in these creeks decrease to 10°C or less, it is likely that the in situ toxicity of the sediments increases at least threefold, even if the pyrethroid concentration were to remain constant.

Toxicity testing: Suspended sediments

Suspended sediment was not tested for toxicity because of the small amount of material that was collected; however, toxicity can be inferred on the basis of toxic units. Although pyrethroid concentrations in suspended sediment are not directly applicable to a benthic organism such as *H. azteca*, this analysis at least indicates the potential for toxicity to benthic invertebrates once those sediments are eventually deposited, if not first diluted with less contaminated material from elsewhere. All three of the suspended sediment samples from Hospital Creek, and two of the three from Ingram Creek, contain pyrethroid concentrations that would be expected to be

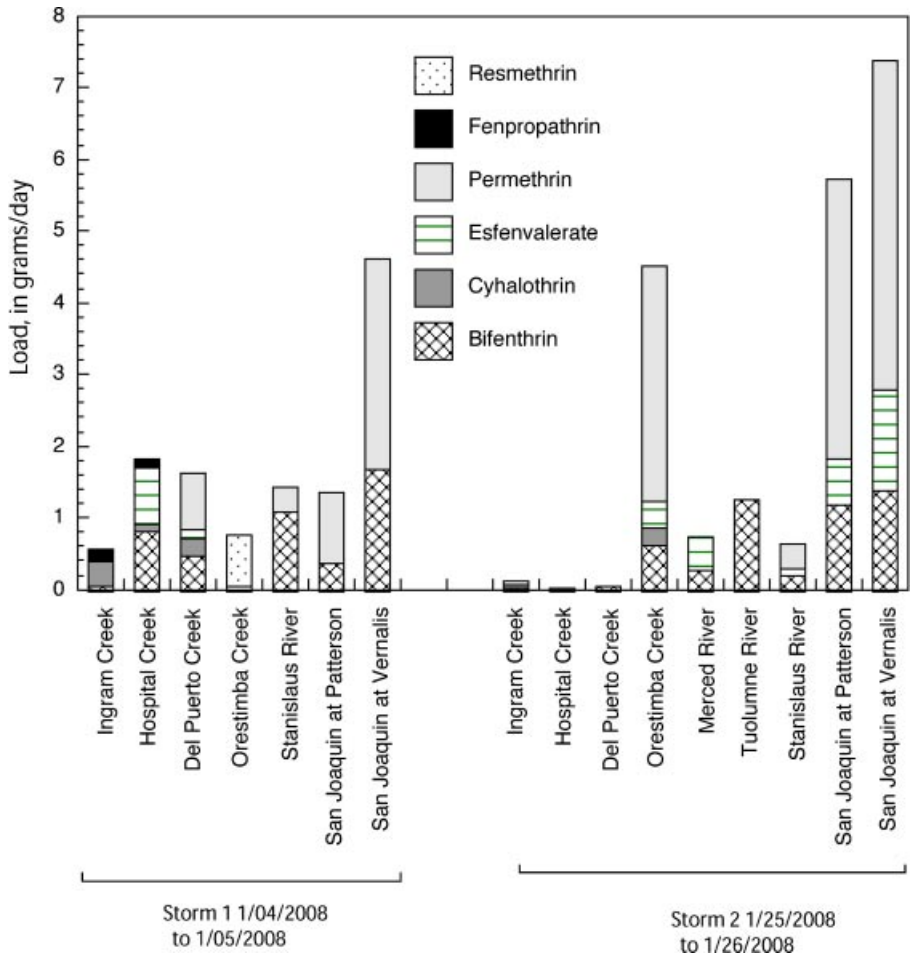

Fig. 5. Loading of pyrethroid insecticides during two storm events from locations in the San Joaquin Valley, California, USA. The pyrethroid insecticide loads were calculated as the amount of each insecticide adsorbed onto suspended sediments. [Color figure can be seen in the online version of this article, available at www.interscience.wiley.com.]

toxic to *H. azteca* (sum of pyrethroid TU $>$ 0.5). One of the three suspended sediment samples from Del Puerto Creek (first storm event) would be expected to be toxic, as would suspended sediment from Stanislaus River on the occasion when it contained 51 ng/g bifenthrin (equivalent to 1.5 TU). All other suspended material (from Orestimba Creek, the other eastern tributaries, and the San Joaquin River) contained less than 0.3 TU and would be likely to cause little or no *H. azteca* acute toxicity following deposition.

Mass loads of pyrethroids during storms

Water samples were collected after two rain events during January of 2008 that resulted in heavy rainfall throughout the study area and associated increases in stream flow. A hydrograph for the upper San Joaquin River site is shown in Figure 4. Samples were collected on the rising limb of the hydrograph at this site during the first storm and near peak discharge during the second. The storm of January 4, 2008, to January 5, 2008, was the first to result in widespread rainfall throughout the study area. Estimated daily loads of pyrethroid insecticides are shown graphically in Figure 5. Pyrethroid insecticide loads in storm runoff were quantified by recovering the suspended sediment in whole water samples and then analyzing the insecticides sorbed to the sediment.

In general, whereas pyrethroid concentrations were usually highest in the western-side tributaries, some of the largest loadings occurred in the eastern-side tributaries and the San Joaquin River because of the much higher flow rates in those water bodies. For example, the discharges of Ingram and Hospital Creeks account for less than 5% of the discharge of the San Joaquin River at the downstream site. Although those two creeks had some of the highest incidences of sediment toxicity during the irrigation, their contribution to the mass loading of pyrethroid insecticides within the San Joaquin River were negligible for these two storm events. Loading of insecticides was less during the second storm at Ingram, Hospital, and Del Puerto Creeks but increased elsewhere, especially for permethrin at Orestimba Creek. Loads at Orestimba Creek might have been higher during the second storm because of more rain, which produced 15 times more runoff than after the first storm. Loads of permethrin were higher at the San Joaquin River sites during the second storm, primarily because of the higher load from Orestimba Creek, which contributed much of the permethrin found in the San Joaquin River on that occasion. During the second storm, Orestimba Creek accounted for approximately 86% of the permethrin load of the San Joaquin River, and other sites, including Merced and the Tuolumne River, contributed to the mass load of pyrethroids for the lower San Joaquin River site. During the first storm, Del Puerto and

the Stanislaus River accounted for much, but not all, of the mass load of pyrethroid insecticides at the lower San Joaquin River site.

After permethrin, the pyrethroid with the second highest loadings was bifenthrin. Loading of bifenthrin was generally similar between the two storms at approximately 1 g/d at times in the Stanislaus, Tuolumne, and San Joaquin Rivers. Some compounds, such as esfenvalerate and cyhalothrin, were detected in some of the western-side creeks during the storms but were not detected in the San Joaquin River, probably because of dilution.

SUMMARY AND CONCLUSION

Pyrethroid insecticide concentrations in the bed sediment of streams of the San Joaquin Valley appear to be controlled by their use within the various watersheds and the potential for deposition of fine-grained sediment. The most frequently detected compounds included bifenthrin, cyhalothrin, and permethrin. Concentrations were elevated in the western tributaries, with generally nondetectable to low concentrations in the eastern tributaries. Because of the greater discharge of the large eastern tributaries, fine-grained sediment is transported to downstream locations, and less mass of pyrethroids accumulates in the limited depositional zones. As a result, sediment toxicity is absent in the eastern tributaries but is common in the western tributaries. Sediment toxicity and pyrethroid insecticides were also low to nondetected in the sandy sediments of the mainstem of the San Joaquin River. Pyrethroid insecticides are present in the suspended sediments of all tributaries and within the San Joaquin River during winter storms as a result of stormwater runoff.

It is difficult to generalize with regard to the sources of pyrethroid insecticides, insofar as the uses of most of the compounds include both agricultural and structural pest control applications. In fact, structural pest control is the largest use, for most of these compounds, within the San Joaquin Basin as a whole. Urban development could, along with agriculture, be a source of pyrethroids to the larger eastern-side rivers, but the smaller western-side watersheds, such as Del Puerto, Ingram, Hospital, and Orestimba Creeks, consist mainly of agricultural land with few structures. In those watersheds, agriculture is likely to be the dominant source. Pyrethroids may be transported to those stream channels as a result of irrigation or stormwater runoff.

Acknowledgement—This work was supported by the 2005 to 2006 Consolidated Grants—Proposition 50 Agricultural Water Quality Grant Program, State of California.

REFERENCES

1. Amweg EL, Weston DP, Ureda NM. 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, California. *Environ Toxicol Chem* 24: 966–972.
2. Liu W, Gan J, Lee S, Kabashima JN. 2004. Phase distribution of synthetic pyrethroids in runoff and stream water. *Environ Toxicol Chem* 23: 7–11.
3. Weston DP, Holmes RW, You J, Lydy MJ. 2005. Aquatic toxicity due to residential use of pyrethroid insecticides. *Environ Sci Technol* 39: 9778–9784.
4. Weston DP, You J, Amweg EL, Lydy MJ. 2008. Sediment toxicity in agricultural areas of California and the role of hydrophobic pesticides. In Gan J, Spurlock F, Hendley P, Weston D, eds, Synthetic Pyrethroids: Occurrence and Behavior in Aquatic Environments. ACS Book Series 991. American Chemical Society, Washington DC, pp 26–54.
5. Amweg EL, Weston DP, You J, Lydy MJ. 2006. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. *Environ Sci Technol* 40: 1700–1706.
6. Starner K, White J, Spurlock F, Kelley K. 2008. Assessment of pyrethroid contamination of streams in high-use agricultural regions of California. In Gan J, Spurlock F, Hendley P, Weston DP, eds, Synthetic Pyrethroids: Occurrence and Behavior in Aquatic Environments. ACS Book Series 991. American Chemical Society Books, Washington DC, pp 72–83.
7. Holmes RW, Anderson BS, Phillips BM, Hunt JW, Crane DB, Mekebri A, Blondina G, Nguyen L, Connor V. 2008. Statewide Investigation of the role of pyrethroid pesticides in sediment toxicity in California's urban waterways. *Environ Sci Technol* 42: 7003–7009.
8. Hladik ML, Kuivila KM. 2008. Occurrence of pyrethroids in bed and suspended sediments in California. In Gan J, Spurlock F, Hendley P, Weston DP, eds, Synthetic Pyrethroids: Occurrence and Behavior in Aquatic Environments. ACS Book Series 991. American Chemical Society Books, Washington DC, pp 55–71.
9. Laskowski DA. 2002. Physical and chemical properties of pyrethroids. *Rev Environ Contam Toxicol* 174: 49–170.
10. Gronberg JM, Dubrovsky NM, Kratzer CR, Domagalski JL, Brown LR, Burow KR. 1998. Environmental setting of the San Joaquin-Tulare Basins, California. Water-Resources Investigations Report 97-4205. U.S. Geological Survey, Washinton DC.
11. Kratzer CR. 1998. Transport of sediment-bound organochlorine pesticides to the San Joaquin River, California. Open-File Report 97-655. U.S. Geological Survey, Washinton DC.
12. Smalling KL, Orlando JL, Kuivila KM. 2005. Analysis of pesticides in surface water and sediment from Yolo Bypass, California, 2004–2005. Scientific Investigations Report 2005–5220. U.S. Geological Survey, Washinton DC.
13. Smalling KL, Kuivila KK. 2008. Multi-residue method for the analysis of 85 current-use and legacy pesticides in bed and suspended sediments. *J Chromatogr A* 1210: 8–18.
14. LeBlanc JL, Orlando JL, Kuivila KM. 2004. Pesticide concentration in water and in suspended and bottom sediments in the New and Alamo Rivers, Salton Sea Watershed, California, April 2003. Data Series 104. U.S. Geological Survey, Washington DC
15. Guy HP. 1969. Laboratory theory and methods for sediment analysis. In U.S. Geological Survey Techniques of Water-Resources Investigations. Book 5. U.S. Geological Survey, Washington DC, p 58.
16. U.S. Environmental Protection Agency. 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. EPA/600/R-99/064. Office of Research and Development, Washington DC.
17. Maund SJ, Hamer MJ, Lane MCG, Farrelly E, Rapley JH, Goggin UM, Gentle WE. 2002. Partitioning, bioavailability, and toxicity of the pyrethroid insecticide cypermethrin in sediments. *Environ Toxicol Chem* 21: 9–15.
18. Weston DP, You J, Harwood AD, Lydy MJ. 2009. Whole sediment toxicity identification evaluation tools for pyrethroid insecticides: III. Temperature manipulation. *Environ Toxicol Chem* 28: 173–180.
19. Weston DP, You J, Lydy MJ. 2004. Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's Central Valley. *Environ Sci Technol* 38: 2752–2759.
20. Weston DP, Zhang M, Lydy MJ. 2008b. Identifying the cause and source of sediment toxicity in an agriculture-influenced creek. *Environ Toxicol Chem* 27: 953–962.
21. Wheelock C, Miller JL, Miller MJ, Phillips BM, Huntley SA, Gee SJ, Tjeerdema RS, Hammock BD. 2006. Use of carboxylesterase activity to remove pyrethroid-associated toxicity to *Ceriodaphnia dubia* and *Hyalella azteca* in toxicity identification evaluations (TIEs). *Environ Toxicol Chem* 25: 973–984.
22. Weston DP, Jackson CJ. 2009. Use of engineered enzymes to identify organophosphate and pyrethroid-related toxicity in toxicity identification evaluations. *Environ Sci Technol* 43: 5514–5520.
23. Anderson B, Phillips B, Hunt J, Voorhees J, Clark S, Mekebri A, Crane D, Tjeerdema R. 2008. Recent advances in sediment toxicity identification evaluations emphasizing pyrethroid pesticides. In Gan J, Spurlock F, Hendley P, Weston D, eds, Synthetic Pyrethroids: Occurrence and Behavior in Aquatic Environments. ACS Book Series 991. American Chemical Society, Washington DC, pp 370–399.