Environ. Sci. Technol. **2010,** *44,* 1833–1840

Urban and Agricultural Sources of Pyrethroid Insecticides to the Sacramento-San Joaquin Delta of California

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Received July 31, 2009. Revised manuscript received January 11, 2010. Accepted January 13, 2010.

While studies have documented the presence of pyrethroid insecticides at acutely toxic concentrations in sediments, little quantitative data on sources exist. Urban runoff, municipal wastewater treatment plants and agricultural drains in California's Sacramento-San Joaquin River Delta were sampled to understand their importance as contributors of these pesticides to surface waters. Nearly all residential runoff samples were toxic to the amphipod, *Hyalella azteca*, and contained pyrethroids at concentrations exceeding acutely toxic thresholds, in many cases by 10-fold. Toxicity identification evaluation data were consistent with pyrethroids, particularly bifenthrin and cyfluthrin, as the cause of toxicity. Pyrethroids passed through secondary treatment systems at municipal wastewater treatment facilities and were commonly found in the final effluent, usually near *H. azteca* 96-h EC_{50} thresholds. Agricultural discharges in the study area only occasionally contained pyrethroids and were also occasional sources of toxicity related to the organophosphate insecticide chlorpyrifos. Discharge of the pyrethroid bifenthrin via urban stormwater runoff was sufficient to cause water column toxicity in two urban creeks, over at least a 30 km reach of the American River, and at one site in the San Joaquin River, though not in the Sacramento River.

Introduction

The confluence of the Sacramento and San Joaquin Rivers forms an area at the head of San Francisco Bay known as the Delta. The land is primarily used for agriculture, though there are some large population centers including Sacramento and Stockton, California. Throughout much of the 1980s and 1990s, winter rains washed organophosphate pesticides off the land, and Delta waters were frequently toxic to the standard testing species, *Ceriodaphnia dubia* (*1*). However use of the organophosphates diazinon and chlorpyrifos has been reduced in agriculture and eliminated in urban environments. Pyrethroid insecticides have taken their place for many uses, with 258 tons used for nonagricultural pest control in California in 2007 and 160 tons used for agriculture.

Pyrethroid residues occur at concentrations acutely toxic to some benthic macroinvertebrates in sediments of agricultural water bodies (*2*) and urban stream sediments in California (*3*), Texas (*4*), and Illinois (*5*). Though the general uses which contribute to these residues are known (e.g., agricultural pest control, professional and homeowner applications around structures or on landscaping) there is little of the detailed information on sources that is needed for mitigation, including pyrethroid concentrations, relative composition of the various pyrethroids for each source type, and seasonal discharge patterns. Our first goal was to gather such information on three possible sources of pyrethroids to Delta waters: (1) urban runoff; (2) municipal wastewater treatment plants (also known as publicly owned treatment works (POTWs)); and (3) agricultural discharges. There are no published data on pyrethroids in POTW effluent, though the compounds have been reported in agricultural (*6*) and residential (*7*) runoff.

Our second goal was to evaluate the potential for discharges to cause toxicity in receiving waters, focusing on urban runoff since it commonly contains pyrethroids at 10 times acutely toxic concentrations (*7*). These concentrations alone do not indicate impacts on receiving waters since there will be considerable dilution at the discharge point, but conversely, most communities have dozens of stormwater outfalls discharging along a watercourse, making cumulative effects possible. Bed sediments have been the focus of prior studies, and few data are available on concentrations in the water column. Given the hydrophobicity of pyrethroids (log K_{oc} values 5−6), water concentrations are likely to be low, but thresholds of toxicity are also extremely low. Concentrations of 2−5 ng/L are toxic to the amphipod, *Hyalella azteca* (*8*), the midge larva, *Chaoborus obscuripes* (*9*), and the shrimp, *Palaemonetes pugio* (*10*). Therefore, we measured pyrethroid concentrations in several watercourses as they passed through urban centers and tested toxicity of these waters using *H. azteca*.

Experimental Section

Urban Runoff. In much of the Delta runoff does not flow by gravity to surface waters since the rivers are flanked by levees. It flows through storm sewers to concrete sumps from which pumps lift it over levees to adjacent rivers. Samples were collected using a stainless steel bailer from two sumps in Sacramento, California (SA-28 and SA-104) and three in Stockton, California (ST-LP, ST-WR, ST-ML) (Supporting Information (SI) Figure S1). All serve primarily residential neighborhoods. Effluent from a single 1.4 m concrete drain serving a residential neighborhood and discharging to Ulatis Creek was sampled in Vacaville, California (site VA-1).

All sites were sampled three times in early 2008 or early 2009 during the winter rainy season (November to April), during or shortly after rain events. Three dry season sampling events (May to October) occurred in 2008. All sumps contained water from summer urban uses (e.g., landscape watering), but the Vacaville drain was not sampled in the dry season because of lack of flow.

POTWs. Three POTWs were sampled on three dry season occasions in 2008, and after three wet season rain events in 2008 and 2009. Site SA-POTW serves the Sacramento region and is permitted for secondary treatment of up to 685 million L/d. The city of Stockton's facility (ST-POTW) is permitted for 208 million L/d, and discharges tertiary-treated effluent. The city of Vacaville's plant (VA-POTW) is permitted for 57 million L/d of secondary treated effluent. Except for a small portion of the Sacramento facility's service area, storm sewer

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10.1021/es9035573
Published on Web 02/02/2010

and sanitary sewer systems are separate in all three communities. However, flows rise after rains at all plants due to inflow of runoff or infiltration of groundwater into the sanitary system. Sampling was delayed 12−20 h after peak rainfall to allow time for runoff to pass through the plants and reach the sampling points at the most downstream locations possible, just prior to discharge to surface waters.

The Stockton facility is unique among the plants sampled in that secondary-treated wastewater is routed through 240 ha of tertiary treatment ponds that provide approximately 30 days residence time prior to discharge. On two occasions after rain events in 2009, wastewater was collected as it entered these ponds, as well as from the final effluent.

Agricultural Discharges. The Delta mostly consists of islands used for agriculture. Field runoff is routed to a canal on each island that leads to a pump station where runoff is lifted over the levee. Water samples were collected at eight pump stations: AID, ETD, LRD, MID, NHTD, RID, VID, and WSD. Samples were collected near the pump intakes using a bailer. The drains were sampled on five occasions during the growing season from May to October 2008 and on three occasions after rains in early 2009.

Receiving Water Bodies. Vacaville, a community of 89,000 people, lies within the watersheds of Ulatis Creek and Alamo Creek (see SI for figures of sampling locations in receiving waters). Both creeks flow through agricultural lands and then enter urban areas. Within Vacaville, the creeks are typically 1−3 m wide and 0.2−0.5 m deep. Samples were taken on Ulatis Creek at the upstream urban boundary and as the creek leaves the city. Alamo Creek enters Vacaville as two forks that merge within city limits. Samples were taken on both the north and south forks as they entered the city and as the combined flow exited the city. All sites were sampled after two rain events in February 2009.

The San Joaquin River has a large, mostly agricultural watershed. Flow is typically 20−60 m^3/s as it enters the Delta. Five sampling sites were established beginning upstream of Stockton (population 244 000), and continuing downstream through the city. Samples were collected after rain in January and February 2009.

The lower American River extends from Folsom Lake to its confluence with the Sacramento River. Upstream of Folsom Lake, the watershed is largely rural or wooded. Downstream of Folsom Lake, the watershed is heavily urbanized as it passes through a continuous succession of cities for over 50 km. River flow is dam-controlled and typically ranges from 22−140 m^3/sec. The lower American River is considered to be a high quality water source. It provides municipal drinking water and supplies a salmon hatchery. Samples were collected after four storms in February to May 2009, and once in March 2009 after two weeks with no rain.

The Sacramento River watershed includes a large portion of northern California. As it passes through the city of Sacramento, it receives urban runoff as well as the discharge of the American River. River flow entering the Delta typically ranges from 200−1100 m^3/sec and was about 850 m^3/sec on most sampling days. Samples were collected along a transect through Sacramento on four occasions following rain events in February to May 2009.

In the reaches sampled, the Sacramento and San Joaquin Rivers are tidally influenced freshwater with a mean tidal range of 0.7−1.0 m. All sampling was conducted within two hours before or after high tide, with the exception of one Stockton event. Water samples were collected just below the surface and held at 4 °C, with toxicity testing usually occurring within 30 h (rarely, 48 h). Chemistry samples were held at 4 °C until extraction within 72 h.

Toxicity Testing. The amphipod, *H. azteca*, was used for toxicity testing since it is far more sensitive to pyrethroids than *C. dubia* which is more typically used. For example, the 96 h *H. azteca* LC_{50}s for the pyrethroids bifenthrin and cypermethrin are 8 and 2 ng/L, respectively (*8*); the equivalent LC_{50}s for *C. dubia* are 50 and 194 ng/L (*11*). *H. azteca* is also resident within the study area. Though it is primarily used for sediment testing, it is an epibenthic organism exposed to the overlying water, and it has occasionally been used in water-only tests (*6, 8, 12, 13*). Testing generally followed U.S. Environmental Protection Agency protocols for acute 96 h tests (*14*). Samples were tested using five replicate 80 mL glass beakers containing 10 *H. azteca*, 7−14 days of age. A 1 cm^2 nylon screen provided a substratum to which amphipods could cling. A 16 h:8 h light:dark photocycle was used. After 48 h exposure, 1 mL of yeast-cerophyll-trout food was added to each beaker, and a 6 h feeding period was provided. Then ∼80% of the water was removed from the beaker and replaced with fresh sample. After an additional 48 h (96 h total), the test was terminated and survivors counted. Pyrethroids are neurotoxins, and it was common for individuals to be alive but immobile. Affected individuals could occasionally rise into the water but swimming movements were uncoordinated and brief. Therefore tests were also scored for number of individuals able to swim normally; the remaining individuals being dead or unable to swim.

Environmentally realistic testing temperatures were used since pyrethroid toxicity increases as temperature decreases (*15*). Temperature was measured in Delta waters during sampling, and the test was performed at that temperature. Test temperatures were held within 13−23 °C even when Delta temperatures exceeded this range, because it was known to provide reliable results within the tolerance range of the species. Test organisms were acclimated to cold temperature over a 3 day period. Subsequent toxicity evaluation identification (TIE) testing was done at 23 °C.

To help establish if pyrethroids or organophosphate insecticides were responsible for toxicity, select toxic samples were evaluated through a focused TIE (*12*). The TIEs used three procedures developed to identify pyrethroid or organophosphate toxicity. First, piperonyl butoxide (PBO) was added to the water at 50 μg/L, a treatment that increases toxicity of pyrethroids, and decreases toxicity of most organophosphates. Second, TIEs were performed at 23 °C with a concurrent test at 17 °C that would cause greater toxicity if due to a pyrethroid. Third, enzymes engineered to hydrolyze specific pesticides reduce toxicity if added to water containing the target substrate (*8*). An E3 enzyme mixture, designed to hydrolyze pyrethroids, contained 50% E3−013 enzyme and 17% each of E3−018, −022, and 025 for a total concentration of 5 mg/L of the crude enzyme preparation, of which the active enzyme variants were a small fraction of the mass. Enzymes were obtained through a research collaboration with the manufacturer (Orica, Melbourne, Australia). Another enzyme, OpdA, was used to mitigate toxicity caused by several organophosphates, including diazinon and chlorpyrifos. A 5 mg/L bovine serum albumin (BSA) treatment was used as a control for reduction in toxicity due to pesticide complexation with dissolved organic matter (DOM) rather than the catalytic activity of the enzymes.

Focused TIEs were usually done as dilution series to quantify the median effective concentration (EC_{50}) for death or impaired swimming in each TIE treatment. The concentration steps varied by a factor of 2 (e.g., 6, 12, 25, 50 and 100% sample). Three replicate beakers were used per concentration, with five replicates for the control and at 100%. This approach allowed statistical comparison between treatments at the 100% concentration or with the corresponding control in instances when an EC_{50} could not be determined.

Statistics were done using CETIS (Tidepool Scientific Software, McKinleyville, CA). A *t* test was used when comparing field samples to their corresponding controls. TIEs were evaluated on the basis of changes in the EC_{50},

TABLE 1. Results of Pesticide Analyses of Water Samples[a]

source type[b]	Bif[c] EC_{50} = 3.3[d]	Cyf EC_{50} = 1.9	Cyp EC_{50} = 1.7	Del (no data)	Esf (no data)	Fen (no data)	Lam EC_{50} = 2.3	Per LC_{50} = 21.1	Chlor EC_{50} = 96
				Frequency of Detection (%)					
urban runoff	79	55	33	12	6	3	45	61	77
POTWs	39	6	6	11	6	0	17	33	40
agric. drains	12	0	0	0	7	5	11	2	72
				Frequency of *H. azteca* EC_{50} or LC_{50} Exceedance (%)					
urban runoff	58	55	30	NA	NA	NA	24	12	0
POTWs	22	0	6	NA	NA	NA	17	0	0
agric. drains	2	0	0	NA	NA	NA	9	0	4
				Maximum Concentration Measured (ng/L)					
urban runoff	29.8	17.8	12.3	3.5	4.3	6.1	6.2	45.8	14.4
POTWs	6.3	1.7	17.0	2.7	3.7	0	5.5	17.2	24.1
agric. drains	5.8	0	0	0	10.1	3.9	17.5	10.3	226

[a] The percentage of samples with detectable concentrations (>1 ng/L) is shown, as well as the proportion exceeding the *H. azteca* 96 h EC_{50} or LC_{50}, and the maximum concentration found. NA indicates not applicable due to the lack of EC_{50} or LC_{50} data. Additional detail in SI Tables S3−S5. [b] Data are derived from 33 urban runoff samples, 18 POTW samples, and 57 agricultural drain samples. [c] Bif = bifenthrin, Cyf = cyfluthrin, Cyp = cypermethrin, Del = deltamethrin, Esf = esfenvalerate, Fen = fenpropathrin, Lam = lambda-cyhalothrin, Per = permethrin, Chlor = chlorpyrifos. [d] *Hyalella azteca* 96 h EC_{50} or LC_{50} values in ng/L are shown for comparison. All from Weston and Jackson (*8*) except lambda-cyhalothrin (*24*); permethrin (*25*); chlorpyrifos (*12*).

derived by the probit method, with significance between two EC_{50}s inferred by nonoverlapping 95% confidence intervals. However, occasionally a comparison at the 100% concentration was made between the control and various TIE manipulations using either *t* test (if only one TIE treatment) or Dunnett's test (two or more treatments).

In order to express pyrethroid concentrations in a format that incorporates their relative toxicity, toxic units (TU) were calculated by dividing the concentration of each compound by its EC_{50} (*8*). The individual TUs in a sample were summed to derive a total TU since pyrethroid mixture toxicity can be considered additive (*16*). In analyzing the data, we attempted to achieve a better prediction of toxicity by consideration of pyrethroid partitioning to suspended sediment and DOM in each sample by the methods of Spurlock et al. (*17*). Predictions were no better than simply using total concentrations, probably because even at 100 mg/L of suspended sediment, approximately two-thirds of pyrethroids remain in the dissolved phase (*17*). In tests with *C. dubia*, 100 mg/L of suspended sediment or 20 mg/L of dissolved organic carbon (DOC) were needed to consistently reduce toxicity (*11, 18*), and only 18% of the samples containing pyrethroids in the present study exceeded either of these benchmarks. Therefore, pyrethroid concentration data were used without adjustment for bioavailability effects of suspended sediment or DOC.

Chemical Analyses. Water samples collected in 1 L glass bottles were preserved with 10 mL of hexane as a keeper solvent. Analytical methods followed Wang et al. (*19*). Briefly, the surrogates, 4,4′-dibromooctafluorobiphenyl and decachlorobiphenyl (Supelco, Bellefonte, PA), were added to the samples. Liquid:liquid extraction (EPA Method 3510C) used three additions of 60 mL of dichloromethane. The combined extracts were concentrated to 1 mL in hexane and added to a dual layer graphitized black carbon and primary/secondary amine column preconditioned with hexane (Supelclean ENVI-Carb II/Supelclean primary/secondary amine column, 3.0 mg /600 mg, 6.0 mL; ResPrep, Bellefonte, PA). The column was eluted with 7.0 mL of 30% dichloromethane in hexane, and the eluate concentrated to 0.5 mL in 0.1% acetic acid in hexane.

Extracts were analyzed on an Agilent 6890 gas chromatograph with a microelectron capture detector (Agilent Technologies, Palo Alto, CA). Two columns, an HP-5 ms and a DB-608, were used. Calibration was performed using the external standard method. Quality control measures included blanks, lab control spikes, matrix spikes, matrix spike duplicates, and field duplicates, all done with every batch of 20 samples.

A primary use of pyrethroid chemistry data was to interpret *H. azteca* toxicity test results. Since the 96 h EC_{50} for this species for several pyrethroids is only 2 ng/L (*8*), and the onset of toxicity would occur at slightly less than that, the high toxicity presents considerable analytical challenges. When analyzing relatively clean matrices, detection limits for most analytes are 0.3−0.7 ng/L, with relative standard deviations (RSDs) of replicate analyses about 10−20% when spiked at 1 ng/L (*19*). However, in analytically difficult matrices, detection limits are typically 0.6−1.6 ng/L, and RSDs increase to 20−30%. Given the need to quantify concentrations near 1 ng/L to interpret the toxicity results, but the challenges of quantification in difficult matrices when <3 ng/L, we report all results above 1 ng/L that we believe to be reliable, but the uncertainty associated with values between 1 and 3 ng/L depends upon sample-specific interferences.

Suspended solids were gravimetrically determined using 934-AH glass fiber filters and drying at 105 °C. Nonpurgeable organic carbon was obtained using 0.7 μm GF/F syringe filters and analyzing the filtrate on a Shimadzu TOC-5000A (Shimadzu, Kyoto, Japan) with ASI-5000A autosampler.

Results and Discussion

Control Performance. Median control survival across all tests was 96% (range 80−100%), and it was rare to find impairment of swimming. In focused TIEs, the median proportion of organisms swimming normally was 96% in the unamended control (84−100%) and 94−98% in all TIE treatments (82−100%), except 89% in BSA treatments (84−100%).

Sources: Urban Runoff. Pyrethroids were found in all but one of 33 urban runoff samples, with bifenthrin most frequently detected (Table 1). It was present in 79% of samples, and exceeded the *H. azteca* EC_{50} in 58% of them. Cyfluthrin, cypermethrin, lambda-cyhalothrin, and permethrin were also detected at toxicologically significant concentrations. Chlorpyrifos was frequently found, though below concentrations causing acute toxicity to *H. azteca*. No longer sold for urban uses, its presence probably reflects homeowner use of remaining stocks. There was consistency in pyrethroid composition of runoff from Sacramento, Stockton, and Vacaville (SI Table S3), suggesting the pesticide

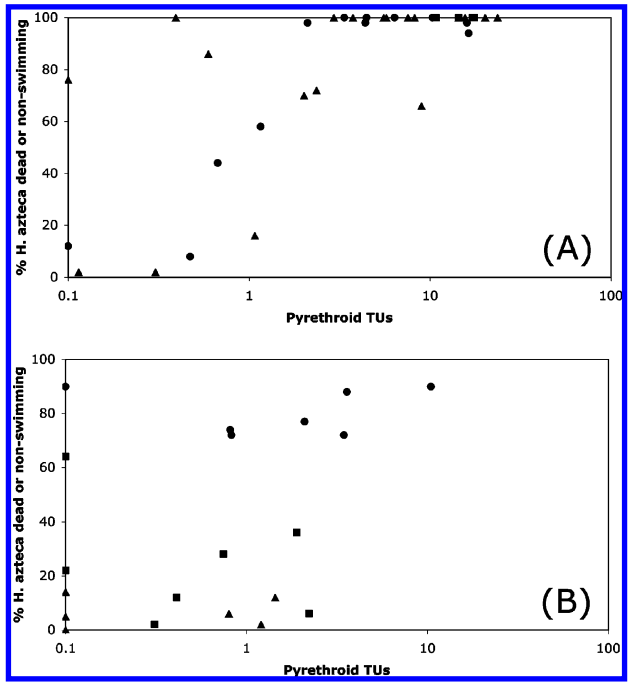

FIGURE 1. Relationship between pyrethroid toxic units (TU) and the proportion of *H. azteca* in the toxicity tests that was dead or unable to swim. Samples with no detectable pyrethroids are plotted at 0.1 TU. ●, Sacramento; ▲, Stockton; ■ Vacaville. Panel A: all urban runoff data; Panel B: all POTW effluent data.

use practices leading to water quality impacts are not unique to specific sampling areas.

Of the 33 runoff samples, 88% caused death or inability to swim in *H. azteca*. Toxicity was strongly related to pyrethroid concentration when expressed as TU (Figure 1). Most samples containing >2 TU caused death or inability to swim in all test organisms. While nonpyrethroid toxicants may be in runoff, in all but three samples (upper left corner, Figure 1a) exhibiting toxicity, there were sufficient pyrethroid concentrations to account for it. Pyrethroid concentrations were higher in the wet season (median 10.5 TU) than in the dry season (median 1.1 TU).

Addition of PBO increased toxicity in all samples by factors of 2−8 (Table 2). Of five samples tested at reduced temperature, four showed doubling of toxicity. Of four samples tested with pyrethroid-degrading E3 enzymes, toxicity was mitigated in every instance. TIE response profiles of all samples were consistent with pyrethroids as the major, if not sole, contributor to toxicity.

The routine presence of pyrethroids in urban runoff at acutely toxic concentrations is consistent with prior work in the Sacramento area (*7*). Pyrethroid input to the Delta via urban runoff was minimal during the dry season, since pump stations discharge little or no water most days. During winter rains, however, over 100 million L/d is discharged from larger pump stations. Pyrethroid loading cannot be determined with precision using the available data, but flows of this magnitude, and typical total pyrethroid concentrations in the sumps, would equate to loadings in the range of 3−9 g/d/pump station during heavy rains.

Sources: POTW Effluent. Twelve of the 18 POTW effluent samples contained quantifiable pyrethroids (50% of samples at Stockton; 67% at Vacaville; 83% at Sacramento). Bifenthrin was the most commonly detected pyrethroid (Table 1), with 22% of samples exceeding the *H. azteca* EC_{50}. Lambda-cyhalothrin was in 17% of the samples and when present always exceeded the EC_{50}. Permethrin was often detected, though below acutely toxic concentrations.

The Stockton facility had the lowest effluent concentrations, but was unique in that secondary-treated wastewater was routed through ponds providing 30 days residence time before discharge. Wastewater collected as it entered the ponds had pyrethroid concentrations far higher than other POTW samples, and comparable to the highest levels in urban runoff. Concentrations in the two samples were: bifenthrin = 12.0−23.9 ng/L, lambda-cyhalothrin = 2.9−9.3 ng/L, permethrin = 94.4−127 ng/L, and cypermethrin = 26.7−42.2 ng/L. These results indicate that during wet weather flow, pyrethroids can pass through secondary treatment systems at concentrations comparable to untreated stormwater runoff. It is also surprising that pyrethroids remained in 50% of Stockton effluent samples, although at low concentrations (<8 ng/L), even after a month in the ponds.

Pyrethroid presence in POTW effluent was surprising considering that these compounds have very high log K_{oc}s of 5−6 (*20*), there is opportunity for partitioning into organic-rich biosolids within the plants, and there is little suspended material in the effluents (<8 mg/L in our samples). Possible sources include sewer disposal of household insecticides, lice control shampoos, pet products containing pyrethroids, and laundering of permethrin-treated clothing used for mosquito protection. Also, all of these plants experience increased flow after rains due to entry of stormwater into sanitary sewer lines. The fact that the wet season concentration of pyrethroids in POTW effluent was comparable to that in the dry season (medians of all samples equal to 4.8 and 2.7 ng/L total pyrethroids, respectively) despite 25−50% higher wet season flows suggests that runoff inflow is at least a partial source.

Given the high effluent volume discharged from some POTWs, and the fact that discharge occurs even in dry weather, POTWs can be a significant source of pyrethroids. The Sacramento facility, for example has an average dry weather flow of 480 million L/d, and a peak wet weather flow of 902 million L/d. A rough approximation of its loading, based on the median total pyrethroid concentration in the three dry weather and three wet weather sampling events (18.2 and 14.2 ng/L, respectively), would be 9 g/d in the dry season and 13 g/d in the wet season. While further study is necessary to refine these estimates, they do indicate large POTWs can be significant pyrethroid sources on a mass basis. The Stockton and Vacaville facilities, with substantially lower flow rates, produced loadings an order of magnitude smaller.

Mortality was observed in 22% of POTW final effluent samples, and mortality or inability to swim was seen in 44% of samples. In every sample of Sacramento POTW effluent, at least 70% of organisms were dead or unable to swim. Similar conditions were observed occasionally at Vacaville (33% of samples), though never at Stockton. When proportions of dead or nonswimming individuals are compared with pyrethroid TU across all plants, there is a significant correlation ($r = 0.48$, $p < 0.05$; Figure 1), driven by the fact that Sacramento usually had relatively high levels of toxicity and pyrethroids. There were two samples that showed toxicity, but contained no measurable pyrethroids (upper left corner, Figure 1b).

TIEs for five POTW samples suggested pyrethroids played a role in toxicity (Table 2). Four samples treated with PBO showed an increase in toxicity of 5- to 10-fold. One sample tested at low temperature also had increased toxicity. Of four samples treated with E3 enzymes, three showed mitigation of toxicity.

Interpretation of TIE results is confounded by the fact that while samples responded as if pyrethroids were a contributor to toxicity, two of these samples had no detectable pyrethroids. Determining cause for toxicity in POTW samples is made difficult by their relatively low toxicity and pyrethroid concentrations in comparison to urban runoff. For example,

TABLE 2. Effect of the TIE Manipulations on Sample Toxicity (Increase, Decrease, Or No Effect)[a]

site and date	analytical results	effect of PBO	effect of low temperature	effect of BSA	effect of E3 enzymes	effect of OpdA enzymes
expected pyrethroid response		increase	increase	no effect	decrease	no effect
expected chlorpyrifos response		decrease	no effect	no effect	no effect	decrease
		Urban Runoff				
SA-28, May 27, 008	lambda-cyhalothrin = 2.7 TU bifenthrin = 0.7 TU	increase	increase	no effect	decrease	
SA-104, Feb. 20, 2008	cyfluthrin = 9.3 TU bifenthrin = 1.0 TU	increase	increase		decrease	
ST-LP, Feb. 3, 2008	cyfluthrin = 5.1 TU	increase	increase			
ST-WR, Sept. 22, 2008	cyfluthrin = 1.8 TU lambda-cyhalothrin = 0.9 TU	increase		no effect	decrease	
ST-ML, Feb. 3, 2008	bifenthrin = 2.9 TU lambda-cyhalothrin = 0.5 TU deltamethrin = 0.5 TU	increase	increase			
VA-1, Feb. 24, 2008	cyfluthrin = 4.8 TU bifenthrin = 2.2 TU cypermethrin = 2.1 TU lambda-cyhalothrin = 1.4 TU	increase	no effect		decrease	
		Municipal Wastewater Treatment Plants				
SA-POTW, May 27, 2008	bifenthrin = 0.8 TU	increase	increase	no effect	no effect	
SA-POTW, Sept. 22, 2008	permethrin = 0.8 TU	increase		no effect	decrease	
SA-POTW, Nov. 2, 2008	none			no effect	decrease	
SA-POTW, Feb. 18, 2009	cypermethrin = 10.0 TU	increase				
VA-POTW, Nov. 2, 2008	none	increase		no effect	decrease	
		Agricultural Drains				
WSD, Apr. 8, 2009	chlorpyrifos = 1.5 TU	decrease		no effect	no effect	decrease
RID, Apr. 8, 2009	lambda-cyhalothrin = 1.2 TU chlorpyrifos = 0.8 TU	increase		no effect	decrease	decrease
NHTD, Aug. 4, 2008	chlorpyrifos = 2.4 TU lambda-cyhalothrin = 1.0 TU	increase	no effect	no effect	increase	decrease
VID, Aug. 4, 2008	lambda-cyhalothrin = 7.6 TU	increase	increase			
VID, Jan. 23, 2009	lambda-cyhalothrin = 1.4 TU	increase		no effect	decrease	

[a] Analytical results are shown for all pesticides with >0.5 toxic units (TU). Blank cells indicate no test done with that TIE treatment. Additional detail in SI Tables S6−S8.

14 runoff samples had >95% of individuals dead or unable to swim, but no POTW samples were as affected. The *H. azteca* 96 h EC_{50} for cyfluthrin, cypermethrin, and lambda-cyhalothrin are all about 2 ng/L, and the onset of toxicity would occur at somewhat less than this value. Yet quantification in a complex matrix such as POTW effluent is difficult below 3 ng/L and impossible by our methods below 1 ng/L. It is likely that pyrethroids could cause a low level of *H. azteca* toxicity, and be implicated by TIE procedures, yet still be analytically undetectable.

Sources: Agricultural Drains. Pyrethroids were detectable in 26% of the 57 agricultural drain samples, yet any given pyrethroid was detected infrequently (Table 1). Only two pyrethroids were found at concentrations above EC_{50}s: bifenthrin in one sample and lambda-cyhalothrin in five samples. Two of these samples, and one other, also contained chlorpyrifos at concentrations approaching or exceeding the *H. azteca* EC_{50}. Thus, seven samples would have been expected to be toxic based on pesticide concentrations, and when tested six of these caused near total mortality or inability to swim. They were the only samples exhibiting toxicity out of 57 agricultural samples, demonstrating the predictive value of the EC_{50}s.

Five of six samples exhibiting toxicity were tested with focused TIEs (Table 2). The WSD sample contained high concentrations of chlorpyrifos (1.5 TU) and was the only sample in which PBO reduced toxicity. Chlorpyrifos toxicity is activated by metabolic transformation to the oxon form, a conversion inhibited by PBO. Thus, it responds to PBO in the opposite direction as pyrethroids (*21*). E3 enzymes had no effect on WSD toxicity, further differentiating it from pyrethroid-containing samples, and OpdA enzymes reduced toxicity.

When both chlorpyrifos and pyrethroids were present (RID and NHTD), PBO increased toxicity as expected for pyrethroids alone. PBO is more effective in increasing toxicity due to pyrethroids than it is in mitigating organophosphate toxicity (*22*). E3 enzymes decreased toxicity in RID, but not in NHTD, possibly because, based on TU, lambda-cyhalothrin was a small contributor to NHTD toxicity compared to chlorpyrifos. Toxicity was increased by addition of E3 enzymes to the NHTD sample for reasons unknown. Because of the unexpected E3 response, and lack of a temperature effect, both inconsistent with pyrethroids, this sample was further tested with the organophosphate-hydrolyzing enzyme, OpdA. It virtually eliminated toxicity, suggesting that an organophosphate was the principal toxicant. The OpdA enzyme was also effective in reducing toxicity in RID where chlorpyrifos comprised about half the TU.

Lambda-cyhalothrin was the only pesticide at potentially toxic concentrations in the two VID samples. They responded to PBO and temperature with the increased toxicity characteristic of pyrethroids. The E3 enzyme treatment exhibited less toxicity than did unamended water, but statistical differences could not be shown because of high variability among the unamended water replicates.

The lower pyrethroid concentrations and less frequent toxicity among agricultural sites, in comparison to urban

TABLE 3. Toxicity and Pyrethroid Concentrations along the Sampling Transects, Shown Following Each of Two Rain Events[a]

sample site	*H. azteca* toxicity (% individuals swimming ± standard deviation)		pyrethroid concentration (ng/L and TU in parentheses)	
	first event	second event	first event	second event
	Ulatis Creek, Vacaville (February 13, 2009 and February 16, 2009)			
U1 (upstream)	84 ± 9*	90 ± 10	ND	ND
U2 (downstream)	26 ± 11*	6 ± 5*	Bif = 10.4 (3.2) Lam = 2.2 (1.0) Per = 2.5 (0.1)	Bif = 11.9 (3.6)
	Alamo Creek, Vacaville (February 13, 2009 and February 16, 2009)			
L1 (upstream)	96 ± 5	98 ± 4	ND	ND
L2 (upstream)	98 ± 4	100 ± 0	ND	ND
L3 (downstream)	0 ± 0*	0 ± 0*	Bif = 17.9 (5.4) Cyf = 6.6 (3.5) Per = 6.0 (0.3)	Bif = 12.4 (3.8) Cyf = 9.6 (5.1) Per = 10.9 (0.5) Lam = 1.0 (0.4)
	San Joaquin River (January 22, 2009 and February 18, 2009)			
J1 (upstream)	60 ± 27	78 ± 44	ND	Per = 4.6 (0.2)
J2	84 ± 11	no sample	ND	no sample
J3	92 ± 8	98 ± 4	ND	ND
J4	86 ± 5	46 ± 21*	ND	Bif = 2.3 (0.7) Per = 6.8 (0.3)
J5 (downstream)	76 ± 21	no sample	ND	no sample
	American River (February 23, 2009 and March 3, 2009)			
A1 (upstream)	no sample	92 ± 8	no sample	ND
A2	no sample	56 ± 15*	no sample	Bif = 2.3 (0.7)
A3	28 ± 26*	94 ± 5	Bif = 1.2 (0.4)	ND
A4	4 ± 9*	24 ± 23*	Bif = 3.1 (0.9)	ND
A5 (downstream)	20 ± 20*	16 ± 11*	ND	ND
	Sacramento River (February 18, 2009 and February 23, 2009)			
S1 (upstream)	64 ± 39*	78 ± 13*	ND	ND
S2	no sample	90 ± 17	no sample	ND
S3	78 ± 15*	62 ± 19*	Bif = 1.6 (0.5)	ND
S4	88 ± 11	78 ± 16*	Bif = 2.7 (0.8)	ND
S5 (downstream)	64 ± 9*	82 ± 11*	ND	ND

[a] ND indicates no detectable concentration (<1 ng/L). Asterisks indicate a statistically significant toxicity difference relative to the control.

runoff or POTW effluent, may result from the fact that water travels in earthen ditches, some containing vegetation, for many kilometers before being released to Delta waters, allowing opportunity for adsorption of dissolved residues and deposition of particulates. In urban environments, water may travel considerable distances, but often through concrete pipes. Agricultural discharges, however, contained acutely toxic concentrations of the more hydrophilic chlorpyrifos, a pesticide that never contributed to urban toxicity in our study.

Receiving Waters: Vacaville Creeks. Before entering Vacaville, Ulatis, and Alamo Creeks flow through agricultural lands, but among six samples upstream of the city, none contained measurable pyrethroids (Table 3) and they showed little evidence of toxicity. After the creeks passed through the city, every sample exhibited high toxicity. In Ulatis Creek, only 6−26% of *H. azteca* were able to swim. In Alamo Creek all test animals were dead or unable to swim. Pyrethroid concentrations were more than sufficient to explain this toxicity, with concentrations 4−10 times the EC_{50}s and bifenthrin and cyfluthrin providing most of the TU.

TIEs were consistent with pyrethroids as the cause of toxicity (Table 4). Addition of PBO increased toxicity in both creeks. Toxicity was reduced by a factor of 3 by adding E3 enzymes to the Alamo Creek sample, and the BSA control had no effect, suggesting pyrethroid hydrolysis mitigated toxicity. The enzyme treatment was not useful in Ulatis Creek since toxicity had been largely lost by the time of the TIE, making it difficult to see further reduction.

Receiving Waters: San Joaquin River. Following the first rain event, pyrethroids were not detected and there was no toxicity to *H. azteca* in the San Joaquin River near Stockton (Table 3). The second rain produced twice the precipitation of the first, and the transect was sampled again at three locations. At J4 on the downstream edge of the city over half the amphipods were unable to swim. Of eight samples from the San Joaquin, this toxic sample was the only one expected to be toxic based on pyrethroid concentrations. It contained 0.7 TU of bifenthrin and 0.3 TU of permethrin. Addition of PBO increased toxicity 5-fold (Table 4), further implicating pyrethroids.

Receiving Waters: American River. Investigation of the American River was triggered by a single sample from the river mouth (site A5) obtained following a February 18, 2009 rain event. At that time, 38% of individuals were dead and 82% dead or unable to swim. The water contained 5.6 ng/L bifenthrin (1.7 TU) and 5.0 ng/L permethrin (0.2 TU). Addition of PBO tripled toxicity (Table 4).

Because of this result, a transect was established from Folsom Lake to the Sacramento River confluence, and sampled after rain events of February 23 and March 3, 2009 (Table 3). In the lake upstream of the urban area (site A1), there was no toxicity and no measurable pyrethroids. In the urbanized reach of the river (A2−A5) with numerous urban runoff inputs, six of seven samples collected over two rain events exhibited toxicity. Only 4−56% of test organisms were capable of swimming. After the first rain, toxicity was apparent from the Sacramento River confluence (A5) to site A3, approximately 31 river km. After the second event, toxicity was intermittently detected nearly to Folsom Lake, approximately 53 river km. The only pyrethroid detected was bifenthrin, found in three samples at concentrations of 1.2−3.1 ng/L (0.4−0.9 TU). Addition of PBO to two samples (A4 and A5, Feb. 23) increased toxicity 4-fold (Table 4). Addition of E3 enzymes to A5 virtually eliminated toxicity.

TABLE 4. Results of TIE Testing with the Samples, Showing EC_{50}s (As Percent Original Sample) and 95% Confidence Intervals in Unamended Water and with Several TIE Treatments[a]

sample site date	unamended water	PBO	BSA	E3 enzymes
		Vacaville creeks		
U2 February 16, 2009	>100	***22.6 (11.6-31.8)***	>100	>100[b]
L2 February 16, 2009	10.9 (8.2−13.6)	***<6 (lowest conc. tested)***	9.2 (7.6−10.8)	***30.0 (24.1−35.6)***
		San Joaquin River		
J4 February 18, 2009	>100	***22.7[c](17.5−27.5)***	no data	no data
		American River		
A5 February 18, 2009	68.7 (57.3−78.5)	***21.7 (12.7−29.2)***	no data	no data
A4 February 23, 2009	59.6 (50.3−67.9)	***16.6 (13.0−20.3)***	no data	no data
A5 February 23, 2009	37.0 (22.0−52.7)	***10.6 (6.5−14.7)***	63.4 (50.2−75.2)	***>100[d]***

[a] Statistical significance inferred by non-overlapping confidence intervals. Those treatments showing a significant effect consistent with pyrethroids as the cause are in bold italics. [b] At the 100% concentration there were 74% swimming normally in unamended water treatment, 66% in the BSA treatment, and 84% in the enzyme treatment. Neither the BSA or enzyme effect was significant (Dunnett's test, $p > 0.05$). [c] In the unamended water treatment there were 70% swimming normally, and none swimming normally in the PBO treatment. [d] At the 100% concentration there were 6% swimming normally in unamended water treatment, 18% in the BSA treatment, and 82% in the enzyme treatment. Only the enzyme effect was significant (Dunnett's test, $p < 0.05$).

The A5 sample was the only TIE sample in which no bifenthrin was detected, though all treatments suggested pyrethroid-related toxicity. We believe the PBO and E3 enzyme results are indicative of pyrethroids slightly below the analytical quantification threshold (<1 ng/L).

Repeat sampling of the four sites in the urbanized reach on March 18, 2009, following two weeks without rain, showed minimal toxicity. Only A5 showed a significant effect, and the proportion of amphipods swimming (64 ± 11%) was relatively high compared to rain event samples. No pyrethroids were detected in any sample.

Finally, a rain event nearly two months later on May 3, 2009 was sampled. No toxicity or pyrethroids were detected. The difference in toxicity results between this rain event and previous events is attributable to river flow. During the previous rain events (February 18, February 23, March 3), river flow was approximately 23 m^3/sec. During the May event, flow was 127 m^3/sec due to releases from the dam at Folsom Lake. Since bifenthrin concentrations in the river during prior rain events had never exceeded 1.7 TU, the 6-fold increase in flow by May would be more than adequate to decrease pyrethroid concentrations below detection limits and eliminate measurable toxicity, even if bifenthrin inputs via runoff were comparable to those prior events.

Taking all American River samples together, there was a significant relationship between the concentration of bifenthrin and degree of mortality and immobility ($r = 0.54$, $p < 0.05$; SI Figure S6). All evidence indicates that repeated toxicity in the river was due to bifenthrin originating in urban runoff, the effects of which were compounded by low flows maintained by water control structures.

Using data from the Sacramento sumps discussed above, wet season runoff from Sacramento contains a median of 6.1 ng/L bifenthrin, in line with medians of 7−17 ng/L from other studies in Sacramento suburbs (*9*). It has been estimated that the greater Sacramento metropolitan area produces 2.66 billion liters of runoff in an average storm, 62% of which reaches the American River (*23*), though undoubtedly these estimates incorporate considerable uncertainty. Using 6.1 ng/L bifenthrin as the concentration in runoff, an average storm would provide 10 g bifenthrin to the American River. If this runoff occurs over a 24 h period, the observed 23 m^3/sec river flow would yield 2 billion liters discharged, and the resulting bifenthrin concentration in the river would be 5 ng/L (1.5 TU). Thus, measured bifenthrin concentrations of 1.2−5.6 ng/L and observed toxicity are consistent with theoretical estimates indicating that bifenthrin-related toxicity would be expected after an average rain event.

Receiving Waters: Sacramento River. The Sacramento River was sampled as it passed through Sacramento following two rain events. Taking the two events together, there were fewer individuals able to swim in seven of nine samples, relative to the concurrent controls (Table 3). However, toxicity was consistently minimal, and in affected samples, 64−78% of individuals showed no adverse effects. No TIEs were pursued given the weak toxicity signal, and the cause for these low-level effects is unknown. Pyrethroids were measurable in two of the nine samples (bifenthrin = 1.6−2.7 ng/L; 0.5−0.8 TU), though there was no relationship between bifenthrin concentration and degree of toxicity. Toxicity was not observed at concentrations that had caused immobility in the American and San Joaquin Rivers. This result may be due to high concentrations of suspended solids in the Sacramento River at the time (185 mg/L), far higher than the American or San Joaquin Rivers (2−20 mg/L). Adsorption of bifenthrin to suspended solids at concentrations comparable to the 185 mg/L found in the Sacramento River can reduce toxicity by a factor of 2−5 (*11*).

The Sacramento transect was again sampled March 3, 2009, after a rain event. Only one site (S1) showed slight toxicity, and no pyrethroids were detected. Three stations were sampled again on May 3, 2009 following rain, and none exhibited toxicity. Whatever the cause of low-level toxicity in February samples, it was limited to those earlier events, and nearly absent in March and May. One possibility is the insecticide diazinon, reported to occur in the river at concentrations toxic to *C. dubia* during the January/February period in the 1990s (*1*).

Lessons for Future Monitoring. This study has shown that surface waters may contain pyrethroids at concentrations sufficient to cause acute toxicity. Urban inputs of pyrethroids repeatedly caused toxicity in Ulatis and Alamo Creeks and in over 30 km of the American River. The San Joaquin River reached toxic thresholds in at least one area. Our study provided no evidence of pyrethroid-related toxicity in California's largest river, the Sacramento River, but given appearance of bifenthrin in the river on one occasion at concentrations that would have been expected to be toxic were it not for the suspended sediments, it would be premature to dismiss the possibility. Toxicity of bed sediments containing pyrethroids is well established (*2*−*5*), but it no longer appears reasonable to limit the potential for toxicity to bed sediments.

This study also indicates it cannot be assumed waterborne pyrethroids are nonbioavailable. Past studies have shown pyrethroid bioavailability to be consistently reduced above suspended solids concentrations of 100 mg/L and DOC concentrations above 20 mg/L (*11, 18*). In the present study, the majority of samples had <17 mg/L suspended sediment

and <7 mg/L DOC. While suspended sediment or DOC can reduce bioavailability, and may have done so on one occasion in the Sacramento River, concentrations were not sufficient in much of our study area to have an appreciable effect.

The appearance of pyrethroids above toxic thresholds, but rarity of previous reports, is probably a consequence of the methods often employed for monitoring and their insensitivity to pyrethroid presence and toxicity. First, pyrethroids are rarely among analytes measured in water samples. Moreover, since *H. azteca* has 96 h EC_{50}s or LC_{50}s ranging from 2−21 ng/L (*8, 24, 25*), detection at toxicologically significant concentrations creates analytical challenges. Second, we used *H. azteca*, but testing is more commonly conducted with *C. dubia* or fathead minnow, *Pimephales promelas*. Pyrethroid 96 h LC_{50}s for *C. dubia* are typically 50−510 ng/L (*11*) and *P. promelas* is considerably less sensitive (*26, 27*). *H. azteca*'s sensitivity to pyrethroids is comparable to the fifth percentile of the LC_{50} distribution for all aquatic species tested, but the sensitivity of *C. dubia* is comparable to the 20th percentile (*28*). The highest concentration of any pyrethroid in effluent samples of the present study was 46 ng/L, and 19 ng/L in receiving waters, so the more commonly used species would have rarely, if ever, shown toxicity. Given that pyrethroids are the dominant urban insecticide, it may be time to reassess the methods used for monitoring surface waters in urban environments. In addition, while agriculture can be a source of pyrethroids, urban sources of the present study were of greater concern in terms of pyrethroid concentrations and frequency of toxicity. The occurrence of pyrethroids, especially bifenthrin, above toxic thresholds in most urban runoff, and their previously unrecognized presence in municipal wastewater, indicate further investigation is needed into how their use or misuse has led to these results.

Acknowledgments

This work was supported by California's Surface Water Ambient Monitoring Program. Assistance was provided by staff of the stormwater utilities (Delia McGrath, Courtney Vasquez) and POTWs (Cameron Irvine, Tony Pirondini, Steve Gittings, Jeff Willett). Micheline Kipf assisted in identifying Stockton sampling sites and Joshua Carr prepared Figures S1−S5.

Supporting Information Available

Sampling locations (Tables S1−S2), pyrethroid concentrations in all discharges (Tables S3−S5), TIE results (Tables S6−S8), maps of study sites (Figures S1−S5) and the relationship between bifenthrin and toxicity in the American River (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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ES9035573