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Pyrethroid Insecticides and Sediment Toxicity in Urban Creeks from California and Tennessee

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Pyrethroid pesticides have replaced organophosphates for many urban applications, including structural pest control, landscape maintenance, and residential home and garden use. This study was intended to determine if pyrethroids are detectable and widespread in diverse urban systems and if concentrations are high enough to cause associated aquatic toxicity. Urban creeks in California and Tennessee were tested on up to four occasions for pesticide residues in sediments, and aquatic toxicity was determined by acute toxicity tests using the amphipod, *Hyalella azteca*. In California, 12 of the 15 creeks tested were toxic on at least one sampling occasion, and sediment pyrethroid concentrations were sufficient to explain the observed toxicity in most cases. The pyrethroid bifenthrin, due to its high concentrations and relative toxicity as compared to other pyrethroids, was likely responsible for the majority of the toxicity at most sites. Cypermethrin, cyfluthrin, deltamethrin, and λ-cyhalothrin also contributed to toxicity at some locations. The source of cypermethrin and deltamethrin was probably almost entirely structural pest control by professional applicators. Bifenthrin, cyfluthrin, and λ-cyhalothrin may have originated either from professional structural pest control or from lawn and garden care by homeowners. None of the sediments collected from the 12 Tennessee creeks were toxic, and pyrethroids were rarely detectable. Regional differences between Tennessee and California are possibly attributable to climate, differences in types of residential development, and pesticide use practices.

Introduction

For several decades, organophosphates were the primary insecticides used residentially by both professional pest control applicators and homeowners. However, as a result of agreements between the U.S. Environmental Protection Agency and the pesticide registrants, some of the most widely used organophosphates were recently withdrawn from residential use. Most products for residential use containing chlorpyrifos were withdrawn in 2001; those containing diazinon were withdrawn in 2004. Currently, there are only a few chlorpyrifos uses still approved in urban environments (e.g., golf courses, road medians, mosquito control by public health agencies, and ant or roach bait in child-resistant packaging).

Just as organophosphates replaced many of the organochlorine products banned in the 1970s and 1980s, pyrethroid pesticides have assumed many roles formerly held by organophosphates. They are extensively used by professional pest control applicators, with over 270 000 kg used for nonagricultural purposes in California in 2003, primarily for structural pest control and landscape maintenance. They also dominate retail insecticide sales to homeowners, although the amounts used, while certainly considerable, are not publicly reported.

Past monitoring of pesticides in urban-dominated creeks has focused on the water column because organophosphates are relatively water soluble. These studies have documented the presence of organophosphates in creek waters following rain events, frequently at concentrations toxic to aquatic life (*1*−*4*). For example, in studies throughout the 1990s, the vast majority of water samples collected from Sacramento, CA and San Francisco Bay Area urban creeks after rain events were toxic to *Ceriodaphnia dubia* in standard 7 day tests. Toxicity identification evaluations found that chlorpyrifos and diazinon accounted for most of the toxicity observed (*2*,*4*). However, there are much less data on sediment quality in urban creeks. The largest urban monitoring program, the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) program, does not monitor pyrethroids in sediments, except permethrin, one of the least toxic of the group (*5*). One study has examined urban creek sediments in a single watershed for a wide variety of pyrethroids and associated toxicity to aquatic life (*6*). This study reported that creeks in a residential subdivision contained the pyrethroids bifenthrin, cypermethrin, and cyfluthrin at concentrations acutely lethal to the standard freshwater sediment testing amphipod, *Hyalella azteca*, and the distribution of resident *H. azteca* in the system was limited to those stream reaches with the least residential development. While this study showed that excess irrigation and/or stormwater runoff were carrying residentially used pyrethroids to nearby creeks, it was limited to one city in California, and the general applicability of the results is unknown.

The present study was intended to determine if pyrethroids and associated aquatic toxicity, such as was seen in one suburban watershed, is also typical of other urban systems with more varied environmental conditions and land uses. A total of 15 California creeks and 12 Tennessee creeks were tested for pyrethroid pesticide residues in the sediments, and aquatic toxicity was determined by acute toxicity tests using *H. azteca*.

Materials and Methods

Sampling Locations (Table 1) and Timing. Sacramento, CA: this study area included seven creeks draining the city of Sacramento and incorporated most of the major creeks in the city. An eighth creek (Curry Creek) was in the residential suburb of Roseville just to the north of Sacramento. To determine seasonal patterns in sediment pyrethroid concentrations, the sampling focused on three critical periods: end of summer when inputs from residential landscape care were expected to be highest, after the first major winter rain event (first flush), and at the end of the rainy season, which in California is confined largely to the months of November to April. The Sacramento sites were sampled on up to four

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TABLE 1. Sampling Locations

water body	coordinates (deg N/W)	time of sampling[a]	stream channel type	land use in sampling area
		Sacramento		
Arcade Creek (site 1)	38.68927/121.29028	S1	natural	mixed commercial and residential
Arcade Creek (site 2)	38.64217/121.36695	S1, FF, W, S2	natural	mixed commercial and residential
Chicken Ranch Slough	38.60393/121.41278	S1, FF, W, S2	natural, but nearby portions of creek in concrete channel	mixed commercial and residential
Curry Creek	38.75813/121.35860	S1, FF, W	sample at transition from underground pipe to natural channel	residential
Elder Creek	38.48122/121.40348	S1, FF, W	channelized in concrete	mixed commercial and residential
Laguna Creek (site 1)	38.44453/121.44297	S1. FF, W, S2	natural	residential
Laguna Creek (site 2)	38.42453/121.37593	FF, W	natural	residential
Laguna Creek (site 3)	38.42453/121.37593	FF	natural	residential
Morrison Creek	38.49138/121.45710	S1, FF, W, S2	channelized in concrete	mixed commercial and residential
Strong Ranch Slough	38.60378/121.39205	S1, FF, W, S2	natural, but nearby portions of creek in concrete channel	mixed commercial and residential
Willow Creek	38.65352/121.18367		natural	commercial
		East Bay		
Glen Echo	37.97500/122.50833	Sp, FF	natural	residential
Kirker Creek	38.01655/121.83914	Sp, S1, FF	natural, but nearby portions of creek channelized open space in sampling area, but upstream watershed predominantly residential	
Lauterwasser Creek		Sp, S1, FF	natural	residential and golf course
Lion	37.76037/122.19512	Sp, FF	channelized in concrete	residential
Pine Creek	37.91624/122.00911	W	channelized (earthen)	residential
San Leandro	37.72547/122.18278	Sp, FF	channelized in concrete	residential
San Pablo Creek	37.88611/122.25500	Sp, FF	natural	commercial
		Nashville		
Cedar Creek	36.23131/86.44473	S1	natural	residential
Drake Creek	36.31261/86.60865	S1	natural with rip/rap	residential
Dry Creek	36.28455/86.70625	S1	natural	mixed commercial and residential
East Fork Station Camp Creek	36.38684/86.48183	S1	natural	mixed commercial and residential
Gills Creek	36.34583/86.44000	S1	natural	commercial
Harpeth River (site 1)	36.02869/86.92424	S1	natural	residential
Harpeth River (site 2)	36.07711/86.95721	S1	natural	commercial
Hays Branch	36.25513/86.55940	S1	natural	mixed commercial and residential
Little Harpeth River	36.01928/86.82078	S1	natural	residential and golf course
Madison Creek	36.31434/86.66566	S1	natural	residential
Mill Creek (site 1)	36.09185/86.68623	S1	natural	mixed commercial and residential
Mill Creek (site 2)	36.11757/86.71921	S1	natural	commercial
Station Camp Creek	36.34674/86.52545	S1	natural	mixed commercial and residential
West Fork Hamilton Creek	36.08896/86.62771	S1	natural	residential

[a] Sp = spring (April 2004); S1 = summer (August to early October 2004); FF = first flush (immediately after first major rainfall, late October 2004); W = winter (December 2004 to March 2005); and S2 = summer (August 2005).

occasions: August to October 2004, late October 2004 after the first major rain event, March 2005, and August 2005.

East Bay, CA: The East Bay is a term locally used to refer to the many communities on or near the eastern shoreline of San Francisco Bay, California. Seven creeks in Alameda and Contra Costa counties were sampled, with sites in the communities of Oakland, Orinda, Pittsburg, Richmond, San Leandro, and Walnut Creek. Four creeks were selected on the basis of past evidence of toxicity (typically water column toxicity related to organophosphates); the remaining three were chosen only because of the availability of soft substrate or ease of access. These sites were sampled up to 3 times: April 2004, mid-October 2004, and late October 2004 after the first major rain event. Pine Creek was sampled only in December 2004.

Nashville, TN: Twelve creeks were sampled within Nashville and in the surrounding communities once in July 2004. These sites represented primarily low-density residential areas with scattered light commercial development. Sites were selected on the basis of availability of soft, fine-grained sediments, excluding the more commonly available areas with rock substrates.

Samples were collected by skimming the upper 1 cm of the sediment with a stainless steel scoop. Since pyrethroids are found primarily in the organic carbon fraction of sediments, fine-grained sediments were preferentially col-

lected at each site when available. Samples for each site were typically collected over a 50 m stream reach and composited in the field, although in some cases, samples were from a single location due to limited availability of soft substrate. Each sample was homogenized by hand mixing in the laboratory and then held at either −20 °C (chemical analysis) or 4 °C (toxicity testing) until analysis.

Toxicity Testing. Sediments were tested for toxicity using the amphipod *H. azteca*, an epibenthic freshwater amphipod widely used for sediment toxicity testing. Samples were tested within 1−3 weeks of sample collection, employing standard U.S. EPA protocols (*7*). Briefly, 400 mL beakers were filled with 50−75 mL of sediment and 250 mL of moderately hard water. Approximately 500 mL of fresh water was added to each beaker over the course of each day, with the excess overflowing through a screened hole. Tests were conducted at 23 °C, without aeration (except one sample that required it: Lion Creek from April 2004) and with feeding of 1 mL of yeast-cerophyll-trout chow daily per beaker. Five replicates were tested with the Nashville samples; eight replicates were tested with the other samples. After 10 days of exposure, the *H. azteca* survival was determined.

Toxicity data were analyzed using ToxCalc Version 5.0 (Tidepool Scientific Software, McKinleyville, CA). Stations with significantly greater mortality than control were identified using Dunnett's Multiple Comparison test. Arcsin squareroot transformation was used when necessary to meet the assumptions of normality and homogeneity of variance. If these assumptions were not met even after transformation, comparison to control was done using Steel's test.

Toxicity Units. Sediment pyrethroid concentrations were used to calculate toxicity units (TUs) to adjust for differences in the relative toxicity of each pyrethroid. Because of the known hydrophobicity of pyrethroids, sediment concentrations were first normalized to total organic carbon (OC) content and then divided by the *H. azteca* 10 day median lethal concentration (LC50) for each compound. The LC50 values used in the TU analysis were bifenthrin = 0.52 μg/g OC, cyfluthrin = 1.08 μg/g OC, cypermethrin = 0.38 μg/g OC, deltamethrin = 0.79 μg/g OC, esfenvalerate = 1.54 μg/g OC, λ-cyhalothrin = 0.45 μg/g OC, and permethrin = 10.83 μg/g OC (*8*, *9*). TUs were calculated as TU = [pyrethroid concentration (μg/g OC)] / [*H. azteca* 10 day LC50 (μg/g OC)].

Therefore, a concentration yielding 1 TU should cause 50% mortality in a 10 day *H. azteca* toxicity test, regardless of which pyrethroid is present. Because pyrethroids share the same mode of action, the pyrethroid TUs were summed, assuming additivity, to determine the cumulative toxic effect of exposure to multiple pyrethroids.

Analytical Chemistry. Chemical analytes included seven pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, λ-cyhalothrin, and permethrin), and chlorpyrifos. Of the organophosphosphates, chlorpyrifos was chosen because it is one of the most hydrophobic of the group and would therefore be more likely to be sediment-associated. Analysis followed the methods described by You et al. (*10*). Briefly, analysis was performed on an Agilent 6890 series gas chromatograph with an Agilent 7683 autosampler, an electron capture detector, and two columns, an HP-5MS and a DB-608 (Agilent, Palo Alto, CA). The qualitative identity was established using a retention window of 1% with confirmation on a second column, and calibration was based on area using external standards. Sediment samples were sonicated with a solution of acetone and methylene chloride, and the extracts were cleaned by column chromatography with deactivated Florisil prior to analysis. Two surrogate standards (4,4′-dibromooctafluorobiphenyl and decachlorobiphenyl) were added to the sediment prior to extraction to verify analytical process performance. The recoveries of target pesticides ranged from 88.7 to 117.3% with relative

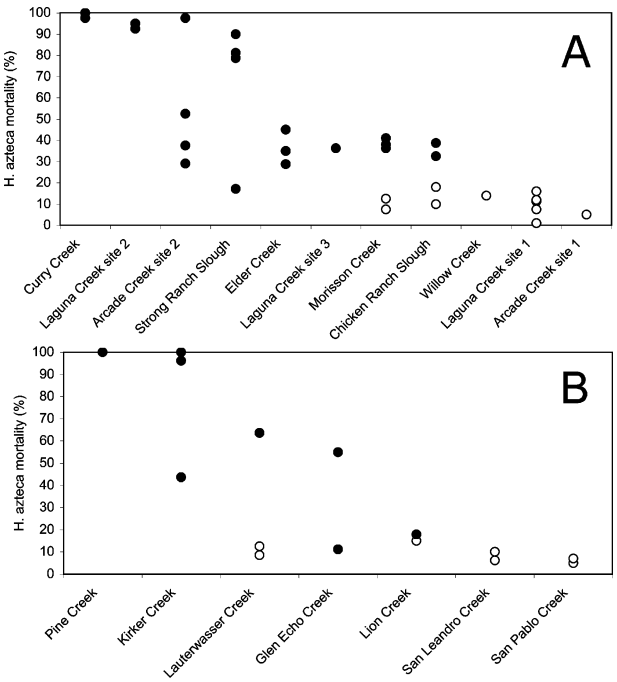

FIGURE 1. Toxicity of urban creek sediments collected to *H. azteca* in 10 day toxicity tests. Open circles indicate nontoxic samples, and darkened circles indicate toxic samples. (A) Sacramento area urban creeks and (B) East Bay urban creeks.

standard deviations of 1.5−9.3% at a spiked concentration level of 5 ng/g. The reporting detection limit for all compounds was 1 ng/g. Two samples were also analyzed by mass spectrometry that confirmed the identity of all pyrethroid analytes.

Total organic carbon was determined on a CE-440 Elemental Analyzer from Exeter Analytical (Chelmsford, MA), following acid vapor treatment to remove inorganic carbon (*11*).

Results and Discussion

Sediment Toxicity. Control survival of *H. azteca* was good in all tests. Control samples associated with the Sacramento samples had mortalities of 1.2−6.2%. Those associated with East Bay and Nashville samples had mortalities of 1.2−2.5 and 4.0−10.0%, respectively. Most of the Sacramento area sediment samples caused acute mortality to *H. azteca* (Figure 1). Twenty-two of 33 samples were toxic, and toxicity was observed in seven of the eight creeks sampled on at least one location. The most extreme toxicity was seen at Curry Creek and Laguna Creek site 2, both of which caused total or near total mortality. These two locations were the only ones in the study located directly in front of storm drain outfalls. The watersheds represented by these two locations consist entirely of subdivisions of single-family homes. In the case of Curry Creek, the entire creek is formed by runoff from a subdivision and emerges from an underground pipe at the sampling location. In the case of Laguna Creek site 2, the sample was taken where a storm drain discharges to the main creek. Laguna Creek sediments not directly in front of storm drain outfalls were less toxic (37% mortality at site 3) or nontoxic (site 1).

The remaining Sacramento area creeks flow through the older portions of the city and represent a mixture of residential and commercial land uses. Arcade Creek sediments were consistently toxic at the more downstream site (site 2), as was Strong Ranch Slough and Elder Creek. Chicken Ranch Slough and Morrison Creek were toxic on some occasions.

East Bay sediments showed only slightly less toxicity than those from Sacramento. Eight of the 15 sediment samples

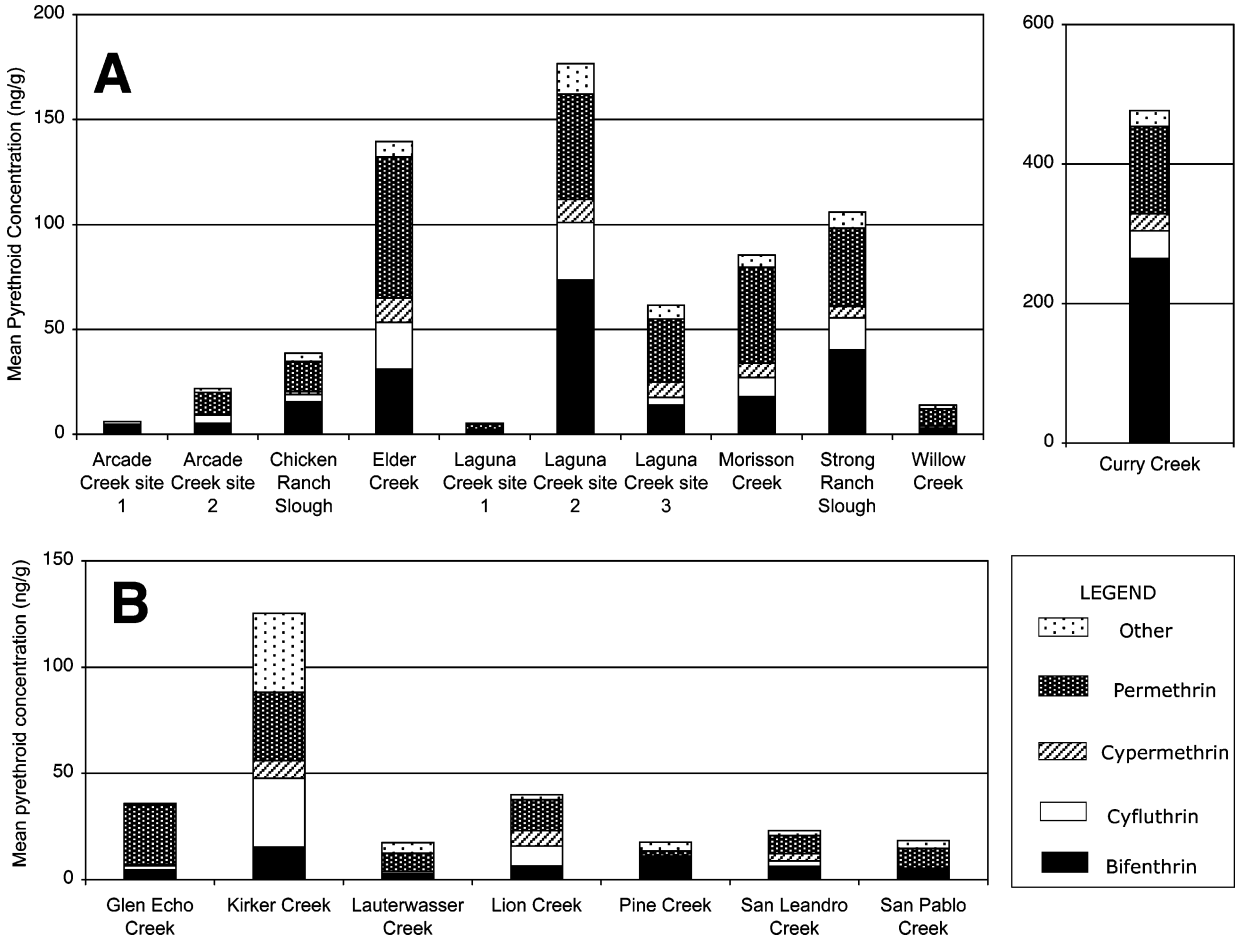

FIGURE 2. Mean sediment pyrethroid concentrations in urban creek sediments from (A) Sacramento and (B) the East Bay. Mean concentrations for each site are shown using values from all sampling time points. Other pyrethroids were usually detected at low concentrations and included esfenvalerate, deltamethrin, and λ-cyhalothrin.

were toxic, and five of the seven creeks had toxic sediments on at least one occasion. Pine Creek, which drains a residential area of Walnut Creek, CA, and Kirker Creek, which drains residential and commercial areas of Pittsburg, CA, had sediments that caused near complete mortality of *H. azteca*. Lauterwasser Creek, serving a residential area and a golf course, was toxic on one occasion, although at that time the sediments collected were finer-grained than on the other occasions, suggesting that differences among the samples may be due to site heterogeneity rather than seasonality. San Leandro Creek and San Pablo Creek sediment samples were consistently nontoxic, and Lion Creek yielded only one sample that was barely significantly toxic.

The absence of toxicity in the Nashville samples was in stark contrast to the California sites. Fourteen samples, representing 12 creeks, were sampled. None showed significant toxicity. Mortality ranged from 0 to 16%, but in no case was mortality significantly higher than the controls.

Sediment Chemistry. Complete chemistry results are provided as Supporting Information (Tables S1−S3). Briefly, all seven pyrethroid analytes were detectable in Sacramento area creeks, and every sample had detectable pyrethroid concentrations (Figure 2). In most samples, at least five of the seven pyrethroids were present. Concentrations of deltamethrin, esfenvalerate, and λ-cyhalothrin were typically less than 10 ng/g. Cypermethrin and cyfluthrin concentrations were higher, usually in the 2−30 ng/g range. Bifenthrin and permethrin concentrations were highest, occasionally greater than 75 ng/g. Curry Creek, the site with the highest toxicity, also contained the highest pyrethroid concentrations measured in the study. All seven pyrethroids were present at this site, and on one occasion (after the first flush in 2004), bifenthrin was detectable at 430 ng/g, 22 times greater than the concentration required to cause 50% mortality in standard toxicity tests with *H. azteca*. (*8*). Chlorpyrifos was detected at concentrations typically 1−2 ng/g in six of the eight creeks on at least one occasion.

In the East Bay, pyrethroids were detected less frequently and at lower concentrations than in Sacramento, with the exception of the Kirker Creek site (Table S2, Figure 2). At sites other than Kirker Creek, pyrethroid concentrations were rarely greater than 20 ng/g for any of the compounds. The Kirker Creek site was unusual in that it also contained relatively high concentrations of deltamethrin. The spring Kirker Creek sample contained the highest concentration of any single pyrethroid measured in the East Bay: 57 ng/g deltamethrin. Chlorpyrifos was detectable at five sites on at least one occasion, at concentrations typically below 10 ng/g. Although the Lion Creek sediment contained the highest chlorpyrifos concentration found in the study (92 ng/g in April 2004), the sediment was not toxic to *H. azteca* on this occasion.

Pyrethroids were rarely detected in Nashville creek sediments (Table S3). Five of the 14 creek sites sampled contained no pyrethroids above the reporting limit of 1 ng/g. Seven more creek sites had only one pyrethroid present in each sample, most at concentrations barely above detection.

Pyrethroids as Contributors to Sediment Toxicity. It is not possible to determine if unanalyzed substances are also contributing to sediment toxicity, but in the Sacramento region, pyrethroids alone are in sufficient concentration to

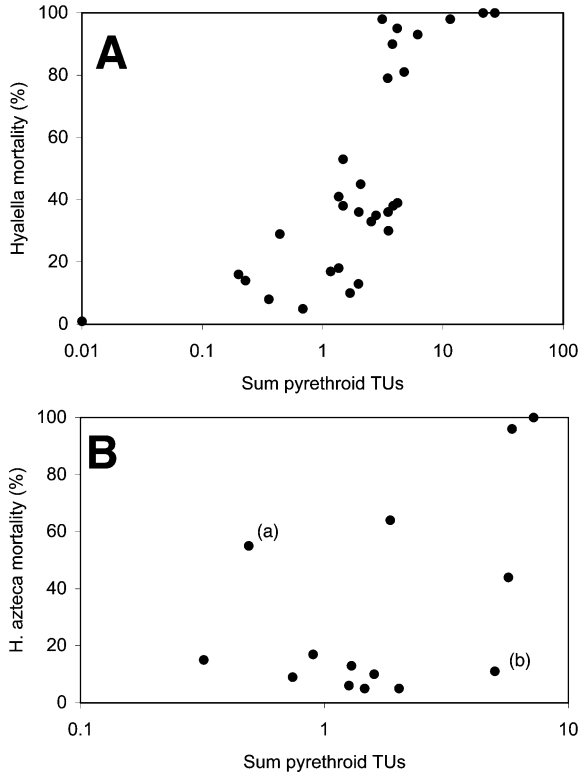

FIGURE 3. Mortality of *H. azteca* exposed to sediments collected from California creeks in comparison to the total pyrethroid toxicity units (TUs) present in the sediment at each site. TUs were calculated from pyrethroid concentrations from the current study and previously reported LC50 data (*8, 9*). (A) Sacramento and (B) East Bay. Points designated by a and b are discussed in the text.

account for virtually all the *H. azteca* toxicity observed. In fact, pyrethroid concentrations, when expressed as TUs to adjust for differences in the relative toxicity among members of the class, proved to be an excellent predictor of *H. azteca* toxicity (Figure 3). Samples with less than 1 TU were nontoxic; those with greater than 2 TU were consistently toxic. Twenty-one of the 22 toxic samples (out of 33 samples total) had at least 1 TU of pyrethroids, indicating a major role for these compounds in explaining the toxicity.

The potential role of pyrethroids in explaining East Bay creek toxicity was less clear. On the basis of the TU analysis, there is good evidence for a role of pyrethroids in the toxicity in Kirker Creek sediments, and potentially Lauterwasser and Pine Creeks, although the latter is indeterminable due to loss of the OC sample during shipment that precluded calculation of TUs. Toxicity in Glen Echo and Lion Creeks cannot clearly be linked to pyrethroids. The two most problematic samples were both from Glen Echo Creek. In one sample (Figure 3B, point a) non-pyrethroids apparently contributed to toxicity. In the other sample (point b), the sediment was only barely significantly toxic (11% mortality) despite the presence of 5 TUs of pyrethroids, suggesting undetermined factors influencing bioavailability. It may be significant that this later sediment was atypical and among the most coarse-grained sediments obtained. Sediments with predominantly medium sands or coarser grain sizes tended to show less mortality than expected based on pyrethroid concentration, although the relationship was not consistent.

When the TUs are apportioned among the individual pyrethroid compounds (Figure 4), it is apparent that bifenthrin alone can account for much of the toxicity. Fifteen of 33 Sacramento area samples contained >1 TU bifenthrin. Although its relative importance varied among the creeks, overall, bifenthrin alone contributed an average of 58% of the total TUs at Sacramento sites and 37% at East Bay sites. Lesser but still substantial proportions of the total TUs were contributed by cypermethrin (average 16% in Sacramento, 17% in East Bay), cyfluthrin (9 and 11%), deltamethrin (4 and 17%), and λ-cyhalothrin (10 and 12%). Kirker Creek was unique in that deltamethrin provided an atypically large fraction of the TUs. Esfenvalerate and permethrin rarely reached concentrations associated with *H. azteca* acute toxicity. Their combined contribution rarely exceeded 0.1 TU and never exceeded 0.5 TU.

Seasonal patterns in pyrethroid sediment concentrations were not clear-cut and varied among the study areas. In the Sacramento area, three of five creeks with seasonal data had the highest total pyrethroid TUs in spring, while the remaining two creeks were highest after the first flush sampling in the fall. Among the East Bay creeks, most creeks had higher pyrethroid TUs in fall, after the first major rain event. Seasonal differences were relatively minor, as expected given that pyrethroid half-lives in sediments are in the range of 0.5–1.5 years (*12*).

Potential Sources. It is apparent that pyrethroid pesticides are widespread in California urban creeks and reach acutely toxic concentrations in many of them. Addressing this condition requires identifying the principal source(s), and the Pesticide Use Reporting (PUR) database, maintained by the California Department of Pesticide Regulation, is helpful in this regard. All urban applications of pesticides by professional pest control applicators, as well as agricultural uses, are reported in the database, although it excludes retail sales to homeowners.

Although agriculture is recognized as a source of pyrethroids in some water bodies (*13*), there is no agriculture in the urban areas investigated in this study. Mosquito control treatment can be eliminated as a potential source as it does not employ the analytes measured. Landscape maintenance by professional applicators is also an unlikely source for most of the pyrethroids since the PUR database indicates the amounts of pyrethroids used are minimal, with the exception of permethrin. For example, 2003 bifenthrin usage for landscape maintenance in Sacramento County, CA totaled 18 kg, as compared to 528 kg used for structural pest control.

The probable sources for most of the pyrethroids studied are retail sales to consumers or structural pest control (applications by professional applicators in buildings, on exterior surfaces, or on the ground around the perimeter of buildings as a barrier treatment). While the amounts used for structural pest control are reported in the PUR database, the volume of retail sales is not publicly reported. Thus, it is not possible to directly compare the magnitude of the sources, and potential importance of retail sales as a pyrethroid source to urban creeks can only be inferred by product availability. We conducted a survey of insecticides available at Home Depot, Lowe's, Ace Hardware, and Orchard Supply Hardware in the San Francisco Bay area in July 2005 to determine retail availability of the various pyrethroid compounds (Table S4) and contrasted the availability of each pyrethroid with the amounts used for structural pest control to obtain a general sense of the potential role of the two uses as sources of pyrethroids to the creek sediments.

Bifenthrin: Over 1400 kg of bifenthrin was used in 2003 in Sacramento County and the East Bay counties (Alameda and Contra Costa) for structural pest control. There are also eight bifenthrin-containing products available to consumers. Four of these products are granules intended for lawn application, which implies use of large amounts of the material and intensive irrigation that could provide a route of transport to nearby creeks.

Cyfluthrin: Cyfluthrin is among the most used structural pest control products in the study area (~2000 kg/year), and there are 15 diverse products available at retail outlets for

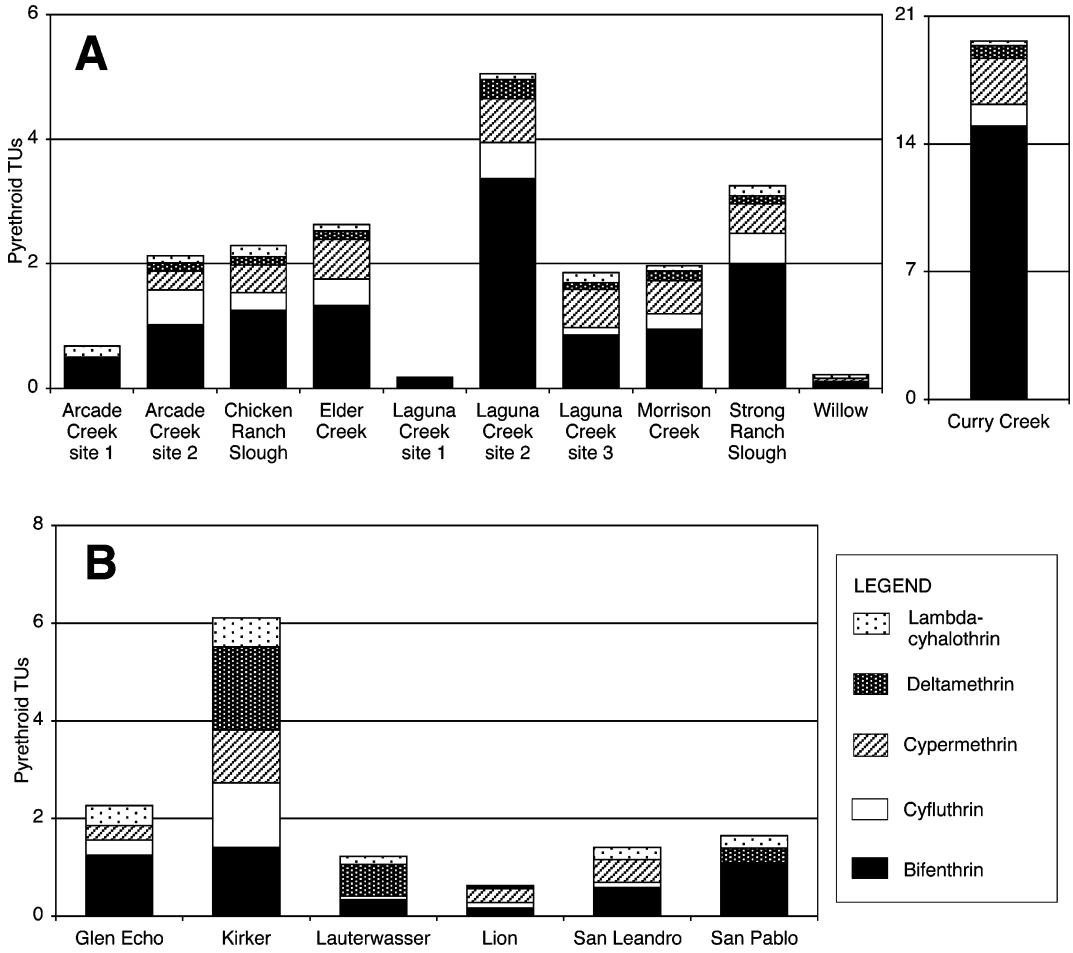

FIGURE 4. Pyrethroid toxicity units (TU) apportioned among the various compounds, using average values over all sampling time points. Esfenvalerate and permethrin are not included as they made only minor contributions to the total TUs. (A) Sacramento area urban creeks and (B) East Bay urban creeks.

lawn and garden use. Both sources could be potential contributors.

Cypermethrin: Structural use of cypermethrin by professionals in the study areas (~12 300 kg/year) is a far greater source to creek sediments than homeowner use. Only a single cypermethrin-containing product was found in the retail shelf survey, and it was not widely available.

Deltamethrin: Only five products containing deltamethrin were found: two pump sprays and three dust treatments. These products were packaged in small volumes and intended for localized treatments. Substantial amounts of deltamethrin (~300 kg/year) are used for aboveground structural pest control in Sacramento and the East Bay, and this use appears to be a more likely source for residues in the creeks than retail sales.

Esfenvalerate: This compound was either undetected or at very low concentrations in creek sediments, an observation consistent with its minimal structural use (~1 kg/year) and limited retail availability.

Lambda-Cyhalothrin: Relatively small amounts of λ-cyhalothrin are used for structural pest control in Sacramento and the East Bay (~100 kg/year). Six retail products containing λ-cyhalothrin were found in the shelf survey. Two products were lawn fertilizer granules containing the insecticide. Both structural pest control and retail products could be contributing to the concentrations detected in creek sediments.

Permethrin: On average, permethrin makes up 38% of the total pyrethroids present in California creek sediments. It is widely used in structural pest control in the study area (~3000 kg/year). However, a substantial fraction of this total probably consists of below-ground termiticide applications. Professional pest control applicators also use some permethrin for landscape maintenance (68 kg/year in Sacramento County), and it is found in over 30 various retail products. Any or all of these sources may have contributed to permethrin in the creek sediments, although because of its relatively low aquatic toxicity as compared to the other pyrethroids, the permethrin residues were not a major contributor to the observed *H. azteca* mortality.

Regional Pyrethroid Distribution. There were substantial differences among the three study areas in the quality of creek sediments. Even between the two California study regions, the Sacramento area showed a greater frequency of toxicity and a clearer role of pyrethroids as contributors to this toxicity. The reason for this difference is unknown but is probably largely a function of land use within the various watersheds. The fact that Sacramento does not meter water use but uses flat rate pricing may also be a factor contributing to excessive landscape watering and a greater potential for pesticide transport to surface water bodies.

The most dramatic difference was between the California sites, as a whole, and Nashville, TN. Whereas pyrethroids and associated toxicity appear to be widespread in California urban creeks, pyrethroids were undetectable or barely detectable in Nashville creeks. Toxicity was observed in 12 of the 15 California creeks on at least one occasion, but no toxicity was found in the 12 Nashville creeks. Total pyrethroid TUs in all Nashville creeks were consistently below levels expected to cause toxicity to *H. azteca*.

Several factors may be contributing to this disparity. First, Sacramento and the East Bay are located in a relatively arid region of California. Summer precipitation is negligible, and runoff from landscape irrigation dominates summer flow in many creeks. Precipitation in Nashville (119 cm/year) is far greater than in San Francisco (51 cm/year) or Sacramento (46 cm/year), but more importantly, it occurs year-round. Abundant flushing in the summer and input of clean sediment from nonlandscaped areas may account for much of the differences in these creeks.

Additionally, the California creeks sampled in this study all drained urban or suburban areas via a storm drain system. The Nashville areas sampled were not served by storm sewers, and runoff reached the creeks by flowing across ground surfaces for considerable distances. This route of water movement permits more limited transport of soil particles and associated pesticides than does a storm drain system, in which water travels to the creeks in a concrete pipe with no opportunity for particle deposition. Some of the highest pyrethroid concentrations and levels of toxicity measured in this study were from Curry Creek and Laguna Creek, just below storm drain outfalls. Previous work in California has shown the highest pyrethroid concentrations in sediments at storm drain outfalls (*6*). When precipitation begins in late-fall, many impervious surfaces are washed for the first time in months flushing any pesticide residues accumulated over the dry season into the storm drain system as well.

Finally, there may be differences in amounts or timing of pesticide use in the two regions, although there are no structural pest control data available from Nashville and no quantitative data on retail sales from either Tennessee or California. Most residential properties in the California study areas are smaller (0.1 hectares) than those in the Nashville study area (0.2−0.4) and have an appearance of more intensive lawn and landscaping care made feasible by the smaller property size. Either quantitative pesticide data are required, or the study areas need to be more carefully matched with respect to land uses, to draw conclusions on relative pesticide use rates. Use differences cannot be ruled out as contributors to the geographic differences observed.

This study clearly indicates that urban pyrethroid use by homeowners or professional applicators can result in creek sediment contamination to levels acutely toxic to sensitive aquatic invertebrates. In at least some urban regions, that toxicity is widespread in most creeks. The TU approach generally provides a good correlation between pyrethroids and toxicity, although it cannot discriminate the effect of other unmeasured contaminants that are potentially contributing to toxicity in these systems, and a reduction in pyrethroid concentrations may not consistently result in a decrease in toxicity if other toxicants co-occur. Pyrethroids are widely used insecticides in urban environments across the U.S., but there are clearly other factors that mitigate surface water degradation, such that the degree of impact is site-specific. Mitigation factors may include patterns of pesticide use, land use differences, or climatic differences. It is not possible, with the limited data from this study alone, to establish whether the pervasive toxicity in Sacramento creeks and the absence of toxicity in Nashville creeks reflects some broad geographic distinction (e.g., climate) or whether the disparate sediment quality impacts simply reflect local land use differences. Nevertheless, the results indicate that pyrethroids are degrading sediment quality in several California areas and show a need for more geographically extensive monitoring of urban and suburban creek sediments to define those areas where aquatic habitat quality is at risk.

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Supporting Information Available

Analytical chemistry results (Tables S1− S3) and pyrethroid pesticides available in San Francisco Bay area retail outlets (Table S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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