Statewide Investigation of the Role of Pyrethroid Pesticides in Sediment Toxicity in California's Urban Waterways

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A statewide investigation of urban creek sediment toxicity was conducted in California in recognition of increased incidences of toxicity linked to pyrethroid pesticides. The goals were to examine the spatial occurrence and magnitude of sediment toxicity in California urban creeks, and to examine the role of pyrethroids in toxic urban creek sediment samples. After a preliminary screening of 90 sites, 30 creeks were sampled in eight geographical regions. Sediment toxicity was assessed using 10 day bioassays with the resident amphipod *Hyalella azteca*. Bioassays were conducted at two test temperatures of 23 °C and at 15 °C to provide evidence of the cause of toxicity, and to more accurately reflect ambient environmental temperatures. Twenty-five of 30 samples were toxic when tested at 23 °C, and all 30 samples were toxic when tested at 15 °C. The magnitude of toxicity increased in samples tested at 15 °C suggesting the influence of pyrethroids, which are more toxic at colder temperatures. Pyrethroids were present in all sediment samples and were the only compounds detected at concentrations toxic to *H. azteca*. Bifenthrin was the pyrethroid of greatest toxicological concern, occurring in all 30 samples at concentrations up to 219 ng/g. Pyrethroid contamination of urban creeks was most severe in the Los Angeles, Central Valley, and San Diego regions, respectively. However, pyrethroids were also linked to urban creek aquatic toxicity in all regions sampled, including the less urbanized areas of the North Coast and Lake Tahoe.

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Introduction

Pyrethroid pesticides have become the dominant urban insecticides used in California (*1*). Pyrethroids are applied in all 58 counties of the State with over 345 000 kg reported used for landscape maintenance, structural pest control, and public health pest control in 2005 (*2*). Approximately 60% of the reported urban-related pyrethroid pesticide use occurs in the four Southern California counties of Riverside, Los Angeles, Orange, and San Diego. The widespread usage of pyrethroid pesticides and dominance in urban environments is of concern particularly because pyrethroids are highly toxic to fish and aquatic invertebrates (*3*).

Several earlier studies identified sediment toxicity associated with pyrethroid pesticides in urban creeks of the Eastern San Francisco Bay and Sacramento areas (*4*, *5*). In the Sacramento area creeks, pyrethroids were present at concentrations greater than amphipod acute toxicity values (*6*) in 95% of the toxic samples. Although a number of pyrethroids were observed in these sediments, bifenthrin contributed the most to the observed toxicity. The highest concentrations of pyrethroids were observed in the sediments near the stormwater outfalls and decreased going downstream. Understanding the role of pyrethroids in urban creek sediment toxicity has become an important issue for statewide stormwater pollution regulation and prevention activities.

The U.S. Environmental Protection Agency (EPA) promulgated the municipal stormwater program under the Clean Water Act (CWA) to address stormwater runoff. The program is currently administered through National Pollutant Discharge Elimination System (NPDES) permits, and in California NPDES permits are issued by the State Water Resources Control Board. To satisfy NPDES requirements, municipalities are required to develop stormwater management plans that outline the pollution prevention control activities to reduce discharge of pollutants, protect water and sediment quality, and satisfy requirements of the CWA. As stormwater management plans are being developed and implemented throughout California, it is not known whether toxicity associated with pyrethroid pesticide contamination is isolated to particular regions or of statewide concern. This is an important question because unnecessary monitoring impacts urban stormwater programs by diverting resources from other potential water and sediment quality problems.

Despite the lack of monitoring of pyrethroids in California's urban waterways, there is extensive evidence of pyrethroid contamination in agricultural waterways (*6*–*14*). These data, in addition to the limited urban data, prompted the Department of Pesticide Regulation, who regulates pesticide sales and use in California, to initiate a reevaluation of more than 600 products containing pyrethroid pesticides in 2006. The registration reevaluation process includes a critical review of all available data and, in some cases, special focused studies, to address significant data gaps, and make determinations on registration. Statewide pyrethroid data for urban-dominated waterways presents a large data gap in California.

Goals of the study were 2-fold. First, to screen urban creeks throughout the State and examine the statewide occurrence of pyrethroids in California's urban waterways. Second, to determine the role of pyrethroid pesticides in toxic urban creek sediments.

Materials and Methods

Site Reconnaissance and Sediment Screening. Ninety sites were sampled on 63 urban waterways statewide during late

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FIGURE 1. Map of California with regions and sampling sites shown.

Summer and Fall 2006 as part of a preproject site reconnaissance phase. A three-replicate 10 day *Hyalella azteca* screening toxicity test was conducted on samples to assess the potential for sediment toxicity and follow up testing. The three-replicate sediment assay was used only for screening sediment samples, and differed from the standard eight-replicate sediment toxicity test only by the number of replicates. The standard eight-replicate toxicity assay is outlined later in the toxicity testing methods section. Most screening samples were collected prior to any rainfall after the summer months. Approximately $^1/_3$ of these samples had caused significant toxicity.

The screening data, although not reported, were used to identify 40 sampling sites for the 23 °C and 15 °C toxicity testing. These samples included 24 of the sites screened during reconnaissance phase, of which 20 were identified as toxic using the screening assay, and 16 new sites. The new sites were added because some regions of the state were not well represented (primarily the Central Coast and San Diego) and most regions of the State were not screened after rainfall due to insufficient rainfall, sampling logistics, and project time frame constraints. Thirty-one of the 40 samples were toxic in the 23 °C test, with approximately 25% resulting in zero percent survival. Thirty-seven of the 40 samples were toxic in the 15 °C test, with approximately $^1/_3$ resulting in 0% survival. The toxicity testing results are presented in Table 3 of the Supporting Information.

Thirty of the 40 sites were selected as the focus for this study, from which all sediments would be included in the chemical analyses, and four would be further investigated using TIEs and reported in a separate manuscript. The primary criteria for selecting sites to include or exclude from the core 30-site list was having a representative statewide spatial distribution. Sites that were excluded were typically close to each other within the same region.

Statewide Site Selection. Thirty urban creek sites were sampled from eight of nine regions of California (Figure 1). Site selection criteria included areas dominated by residential urban land use, perennial creek flow, natural habitat (named waterways) of ecological importance, presence of sediment depositional zones, the presence of stormwater outfalls, and evidence of toxicity from the screening studies. The number of sampling sites in a region was reflective of pyrethroid pesticide use, urban residential land use, and availability of sites meeting the site selection criteria. Sampling sites were not identified in the Colorado River region due to the lack of permanent creek flows and dominance of agriculture in certain parts of this region. Also, sampling sites were not identified in the southern part (south of Stockton) of the Central Valley because urban stormwater runoff is primarily routed to dry wells and not natural named creeks. Sampling site location information is available in Table 1 of the Supporting Information.

The existing data, while limited, suggest that pyrethroids are persistent in the sediment (*15*), hydrophobic, and rapidly adsorb to sediments in aquatic environments (*16*), so it is not surprising pyrethroids have been reported as most concentrated in the sediments near the point of discharge to a waterway (*4*). Therefore, only creek reaches located within or immediately downstream of urban areas were selected. Sampling site locations targeted those areas of sediment deposition within an identified 50 m of urban stormwater outfalls. Sampling reaches that could be influenced by agricultural practices were avoided.

Sediment Sampling Procedures. Sampling was conducted after significant rainfall had occurred in each watershed (≥1.3 cm) since the beginning of the water year on July 1. All sediment samples were collected during January through March 2007. Exceptions include samples collected from the Lake Tahoe region in October 2006, and samples from the North Coast and Central Valley, which were collected in November 2006.

Sediment samples for toxicity testing and chemical analyses were collected by skimming the upper 2 cm of sediment from depositional zones using precleaned Teflon polycarbonate or stainless steel scoops. Sediments were placed into precleaned 2 L glass jars and transported to the laboratory on ice. Approximately 4 L of sediment were collected from each site. Sediments were homogenized on a roller apparatus (Wheaton Instruments, Millville, NJ), and aliquots of sediment were held at 4 °C (sediment toxicity testing samples) or −20 °C (analytical chemical samples), prior to analyses.

Toxicity Testing. Sediment toxicity was assessed using the 10 day survival toxicity test with *H. azteca* (*17*), an amphipod species that occurs in California waterways. Eight replicate test containers, each containing 10 7−14-day old amphipods, were used for the test. Laboratory control sediment consisted of a formulated sediment prepared in accordance with Anderson et al. (*18*),. Testing was done in 250 mL beakers containing 50 mL of sediment and 200 mL of overlying water. Tests were conducted using the standard test temperature of 23 °C, in addition to the temperature of 15 °C, to reflect fall and winter creek temperatures. The overlying water was renewed twice daily, and 1.0 mL of YCT (yeast, cerophyll, trout chow; Aquatic Biosystems, Fort Collins, CO) was added daily to each test container. About half of the samples required aeration, due to low dissolved oxygen. After a 10 day exposure, surviving amphipods were recovered and their number recorded.

Analytical Chemistry. Sediment chemical analytes included eight pyrethroids, 30 organochlorine pesticides (OCs) or their degradation products, and the pyrethroid synergist piperonyl-butoxide (PBO). OCs include highly persistent legacy compounds such as chlordanes and DDT that may co-occur with pyrethroids, and their measurement may help resolve relationships between contaminants and toxicity. PBO is commonly used in pesticide formulations with pyrethroids to potentiate their toxicity, and its measurement may help resolve relationships between pyrethroids and magnitude of toxicological effect. All sediment samples were extracted twice

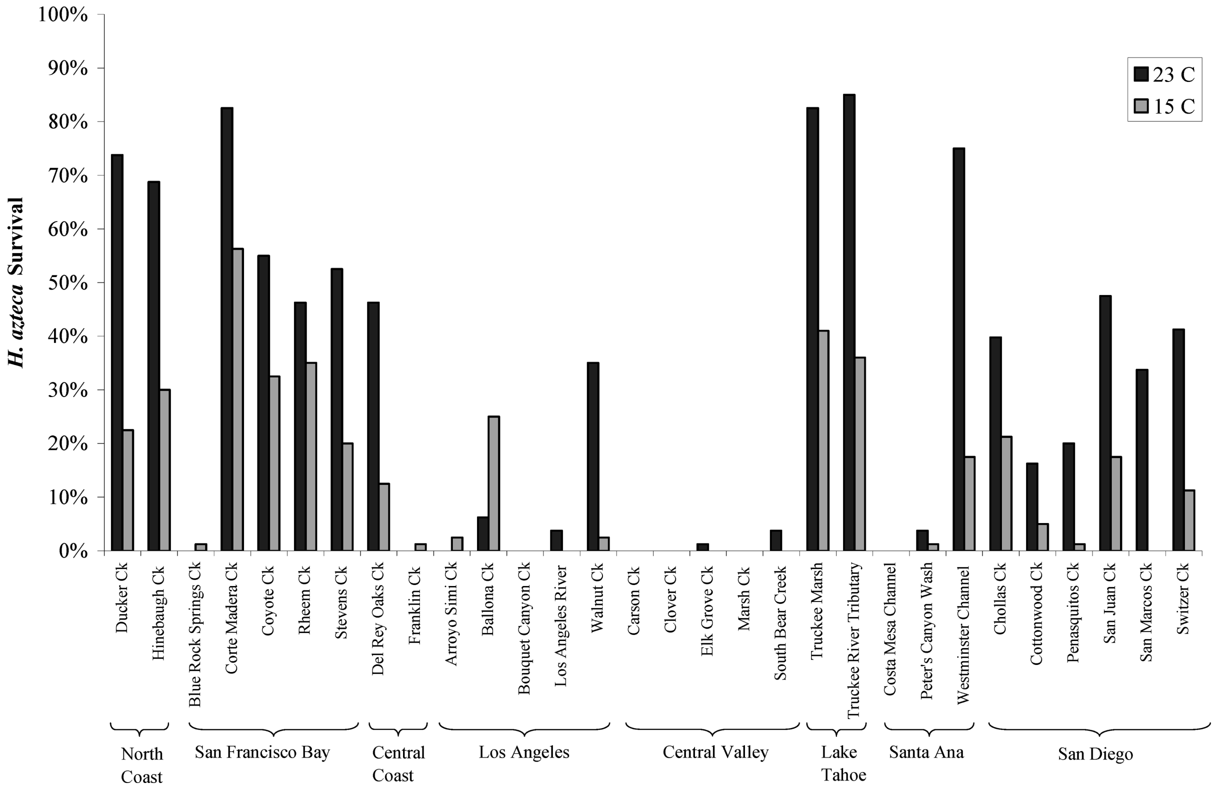

FIGURE 2. ***H. azteca*** **percent survival from sediment toxicity tests conducted at 23C and 15C with sediments from each urban creek.**

using method 3545A modified pressurized fluid extraction (*19*). In addition, two organophosphate pesticides (OPs; diazinon and chlorpyrifos) were also analyzed in interstitial water samples following procedures recommended by Sullivan and Goh (*20*). While these OPs are phased out for residential use, they are commonly found in urban creeks, and their measurement aids in identification of chemicals associated with toxicity. Further, both diazinon and chlorpyrifos are highly toxic to invertebrates, relatively water soluble, and have been observed in toxic concentrations exceeding amphipod toxicity values in interstitial water samples collected from agricultural waterways in California (*9*). See Table 5 in the Supporting Information for a more detailed outline of the chemistry methods. Metals were not measured in sediment samples.

Hardness, alkalinity, conductivity, pH, and ammonia were measured at the beginning and end of each test. Temperature and dissolved oxygen were monitored daily. Ammonia did not exceed any established toxicity values for *H. azteca* (*21*). Total organic carbon and grain size were measured in each sediment sample using method 9060A (*19*) on an elemental analyzer by Applied Marine Sciences in League City, TX.

Data Analyses. Toxicity testing data were analyzed by comparing sample results to laboratory controls with separate variance *t* tests ($\alpha = 0.05$). A sample from a site was deemed toxic if there was significant response difference ($p < 0.05$) from laboratory control response, and if the sample survival percentage was at least twenty percentage points below the control survival percentage.

Results and Discussion

Sediment Toxicity Testing. Twenty-five of the thirty samples were toxic at the 23 °C test temperature and all thirty were toxic at the 15 °C test temperature (Figure 2). An overall increase in the magnitude of toxicity was observed in samples tested at 15 °C, with the exception of the Ballona Creek site, which was more toxic at 23 °C than 15 °C (see discussion below). Of the five samples that became toxic with the cold exposure, two were samples from the Lahontan region (Truckee River swale and the Truckee Marsh), and one sample each was from the North Coast, northern San Francisco Bay, and Santa Ana regions. Sites with the lowest *H. azteca* survival were observed in the Central Valley, Los Angeles, and San Diego regions (Figure 2).

Chemistry. Organochlorine pesticides were detected in 23 of the 30 samples. However, none were reported above concentrations associated with toxicity to *H. azteca*, (see Table 4 in the Supporting Information). Diazinon was observed in interstitial water below the toxicity threshold for *H. azteca* (LC50 = 6.51 ug/L (*22*),), but above the reporting limit in Franklin Creek and the Truckee River swale at 0.120 ug/L and 0.277 ug/L, respectively. Chlorpyrifos was observed in samples (Franklin Creek, Costa Mesa Channel, and Chollas Creek) above the detection limit (0.050 ug/L) but below the reporting limit (0.100 ug/L). The *H. azteca* LC50 for chlorpyrifos is 0.086 ug/L (*22*), so it is possible that we did not detect slightly toxic concentrations of chlorpyrifos.

Seven of eight pyrethroid analytes were detected in this study, but deltamethrin and esfenvalerate were observed infrequently. Fenpropathrin was not detected in any samples. PBO was detected in five samples (Franklin Creek, Bouquet Canyon Creek, Walnut Creek, South Bear Creek, and Switzer Creek) at concentrations ranging from 1.5 to 48.7 ng/g. Amweg et al. (2005) reports that sediments spiked with permethrin became more toxic with as little as 12.5 ng/g PBO in sediment. See Table 2 in the Supporting Information for pyrethroid pesticide and PBO analytical chemistry results. Quality assurance results for all analytes were within acceptable ranges and available upon request.

Bifenthrin was observed in all thirty urban creek samples with concentrations ranging from 2.19 to 219 ng/g dry weight. These results are comparable to earlier studies in the Eastern San Francisco Bay, and Sacramento areas (*4, 5*). As reported previously, the highest concentrations of bifenthrin continue to be observed in the Central Valley region, with the maximum concentration of bifenthrin measured in the current study

(219 ng/g) from Clover Creek in Redding. Although this concentration is only about half the maximum concentration recorded from earlier work in the Sacramento area (430 ng/g from Curry Creek), these data show high concentrations occurring in a part of the northern Central Valley region where ambient pesticide and sediment toxicity monitoring has not been conducted. The second highest concentration of bifenthrin from the current study was observed in the Los Angeles region (173 ng/g) followed by the remaining Central Valley samples (65.1−114 ng/g), and Cottonwood Creek (69.1 ng/g) and Penasquitos Creek (56.8 ng/g) in the San Diego region.

Permethrin was the second most commonly observed pyrethroid, occurring in 26 of 30 samples. Cyfluthrin was measured in 16 samples. The five Central Valley samples had the highest concentrations of cyfluthrin with South Bear Creek in Stockton having the highest concentration of 127 ng/g dry weight. Cypermethrin was measured in 10 samples collected from the Central Valley, Los Angeles, and San Diego regions. Maximum concentration of 102 ng/g dry weight was observed in Cottonwood Creek in San Diego. Lambda-cyhalothrin was also measured in 10 samples with observations occurring in every region except the North Coast and Lake Tahoe regions.

The widespread occurrence of pyrethroids in urban creek sediments suggests a need for increased monitoring for aquatic life impacts due to pyrethroids in urban creek habitats statewide.

Role of Pyrethroids in Sediment Toxicity. Pyrethroid concentrations were converted to toxic units (TUs) to better understand the relative toxicities of each pyrethroid to *H. azteca*. Pyrethroid TUs were calculated by dividing the organic carbon normalized concentration of pyrethroid in the sediment by the organic carbon normalized pyrethroid *H. azteca* LC50 reported from earlier studies (*6, 23*). Pyrethroid TUs were calculated using LC50 data derived at the standard test temperature of 23 °C. Therefore, the TU approach will tend to under-predict observed toxicity at 15 °C due to the enhanced toxicity of pyrethroids at the lower temperature.

There is a clear relationship between total pyrethroid TUs and *H. azteca* toxicity both in tests conducted at 23 °C and 15 °C (Figure 3). For example, nearly all samples tested at 23 °C with greater than 0.5 TUs displayed significant toxicity. Sediments from 26 sample sites contained at least 0.5 TU of pyrethroids, indicating these pesticides likely play a major role in sediment toxicity in these urban creeks.

Toxicity of samples tested at 15 °C may provide a more ecologically relevant indicator of pyrethroid toxicity, particularly during winter months. All of the urban creeks demonstrated significant toxicity when tested at 15 °C. This observation is not surprising, since pyrethroids occurred in all samples, and pyrethroids have been shown to be more toxic at colder temperatures (*24*), largely due to the slower metabolism at lower temperatures (*25*). The overall increase in the magnitude of toxicity observed in samples tested at 15 °C provide further evidence of the role of pyrethroids (Figure 3). Most of the urban creeks assessed as part of the current study have winter temperatures well below the lowest tested temperature of 15 °C. In fact, the Truckee Marsh in the Lake Tahoe region has typical winter temperatures of 4 °C. Typical urban waterway temperatures in the Sacramento area are closer to 10 °C.

The occurrence of pyrethroids at toxicologically significant concentrations to *H. azteca* is of particular concern since this species is also a resident in many California urban habitats. Weston et al. (*4*), studied pyrethroid occurrence, toxicity patterns, and resident *H. azteca* abundance in a Sacramento area urban watershed. The abundance of resident *H. azteca* was inversely correlated with pyrethroids TUs. In the current study the toxicity observed in the Truckee

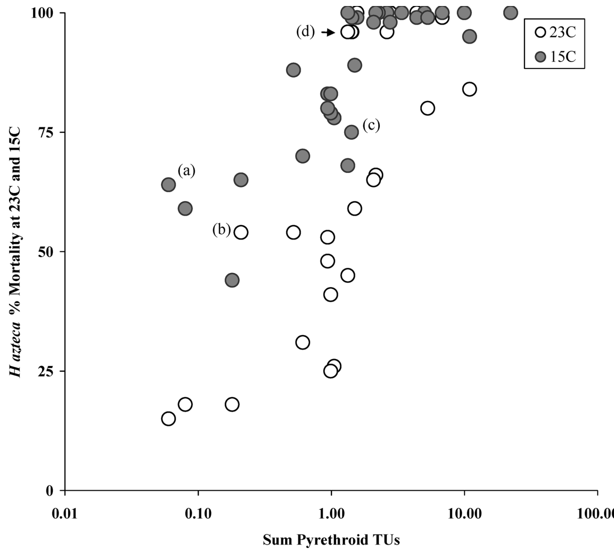

FIGURE 3. Relationship between the sum of pyrethroid TUs in California urban creek sediments and the toxicity to *H. azteca* in 10 day laboratory sediment toxicity tests conducted at 23C and 15C. Pyrethroid TUs are based on *H. azteca* 10 day sediment toxicity tests conducted at 23C, and are calculated using organic carbon (oc) normalized pyrethroid pesticide concentrations. The points designated as a, b, c, and d are discussed in the text.

Marsh is also of particular concern because earlier data indicate the occurrence of resident *H. azteca* in the Truckee Marsh (*26*). Studies conducted in the Santa Maria and Salinas Rivers have also documented declines in amphipods and other macroinvertebrates at sites demonstrating sediment toxicity due to pyrethroids and other pesticides (*7*−*9, 13*).

Results of *H. azteca* toxicity tests and pyrethroid TU analyses suggest a major role of pyrethroids in sediment toxicity in California's urban creeks. However, the potential role in explaining toxicity at three sites was less evident. The sample from the Truckee Marsh in the Lake Tahoe region had caused significant *H. azteca* mortality when tested at 15 °C at only 0.08 TU of pyrethroids (Figure 3, point a). Similarly, the Rheem Creek sample, from eastern San Francisco Bay, had significant *H. azteca* toxicity at 23 °C with less than 0.5 TU of pyrethroids (Figure 3, point b). Both sample results suggest the possibility that other unanalyzed substances may also be linked to the toxicity at these sites. Ballona Creek, in the Los Angeles region, was the other site where the role of pyrethroids was less clear since this site was the only site to be more toxic at 23 °C than 15 °C (Figure 3, points c and d). Since there are greater than 1.4 TUs of pyrethroids in the Ballona Creek sediments it would be expected to have an increase in the magnitude of toxicity at the colder temperature, since pyrethroids are more toxic at colder temperatures. However, it is not possible to determine if unanalyzed substances could be linked to or affecting any of the observed toxicity.

The organic carbon content and grain size (percent fines) of sediments influences pyrethroid bioavailability and toxicity. Organic carbon content ranged from 0.62% (Arroyo Simi Creek in Los Angeles) to 32.89% (Truckee Marsh in Lahontan). The relationship between organic carbon content and bioavailability of hydrophobic organic compounds is well established. Recent studies have shown that organic carbon quality also affects chemical bioavailability and thus, toxicity (*27*−*29*). While there was very high TOC in the Truckee Marsh sediment (∼33%), this was mainly comprised of intact reeds and leaves, a carbon source that is likely less effective at binding hydrophobic chemicals than more humified plant

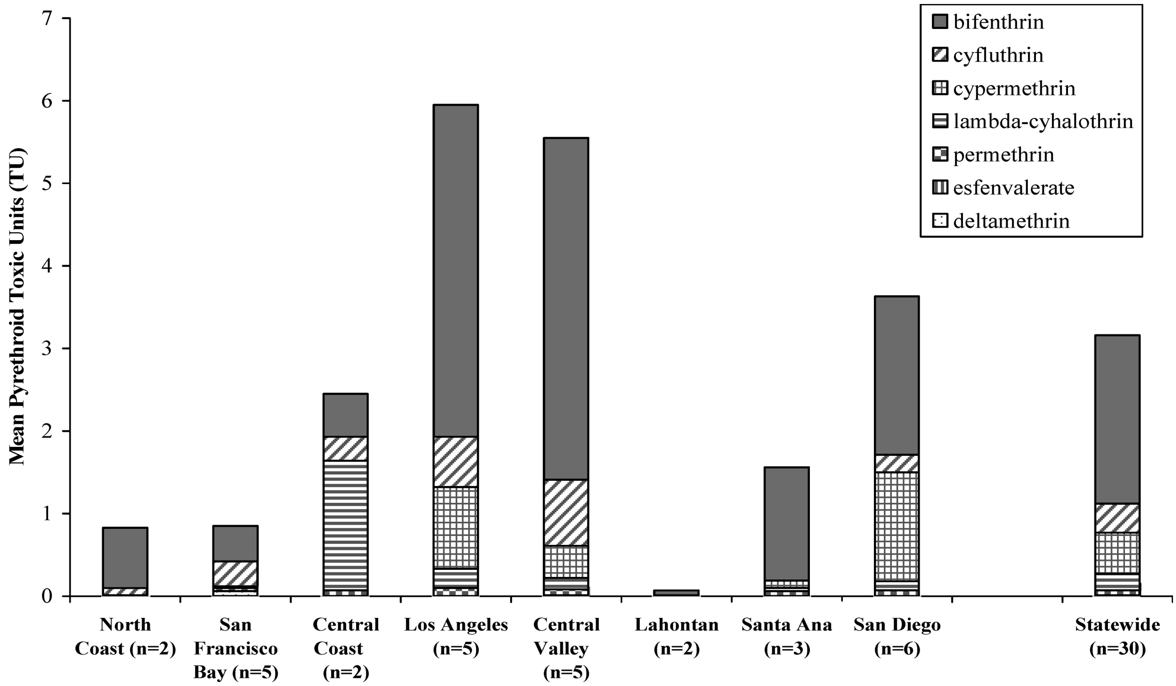

FIGURE 4. Comparison of mean pyrethroid pesticide TUs in urban creek sediments in regions of California and Statewide, and the contribution of the various pyrethroids to the total TUs. Pyrethroid TUs are calculated using organic carbon normalized (oc) pyrethroid pesticide concentration data to compare the concentrations of pyrethroids that would be sufficient to cause 50% mortality to *H. azteca* in 10 day sediment toxicity tests. Calculation of TUs is based on *H. azteca* 10 day sediment toxicity tests conducted at 23C.

materials (*28*). Therefore, the oc-normalized TUs calculated for the Truckee Marsh sediment would likely underestimate its potential for toxicity. Although the analyte list was relatively complete, other contaminants (e.g., metals) could have played a role in the toxicity occurrences. However, test organism mortality due to sediment metals would likely have been increased with an increase in temperature, opposite of that which occurs with pyrethroids.

Grain size ranged from 1.8% (Costa Mesa Channel) fines less than 0.0625 to 97.5% (Truckee Marsh). Pyrethroid pesticide occurrences in sediment were not limited to sampling sites with high percent fines. However, the sampling sites with the highest percent fines generally contained higher concentrations of pyrethroids, with the exception of the Lahontan region sites. Pyrethroid linked toxicity was also observed in sampling sites with the lowest percent fines (e.g., 1.84% in Costa Mesa channel at both test temperatures). Average and median percent fines were 52 and 57% for the thirty statewide urban creeks, respectively.

Statewide Significance of Pyrethroids in Urban Waterways. When the pyrethroid TUs are partitioned among regions and individual pyrethroid analytes (Figure 4), it is apparent that the level of pyrethroid contamination and toxicity varies regionally, ranging from less than 1.0 TU to over 5.0 TUs. Statewide, the mean level of pyrethroid contamination is approximately 3 TUs. The most contaminated regions sampled were the Los Angeles, Central Valley, and San Diego regions, whereas the regions with the least amount of pyrethroid contamination were the North Coast, San Francisco Bay, and Lahontan regions. The San Francisco Bay region, while less contaminated by pyrethroids than the statewide average, was dominated by a prevalence of coarse-grained sediments in the regional creek samples. The fate of pyrethroids in streams dominated by coarse grained sediment has not been studied. However, coarse grained sediments do not present a suitable matrix for the sampling and analysis of sediment-bound organic contaminants, such as pyrethroids. Other factors (e.g., usage patterns, management practices, land use) could also be associated with regional differences in pyrethroid contamination, which, an analysis of is beyond the scope of the current screening investigation.

When the individual pyrethroid TUs are partitioned, it is also apparent that bifenthrin accounts for approximately 67% of the mean observed pyrethroid toxicity statewide. This finding is consistent with the earlier studies in the Sacramento and Eastern San Francisco Bay urban creeks (*5*). However, bifenthrin is not the only contributor to pyrethroid linked toxicity, cyfluthrin and cypermethrin, also played large roles in the pyrethroid linked toxicity on a statewide basis. Ng et al. (*30*), reported the occurrence of cypermethrin in sediment samples collected from three agricultural and urban mixed land use streams in the Central Coast region, and noted that the occurrence of cypermethrin as being more typical of the agricultural rather than the urban stream reaches in the sites surveyed. Cypermethrin was not detected in urban creek samples from the Central Coast in the current study. However, cypermethrin occurred in 1/3 of the samples collected statewide from the current study, in other regions and watersheds without agricultural influence. This finding is not surprising as both cyfluthrin and cypermethrin are used extensively in commercial structural pesticide applications in California, explaining one possible reason they were observed in the urban creek samples.

Budd et al. (*31*), also surveyed pyrethroid occurrence in a mixed land use watershed, in the San Diego Creek/Newport Bay area of the Santa Ana region. Similar to the current study, bifenthrin was the most commonly observed pyrethroid in sediment samples. However, fenpropathrin, a pyrethroid pesticide registered only for use in agriculture and nurseries, was the second most commonly observed pyrethroid. These findings are not surprising because the sampling areas were in close proximity to several commercial nurseries. Fenpropathrin was not detected at any sites in the current study, probably because it is not used much in California. In addition, fenpropathrin has not been identified as being a contributor to aquatic toxicity observations in any earlier urban-dominated creek studies.

This study documented the occurrence of pyrethroids in urban creek sediments of California. Thirty urban creeks were sampled from eight regions of California, including the State's largest urban areas (e.g., Los Angeles, San Diego, San Francisco Bay) and in less urbanized but also ecologically important environments elsewhere in California (e.g., South Lake Tahoe, North Coast). Sampling sites were targeted in close proximity to urban residential stormwater outfalls to provide a screening level assessment of pyrethroid occurrence and toxicity. These data were intended to provide water quality and pesticide regulators, and stormwater managers, the potential statewide significance of pyrethroid pesticides in urban creeks of the State of California. Pyrethroid pesticides were observed in sufficient concentrations in every region to explain the observed toxicity to *H. azteca*. Bifenthrin accounted for 67% of the statewide urban creek pyrethroid TU's observed. Cypermethrin, cyfluthrin, and lambda-cyhalothrin were also important contributors to the pyrethroid toxicity in urban waterways of California.

Acknowledgments

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Supporting Information Available

Sampling locations (Table 1), analytical results for physical properties, pyrethroid pesticides, and piperonyl butoxide (PBO) in sediment samples (Table 2), toxicity testing results for 10 day *H. azteca* sediment toxicity tests (Table 3), analytical results for organochlorine pesticides in sediment samples (Table 4), and analytical methods information (Table 5). This material is available free of charge via the Internet at http://pubs.acs.org.

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