Environmental Science & Technology

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Occurrence and Potential Sources of Pyrethroid Insecticides in Stream Sediments from Seven U.S. Metropolitan Areas

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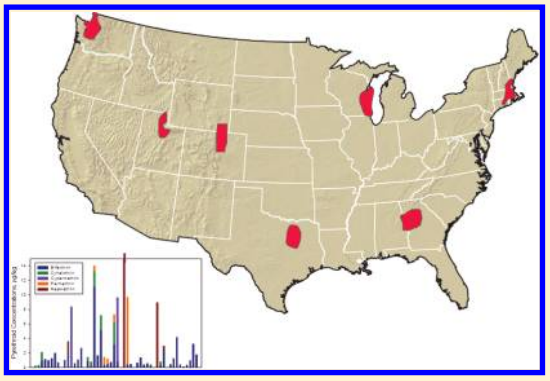
Supporting Information

ABSTRACT: A nationally consistent approach was used to assess the occurrence and potential sources of pyrethroid insecticides in stream bed sediments from seven metropolitan areas across the United States. One or more pyrethroids were detected in almost half of the samples, with bifenthrin detected the most frequently (41%) and in each metropolitan area. Cyhalothrin, cypermethrin, permethrin, and resmethrin were detected much less frequently. Pyrethroid concentrations and *Hyalella azteca* mortality in 28-d tests were lower than in most urban stream studies. Log-transformed total pyrethroid toxic units (TUs) were significantly correlated with survival and bifenthrin was likely responsible for the majority of the observed toxicity. Sampling sites spanned a wide range of urbanization and log-transformed total pyrethroid concentrations were significantly correlated with urban land use. Dallas/Fort Worth had the highest pyrethroid detection frequency (89%), the greatest number of pyrethroids (4), and some of the highest concentrations. Salt Lake City had a similar percentage of detections but only bifenthrin was detected and at lower concentrations. The variation in pyrethroid concentrations among metropolitan areas suggests regional differences in pyrethroid use and transport processes. This study shows that pyrethroids commonly occur in urban stream sediments and may be contributing to sediment toxicity across the country.



INTRODUCTION

Synthetic pyrethroid insecticides have been steadily increasing in use over the past two decades and are now one of the most widely used classes of insecticides.[1] Currently, pyrethroids are registered for numerous uses on a wide variety of crops, golf courses, home and garden, landscaping, nurseries, structural sites, and vector control.[1] Relatively hydrophobic,[2] pyrethroids preferentially sorb to sediments including to suspended sediments in the water column.[3−5]

The earliest known pyrethroid detection in California surface waters was bifenthrin measured on suspended sediments collected in 1997 in San Francisco Bay.[6] In the early 2000s, the phase-out of residential use of diazinon and chlorpyrifos[7] resulted in a corresponding increase of pyrethroid use in urban areas.[1] Since then there has been more frequent analysis of pyrethroids in California stream sediments. In a survey of bed sediments in agriculturally dominated irrigation canals and small streams in the California's Central Valley, multiple pyrethroids were detected frequently at elevated concentrations.[8] Another study which focused on residential sources of pyrethroids found even higher concentrations in bed sediments of streams within a new suburban development in Roseville, California.[9]

Pyrethroids are highly toxic to invertebrates and fish in both freshwater and marine environments.[10−12] The 10-d LC_{50} values for various pyrethroids range from 4 to 110 μg/kg in sediments for the amphipod *Hyalella azteca*.[13,14] In a number of small urban streams throughout California, previous studies found that bed sediment samples showed reduced survival of *H. azteca* in 10-d toxicity tests and measured pyrethroid concentrations were sufficiently high to cause the observed toxicity.[9,15,16] Typically, these studies sampled streams in small basins and in close proximity to direct stormwater inputs from intensely urbanized areas. Subsequent studies outside of California found lower concentrations and lower toxicity to *H. azteca* in urban stream sediments in Illinois[17] and Texas.[18] One California study that assessed the spatial distribution of pyrethroids along downstream transects in several creeks and

Received: March 25, 2011
Revised: March 13, 2012
Accepted: March 14, 2012
Published: March 28, 2012

dx.doi.org/10.1021/es2044882 | Environ. Sci. Technol. 2012, 46, 4297−4303

their tributaries found that sediment contamination was localized near storm drain outfalls and concentrations substantially decreased away from the source.[9] The frequent detection and toxicity of pyrethroids in urban streams is of concern and raises the question of the geographic extent of the problem.

The overall study was designed to evaluate the occurrence and toxicity of a wide variety of contaminants in 98 bed sediments collected in 2007 from streams in seven metropolitan areas across the United States.[19] This paper, focused only on pyrethroids, characterizes their occurrence and potential sources in urban stream sediments for the first time in a nationally consistent approach across the United States. The relationship between pyrethroid concentrations and toxicity to *H. azteca* in 28-d whole-sediment toxicity tests is also discussed. Other aspects considered elsewhere[19] include analysis of all five classes of measured sediment contaminants in relation to urbanization and other factors, evaluation of sediment contamination in the context of sediment quality guidelines, and more detailed assessment of sediment toxicity using a reference envelope approach and growth endpoints in addition to measuring effects on survival.

MATERIALS AND METHODS

Study Design. Samples were collected from 98 urban streams within seven metropolitan areas (study areas): Atlanta (GA); Boston (MA, NH); Milwaukee−Green Bay (WI); Dallas−Fort Worth (TX); Denver (CO, WY); Salt Lake City (UT); and Seattle−Tacoma (WA). In each study area, there were 12−14 sampling sites, except the Seattle−Tacoma area had 21 sampling sites. Sampling sites were "representative" stream reaches within wadable streams, selected so that there were no significant inflows or outflows over the course of the reach. Stream reaches were a minimum of 150 m long, had an average basin size of 369 km^2, and an average Strahler stream order of 2.5 ± 1. More details are provided in Moran et al.[19]

The sites within a study area spanned a wide range of urbanization. The 2006 land-use data were based on the National Land Cover Data (NLCD) 2006 data set[20] with the percentage of urbanization and agriculture in each basin calculated as described in Moran et al.[19] Sites ranged from 0.2 to 99.7% urban (Supporting Information (SI) Table S1). The remaining land cover varied by study area, but was typically agriculture or undeveloped (e.g., forest or rangeland).

Sample Collection and Processing. Each sediment sample was a composite of multiple grab samples collected from the top 2 cm in depositional zones from the stream reach. Once homogenized, the sediment was subsampled for various analyses. One subsample was passed through a 2.0-mm stainless steel sieve for analysis of pyrethroid insecticides and organic carbon, and one was used for toxicity testing. Moran et al.[19] described details on sediment handling and processing.

Chemical Analysis. Sediment samples were analyzed for trace elements, organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pyrethroids, total organic carbon (TOC), and grain size.[19]

Fourteen pyrethroid insecticides were analyzed in the bed sediments.[21] Briefly, wet sediments (about 50% moisture) were extracted with microwave-assisted solvent extraction using dichloromethane and methanol. Sediment matrix interferences were removed using stacked graphitized-carbon and alumina solid phase extraction cartridges, followed by gel permeation/high-pressure liquid chromatography. Prior to instrumental analysis, deuterated PAH standards from Cambridge Isotope Laboratories (Andover, MA) were added to each sample extract as internal standards. The final extracts (1 μL injection) were analyzed on a Varian (Walnut Creek, CA) CP-3800 gas chromatograph coupled to a Saturn 2000 ion-trap mass spectrometer in both single and tandem mass spectrometry modes. Neat pyrethroid standards purchased from Chem Service (West Chester, PA) were dissolved in acetone or methanol for an initial concentration of 1 mg/mL. Stock solutions were diluted to make calibration standards with concentrations ranging from 0.0025 to 2.5 ng/μL and a constant internal standard concentration of 2.0 ng/μL. Method detection limits (MDL) ranged from 1.0 to 2.6 μg/kg dry weight using GC/MS and 0.2 to 0.5 μg/kg dry weight using GC/MS/MS. Complete details of the analytical method and validation are given elsewhere.[21,22]

A comprehensive set of performance-based quality control parameters used for concentration validation included laboratory blanks, matrix spikes, replicate samples, and surrogate recovery. No pyrethroids were detected in any of the blanks. Replicate samples were within 25% agreement for all pesticides detected above the MDL. Matrix spikes added to environmental samples had recoveries ranging from 77 to 126%. Mean percent recoveries (and standard deviations) of surrogates in the samples, ^{13}C-labeled *p,p′*-DDE and cis-permethrin (Cambridge Isotope Laboratories Inc., Andover, MA), were 87 ± 10 and 93 ± 13, respectively.

Sediments were analyzed for organic carbon content using a Perkin-Elmer CHNS/O analyzer (Perkin-Elmer Corporation, Norwalk, CT). Before analysis, sediments were dried to a constant weight at 110 °C for 3 h. Sediments were combusted at 925 °C in silver boats after being exposed to concentrated hydrochloric acid (HCl) fumes in a desiccator for 24 h to remove inorganic carbon. Acetanilide was used for instrument calibration of elemental carbon.

Toxicity Testing. Whole-sediment toxicity tests were conducted with *H. azteca* starting with 7-d-old test organisms in 28-d exposures.[19] Toxicity endpoints included survival, weight, and biomass.[23,24] Amphipods were exposed to 100 mL of sediment with 175 mL of overlying water in 300-mL beakers with a total of four replicates per treatment. The source of the overlying water was well water diluted with deionized water to a hardness of 100 mg/L as $CaCO_3$. Toxicity tests were conducted in four batches (all samples from a study area in the same batch) and were started within one month of sediment collection. A control sediment collected from West Bearskin Lake, MN (about 3% TOC)[25] was tested with each batch of sediments. Test protocols include a photoperiod of 16:8 h light/dark, an exposure temperature of 23 °C, and daily feeding of test organisms.[23,24] Differences in toxicity endpoints relative to control sediment were determined by analysis of variance (ANOVA) with mean separation by Duncan's multiple-range test at $p < 0.05$ performed using SAS statistical software (SAS/STAT version 9.2; SAS Institute, Cary NC). Additional details on methods and statistical analyses can be found in Moran et al.[19]

Toxic Units. The contribution of pyrethroids to the observed toxicity in 28-d tests was evaluated using a toxic unit approach (TUs). First the organic-carbon normalized concentration was calculated by dividing the pyrethroid concentration by the organic carbon concentration (SI Table S1); then this value was divided by the organic-carbon (OC)

Table 1. Summary of Pyrethroid Detections and Organic-Carbon Normalized 10-d LC_{50} Values for *H. azteca*

pyrethroid	Log K_{oc}[21]	detection frequency (%)	study areas where pyrethroids were detected	maximum concn. (μg/kg, dry weight)	median detected concn. (μg/kg, dry weight)	method detection limit (μg/kg, dry weight)	10-d LC_{50} value for *H. azteca* (μg/g OC)[19]
bifenthrin	5.3	41	all 7 study areas	11.2	0.9	0.2	0.25
cyhalothrin	5.1	11	Atlanta, Dallas−Fort Worth, Milwaukee−Green Bay, Seattle−Tacoma, Salt Lake City	3.0	0.5	0.2	0.44
cypermethrin	7.8	1	Dallas−Fort Worth	8.9		0.4	0.38
permethrin	6.1	5	Dallas−Fort Worth, Denver	9.3	1.0	0.2	9.8
resmethrin	5.0	4	Boston, Denver, Seattle−Tacoma	38.3	5.3	0.5	2.17[a]

[a]Screening-level toxicity value (not specifically for *H. azteca*) from U.S. EPA Registration Eligibility Decision.[27]

normalized lethal concentration (LC_{50}) for *H. azteca*. Because 28-d LC_{50} values were not available, these values were estimated by dividing 10-d LC_{50} based on spiked sediment toxicity tests in the literature (listed in Table 1) by a factor of 2.[26] No sediment toxicity data were available for resmethrin so a screening-level toxicity value,[19] computed using the water-column 96-h LC_{50} value for the most sensitive invertebrate (pink shrimp), was used from the U.S. Environmental Protection Agency Registration Eligibility Decision[27] (Table 1). Toxicity from all the pyrethroids was assumed to be additive[28] so individual TUs were summed.

RESULTS AND DISCUSSION

Occurrence of Pyrethroids. Almost half (45%) of the 98 samples contained detectable concentrations of one or more pyrethroids (SI Table S1). Five of the fourteen pyrethroids measured were detected in this study: bifenthrin, cyhalothrin, cypermethrin, permethrin, and resmethrin (Table 1). Bifenthrin was detected the most frequently (41% of samples) and was often the only pyrethroid detected (Figure 1; Table 1). About a third of the samples with pyrethroid detections had at least two pyrethroids detected and the most frequent combination was bifenthrin with either cyhalothrin or permethrin (Figure 1). Bifenthrin concentrations ranged from less than the detection limit (0.2 μg/kg) to 11.2 μg/kg. The range of permethrin concentrations was similar, with a maximum of 9.3 μg/kg, while cyhalothrin concentrations were lower, with a maximum concentration of 3.0 μg/kg. In contrast, resmethrin was only detected in 4 samples but had the highest maximum concentration (38.3 μg/kg) of any pyrethroid (Table 1). Cypermethrin was only detected in one sample, at 8.9 μg/kg.

Bifenthrin also was the most frequently detected pyrethroid in urban streams in California,[9,15,16] Illinois,[17] Oregon/Washington,[29] and Texas.[18] As in the present study, the next most frequently detected pyrethroids in these previous studies were typically cyhalothrin and permethrin. Many of the California sites also contained elevated concentrations of cyfluthrin and cypermethrin. In contrast, bifenthrin was not detected at all in urban creeks in Tennessee.[15]

Concentrations of pyrethroids in most previous studies were generally higher than those reported here, especially in northern California[9,15,16] where bifenthrin and permethrin concentrations were up to 40 times higher than those detected in the current study (SI Table S1 and Figure S1). This difference may be partially due to contrasting study objectives and site selection criteria. In the current study,[19] sampling sites had no significant inflows over the stream reach; however, sites sampled in the California statewide urban study were located within an identified 50 m of urban stormwater outfalls and had previously demonstrated sediment toxicity to *H. azteca* in 10-d

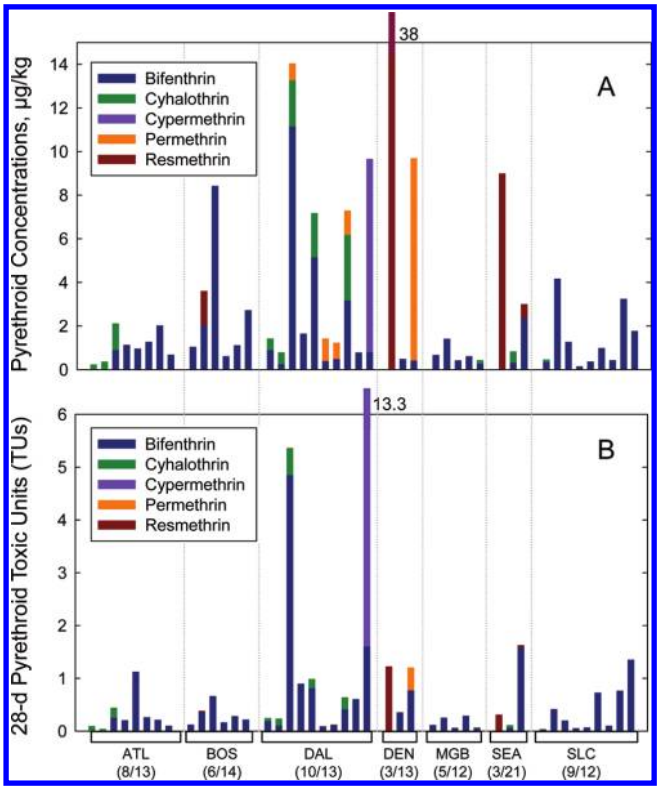


Figure 1. Stacked bar graphs by individual pyrethroids of (A) sediment pyrethroid concentrations and (B) TUs calculated for 28-d *H. azteca* tests. Only samples with pyrethroids detected (44 of the 98 total samples) are shown and the number of samples with detectable pyrethroids per number of total samples are shown in parentheses for each of the seven metropolitan areas. Samples within each area are arranged in order from low to high urban landuse in the watershed (ATL = Atlanta, GA; BOS = Boston, MA, NH; DAL = Dallas−Fort Worth, TX; DEN = Denver, CO; MGB = Milwaukee−Green Bay, WI; SEA = Seattle−Tacoma, WA; SLC = Salt Lake City, UT).

toxicity tests measuring effects on survival.[16] Although two other California studies varied in their site selection, samples with the highest concentrations were often collected just below storm drains outfalls.[9,15] In Texas, all sites were in close proximity to or receiving direct input from impervious surfaces draining residential single-family neighborhoods[18] and most of the urban samples in Illinois were taken from constructed storm drains.[17] In contrast, urban creeks in Tennessee, located in primarily low-density residential areas which were not served by storm sewers, reported concentrations of cyhalothrin, cypermethrin, and permethrin that were similar to the current study.[15]

dx.doi.org/10.1021/es2044882 | Environ. Sci. Technol. 2012, 46, 4297−4303

One previous study sampled urban streams in Oregon and Washington,[29] including five streams that were sampled in this study. About one-third of the 35 sediment samples contained detectable levels of pyrethroids with bifenthrin concentrations similar to the current study. Only one of the five overlapping locations (Juanita Creek near Kirkland, WA) had detectable bifenthrin concentrations in both the previous study[29] (4.8 μg/kg) and the current study (2.4 μg/kg).

Relationships between Pyrethroid TUs and Sediment Toxicity to *Hyalella azteca*. After converting pyrethroid concentrations to 28-d TUs, there was a shift in the overall pattern due to organic-carbon normalization and differing toxicity of the various pyrethroids (Figure 1B). The Dallas–Fort Worth samples had both the highest concentrations and the highest pyrethroid TUs compared to the other study areas. Although the Boston samples had somewhat similar concentrations, the TUs were much lower due to the higher organic carbon content of the sediments (SI Figure S2 and Table S1). The LC_{50} values for permethrin and resmethrin are about an order of magnitude higher than those of bifenthrin, cyhalothrin, or cypermethrin (Table 1). This lower estimated toxicity of permethrin and resmethrin was evident in the lower TU values, in comparison to other sites, for the Denver sample with high permethrin, the Denver sample with high resmethrin, and the Seattle–Tacoma sample with high resmethrin (Figure 1A and B).

The highest TU value, 13.3 in one stream in Dallas–Fort Worth area, was primarily due to cypermethrin (88% of the TU value). Although the sample with the next highest TU value (5.4) was from the same study area, the main contributor was bifenthrin (90%). The majority of the samples had TUs less than 1.0 (Figure 1B). On average, bifenthrin contributed the most to the pyrethroid TUs (81%), followed by cyhalothrin (11%). Previous urban studies in California, Illinois, and Texas[15−18] have also found that the majority of the pyrethroid TUs were due to bifenthrin.

In sediment toxicity tests with *H. azteca,* 25 of the 98 sediment samples (26%) had significant reduction in survival relative to the control during a 28-d exposure, and total (100%) mortality was not observed in any of the sediment samples (SI Table S1). Survival was the most sensitive endpoint in the amphipod test.[19] Sediment from the current study was considerably less toxic than in most of the previous 10-d toxicity tests conducted with pyrethroid-contaminated sediments, which is consistent with the correspondingly lower pyrethroid concentrations.[9,15−18]

Specifically, samples contaminated with pyrethroids collected near direct urban inputs in California and Texas[9,15,16,18] showed considerably higher toxicity to *H. azteca* in in 10-d exposures than was observed during the current study in 28-d exposures; moreover, 100% mortality was frequently observed in these previous studies. Results from urban streams in Illinois[17] were intermediate, with significant effects on survival of *H. azteca* in sediment from 59% of urban sites, but with no samples exhibiting 100% mortality in 10-d exposures. Sediments from only one site (of the 30 sites sampled) in Oregon/Washington[29] were acutely toxic to *H. azteca*. None of the samples from Nashville, TN showed significant effects on survival of *H. azteca* in 10-d exposures, consistent with low concentrations of pyrethroids and no detections of bifenthrin.[15]

Relationships between survival of *H. azteca* in the 28-d exposures and pyrethroid TUs are presented in Figure 2. Samples with no detectable pyrethroids were assigned a TU of 0.01 (one-half of the lowest measured total TU). The correlation between log-transformed total pyrethroid TUs and observed *H. azteca* survival relative to control was significant ($p < 0.001$; Figure 2). Eight samples contained one TU or more, and half of these samples reduced survival of *H. azteca* in 28-d exposures. The four samples in which survival was not significantly reduced relative to control had TUs between 1.1 and 1.4. Previous toxicity studies have also noted lower than predicted mortality in sediment with 1−3 pyrethroid TUs.[9,15,18] In the current study, there were 36 samples with detectable pyrethroids but less than one TU, and 44% (16) of these samples reduced survival of *H. azteca* in 28-d exposures. A similar pattern was seen in Illinois urban streams where 7 of the 12 samples with TUs between 0.08 and 0.65 TUs reduced survival of *H. azteca* in 10-d toxicity tests.[17] The remaining 54 samples in the current study did not contain any detectable pyrethroids but seven of these were toxic, suggesting contaminants other than pyrethroids were contributing to the toxicity.[19]

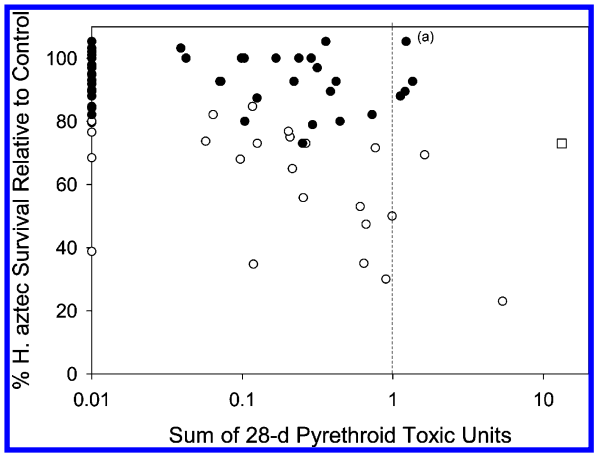


Figure 2. Relationship between the sum of pyrethroid TUs in stream sediments and the toxicity to *H. azteca* in 28-d laboratory sediment toxicity tests. Open symbols are samples with survival significantly less than the control; filled symbols are not significantly less than the control. Square is sample with cypermethrin as main contributor to TU. Samples with no detectable pyrethroids were assigned a TU value of 0.01. The point designated as (a) is discussed in the text.

The high cypermethrin concentration in the Dallas–Fort Worth sample (Figure 1B) resulted in the highest TU for any sample (13.3). Although significantly different from the control, *H. azteca* survival (73%) was much higher than predicted from the TU value (Figure 2; SI Table S1). This type of an outlier has been seen in other studies.[15,17,18] The lower-than-predicted toxicity suggests that other factors, such as the high sand (75%) and low organic carbon content (0.4%) (SI Table S1), may be influencing the bioavailability of cypermethrin in this sample. The results of a study comparing chemical availability and sediment toxicity[30] showed that sorption to sandy sediments with low organic carbon content may decrease pyrethroid bioavailability and toxicity to *H. azteca*.

One of the nontoxic samples from the Denver area (point designated as (a) in Figure 2) had a very high concentration of resmethrin (38.3 μg/kg) which accounted for the 1.2 TUs. The screening-level toxicity value for resmethrin[27] was computed using the equilibrium sediment partitioning approach and assumes the same toxicity to benthic organisms as water-column species. It is likely that the LC_{50} value used for

resmethrin (Table 1) was too low and overestimated the toxicity.

The significant correlation between calculated TUs and observed *H. azteca* survival suggests that pyrethroids are likely a major cause of the observed toxicity. In addition to the 14 pyrethroids, 94 chemical analytes were quantified in this study, including PAHs, OCPs, PCBs, fipronil compounds, priority trace, and other major elements.[19] Of all the contaminants analyzed, bifenthrin was the best single predictor of toxicity to *H. azteca*.[19] A more detailed assessment of the potential contribution of contaminants other than pyrethroids to the sediment toxicity is beyond the scope of this paper.

Sources of Pyrethroids. In urban areas, pyrethroids are commonly used for golf course turf, ornamentals, residential lawns, rights-of-way, and structural pest control. Because the sampling sites for this study spanned a range of urbanization, other potential sources of pyrethroids need to be considered including use for agriculture, animal premises, and vector control. The relative importance of urban versus other sources can be separated using land cover statistics for the sampled sites (Figure 3; SI Table S1).

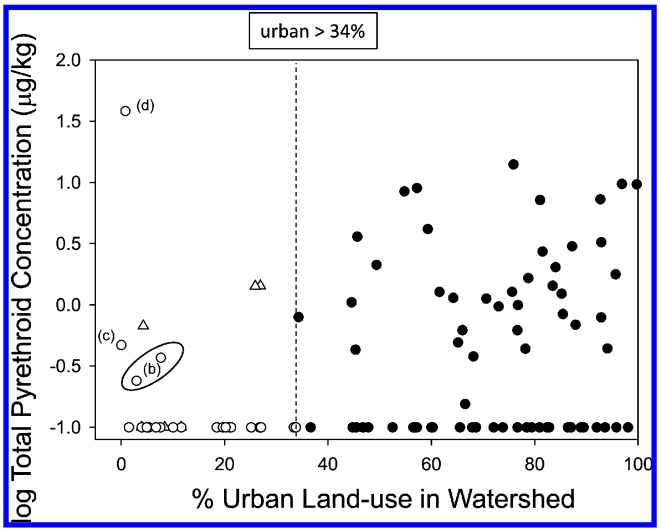


Figure 3. Relationship between total pyrethroid concentrations and land use. Closed circles indicate urban land use >34%, open triangles indicate agricultural land use >28%, and open circles indicate undeveloped land use >50%. Nondetects are plotted as half the method detection limit (0.1). The points designated as (b), (c), and (d) are discussed in the text.

The log-transformed total pyrethroid concentration was significantly correlated to the percent urban land in the basin (p value <0.01; Figure 3). Sixty-nine of the 98 sites (70%) were primarily urban, which was defined as having urban land use >34% and more urban than agricultural area within the watershed. The majority of samples with detectable pyrethroids (84%) were observed in these primarily urban streams (Figure 3; SI Table S1).

Pyrethroids are also used on a variety of crops. Six sites have some agricultural influence (defined as having agricultural land use that is >28% and also greater than urban land use; SI Table S1); half of these sites had pyrethroids detected (Figure 3). In the remaining 23 sites, the land use is relatively undeveloped (urban <34% and agricultural <22%) and pyrethroids were only detected at four of these sites (Figure 3). Cyhalothrin was detected at two Atlanta sites with 10−22% agriculture and very low urban percentage (points designated as (b) in Figure 3) and could have come from registered use on nearby poultry farms. Two undeveloped sites (with combined urban and agricultural land use of <2%) had detectable pyrethroid concentrations. Of these, one sample from Salt Lake City (point designated as (c) in Figure 3) had very low concentrations of bifenthrin (0.35 µg/kg) and cyhalothrin (0.12 µg/kg), but the source of these pyrethroids is unknown. The other is a sample from Denver (point designated as (d) in Figure 3), which contained only resmethrin and is discussed below.

Resmethrin was detected infrequently (in only 4% of the sediment samples) and its occurrence did not appear to be related to urban or agricultural use. Registered for use in animal premises, commercial buildings, homes, and industrial settings, resmethrin is primarily used to control adult mosquitoes for public health.[27] The highest concentration (38.3 µg/kg) detected in this study was at a site within Estes Park, CO (point designated as (d) in Figure 3) which is considered an undeveloped watershed. Possible sources of the resmethrin[27] may be aerial transport from applications to control mosquitoes that may carry West Nile virus, or use for insect control at a nearby horse stable. Few previous pyrethroid studies included the analysis of resmethrin, so there are limited data for comparison. The highest resmethrin sediment concentration reported previously was 18.7 µg/kg on suspended sediments in a small agricultural watershed in the San Joaquin Valley of California.[31]

National Perspective. For comparison with prior studies of urban streams, results from the current study were limited to the 69 sites that are primarily urban (>34% urban land in the watershed). Pyrethroid occurrence for these urban sites was compared across the seven study areas in the current study (Figure 4A, B). Dallas had the highest number of sites with pyrethroid detections (9 out of 10 sites), the most samples (7) containing multiple pyrethroids, and the highest concentrations of pyrethroids. Consistent with these high concentrations, Dallas also had the highest observed frequency of toxicity to *H. azteca* in 28-d exposures (8 of the 10 samples). In contrast, Salt Lake City had a similar number of sites with detections, but bifenthrin was the only pyrethroid detected, concentrations were generally lower than those in Dallas, and only one-third of the samples reduced survival of *H. azteca*. Both Atlanta and Boston had pyrethroid detection frequencies ≥50% and had lower concentrations of pyrethroids compared to Dallas. One-third or less of the urban samples contained detectable concentrations of pyrethroids in the Denver, Milwaukee−Green Bay, and Seattle study areas.

The results of the current study suggest that there are major regional differences in pyrethroid concentrations and corresponding toxicity in urban stream sediments across the United States. The high concentrations and detection frequency in Dallas are likely due to elevated use of pyrethroids to control fire ants, grub worms, and termites.[18] The infrequent detection of pyrethroids in Atlanta is surprising considering the presence of fire ants, but other insecticides such as fipronil are available and may be used instead of pyrethroids. In Salt Lake City, bifenthrin is used to control a variety of pests such as grasshoppers, lilac-ash borer, spiders, and scorpions. Pyrethroid use likely varies across the country but quantitative data on amounts applied or retail sales data are not available. Besides differences in pesticide-use patterns, hydrologic processes responsible for transporting pyrethroids from their application

dx.doi.org/10.1021/es2044882 | Environ. Sci. Technol. 2012, 46, 4297−4303

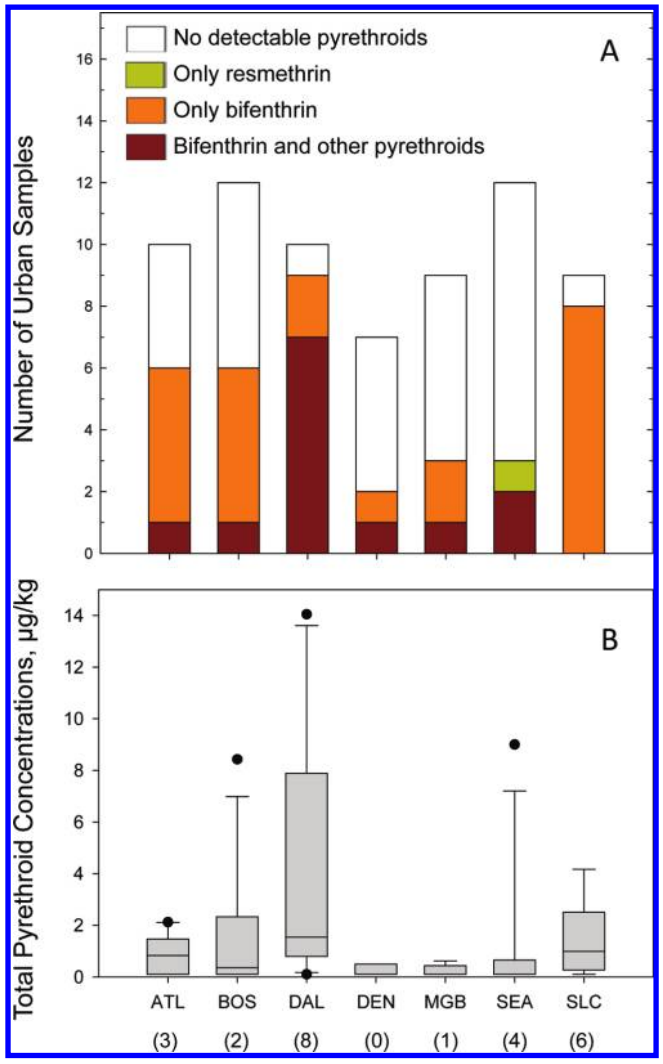


Figure 4. Comparison of pyrethroid occurrence for the primarily urban sites (>34%) across the seven metropolitan areas. (A) Number of samples with pyrethroid detections or no detections. (B) Boxplot of total pyrethroid concentrations (nondetects are included as half the method detection limit). Number of samples that had significant reduction in survival relative to the control are listed in parentheses.

site to urban streams also can vary considerably across the country. Previous studies have pointed out the potential importance of timing and amount of rainfall and presence/absence of storm drain systems.[9,15,18] In the present study, natural environmental setting (e.g., climate, elevation, slope, soils) varied substantially among study areas but comparatively little within a study area.[19] A detailed analysis of the relative importance of all these potential factors is beyond the scope of this paper.

A national perspective can be gained by qualitatively comparing the results of the current study with previous urban studies (SI Figure S1). A direct comparison is limited because of differences in study design, ranging from targeted sampling near contamination sources[16,18] to sampling stream reaches with no significant inflows in the current study.

In previous studies within California,[9,15,16] "hot spots" of pyrethroid contamination and related sediment toxicity were detected, specifically in the Central Valley, Los Angeles, Roseville, Sacramento, and San Diego. Compared to these areas, other watersheds in California, including the San Francisco Bay area and East Bay, had significantly lower pyrethroids concentrations and a lower incidence of toxicity.[15,16] Still lower concentrations were detected in Texas and Illinois.[17,18] In comparison, the highest concentrations in the current study were detected in Texas (Dallas), albeit at considerably lower concentrations compared to a previous urban-source targeted study in central Texas.[18] The pyrethroid concentrations in the other six areas from the current study were even lower. Finally, sites sampled in Nashville, TN[15] had pyrethroid concentrations equal to or lower than the current study. As expected from pyrethroid concentrations observed in these studies, toxicity of sediments to *H. azteca* in 28-d exposures in the current study was lower than previously reported for urban streams in California, Texas, and Illinois, but higher than in Nashville, TN.

The results of the nationally consistent approach used in the current study suggest that pyrethroids commonly occur in urban stream sediments and may be contributing to sediment toxicity across the country. Although none of the sediment samples caused total (100%) mortality to *H. azteca* during a 28-d exposure, decreased survival was observed in approximately one-quarter of the samples and is likely due to pyrethroids. In particular, the frequent occurrence of bifenthrin and its likely contribution to toxicity demonstrates the need for additional monitoring and assessment. Further evaluation of the factors influencing bioavailability of pyrethroids in stream sediments[30] and laboratory studies of resmethrin toxicity to benthic organisms is needed.

■ ASSOCIATED CONTENT

Supporting Information

Analytical results for organic carbon, percent sand, and pyrethroid insecticides, calculated TUs, percent survival of *H. azteca* in 28-d toxicity tests, and land use within each basin (Table S1), boxplots of bifenthrin concentrations from previous and current studies (Figure S1), and boxplots of organic carbon concentration of samples with detectable pyrethroids by study area (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Kelly Smalling, James Orlando, and Kristi Jones for their help in processing and analyzing field samples and interpreting data. This study was a joint effort between the USGS Toxic Substances Hydrology Program, the USGS National Water Quality Assessment Program, and the USGS Contaminant Biology Program. We express our appreciation to Steve Corsi and Jason Belden for reviewing the manuscript and making helpful suggestions. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government. This manuscript has been reviewed in accordance with USGS policy.

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