Journal of Hazardous Materials 324 (2017) 258–271

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Review

Global occurrence of pyrethroid insecticides in sediment and the associated toxicological effects on benthic invertebrates: An overview

Huizhen Li[a], Fei Cheng[b,d], Yanli Wei[b], Michael J. Lydy[c], Jing You[a,*]

[a] School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou, 510632, China
[b] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
[c] Center for Fisheries, Aquaculture and Aquatic Sciences and Department of Zoology, 251 Life Science II, Southern Illinois University, Carbondale, IL, 62901, United States
[d] University of Chinese Academy of Sciences, Beijing, 100049, China

HIGHLIGHTS

- Current knowledge on pyrethroids in sediment is reviewed on a global scale.
- Toxicity of sediment-associated pyrethroids to benthic invertebrates is evaluated.
- Potential risk of pyrethroids to benthic community is simulated based on SQC.
- Sediment-bound pyrethroids exhibited potential risk to benthic organisms globally.
- Factors influencing sediment risk assessment of pyrethroids is discussed.

ARTICLE INFO

Article history:
Received 12 April 2016
Received in revised form 17 October 2016
Accepted 24 October 2016
Available online 25 October 2016

Keywords:
Pyrethroid insecticides
Sediment
Global occurrence
Toxicity
Benthic invertebrates

ABSTRACT

Pyrethroids are the third most applied group of insecticides worldwide and are extensively used in agricultural and non-agricultural applications. Pyrethroids exhibit low toxicity to mammals, but have extremely high toxicity to fish and non-target invertebrates. Their high hydrophobicity, along with pseudo-persistence due to continuous input, indicates that pyrethroids will accumulate in sediment, pose long-term exposure concerns to benthic invertebrates and ultimately cause significant risk to benthic communities and aquatic ecosystems. The current review synthesizes the reported sediment concentrations of pyrethroids and associated toxicity to benthic invertebrates on a global scale. Geographically, the most studied area was North America, followed by Asia, Europe, Australia and Africa. Pyrethroids were frequently detected in both agricultural and urban sediments, and bifenthrin and cypermethrin were identified as the main contributors to toxicity in benthic invertebrates. Simulated hazard quotients (HQ) for sediment-associated pyrethroids to benthic organisms ranged from 10.5 ± 31.1 (bifenthrin) to 41.7 ± 204 (cypermethrin), suggesting significant risk. The current study has provided evidence that pyrethroids are not only commonly detected in the aquatic environment, but also can cause toxic effects to benthic invertebrates, and calls for better development of accurate sediment quality criteria and effective ecological risk assessment methods for this emerging class of insecticides.

Contents

* Corresponding author.
E-mail address: youjing@jnu.edu.cn (J. You).

http://dx.doi.org/10.1016/j.jhazmat.2016.10.056
0304-3894/

1. Introduction

Pesticides are intentionally applied in large quantities in agriculture to boost yields, as well as in urban areas for landscape maintenance and household use. Pesticides are designed to kill pests; however, these chemicals threaten not only target pests, but also many non-target species [1]. The cost of pesticide use is great in regard to product costs, but also in terms of the toxicological effects to the environment [1,2]. Pesticides, particularly insecticides, are among the most ecologically toxic chemicals in aquatic ecosystem worldwide [1,3–5]. There are increasing concerns about pesticide residues in surface water due to their potential impact on freshwater biodiversity and ecosystem functioning [1,6–8].

To reduce pest resistance and undesired toxicity to non-target organisms, newer generations of insecticides, such as pyrethroids and neonicotinoids, have been developed to replace older classes of pesticides including organochlorine, organophosphate and carbamate insecticides [9]. Due to their high efficiency, broad spectrum of effects and low mammalian toxicity, pyrethroids have been increasingly used in agricultural and residential pest control since the early 2000 s [10,11]. Currently, pyrethroids are among the most important classes of insecticides in crop and human protection, i.e. accounting for 38% of the world insecticide market share in 2015 [12]. Surprisingly, recent studies have found that pyrethroids have higher aquatic risk associated with their use compared with older-generation insecticides [1,8].

Pyrethroid residues are frequently detected in different environmental compartments including sediment, which serves as a major sink for this class of hydrophobic insecticides [13]. After entering an aquatic system, pyrethroids rapidly dissipate from the dissolved water phase and bind to organic carbon in sediment particles [14,15]. Sediment-associated pyrethroids not only pose risk to sediment-dwelling non-target organisms [16,17], but also act as a secondary source of contaminants releasing into surface water and causing adverse effects to water column species [13]. Stehle and Schulz [8] suggested that pyrethroids were the greatest emerging concern of the pesticide classes in sediment. The application, fate and toxic effects of pyrethroids in water have been previously reviewed at the regional scale [18–20], but the occurrence, toxicity and risk of pyrethroids in sediment have not yet been summarized. While studies on the occurrence of sediment-associated pyrethroids have been reported, they have been limited to certain regions, mainly in the United States and China. Therefore, a review of the occurrence and risk of sediment-associated pyrethroids on a global scale is warranted.

The current review synthesized available data on pyrethroid insecticide residues in sediment and the associated toxic effects to benthic invertebrates. It also provides an overview of their spatial distribution and relationship to global land use patterns. Finally, this review discusses the importance of bioavailability in defining sediment toxicity of pyrethroid insecticides and the extrapolation from sediment toxicity to ecological risk in aquatic systems.

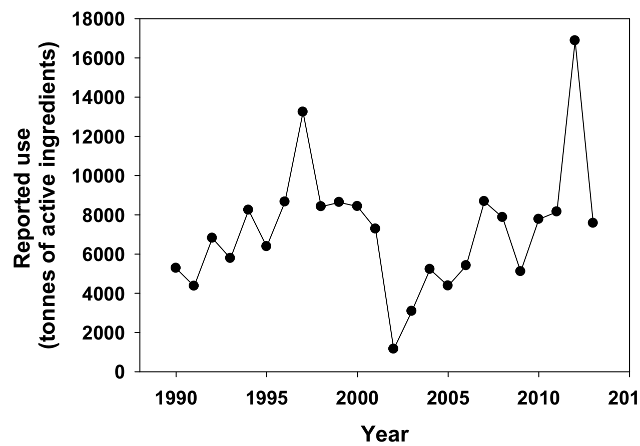

Fig. 1. The worldwide annual use of pyrethroid active ingredients reported by FAOSTAT (http://faostat3.fao.org/search/pyrethroid/E).

2. Properties and use of pyrethroid insecticides

Pyrethroids are a group of synthetic insecticides derived from pyrethrins, which are the insecticidal active substances in chrysanthemum flowers (*Chrysanthemum cinerariaefolium*). Pyrethroid insecticides are neurotoxicants, acting upon voltage-gated sodium channels on nerves and prolonging the time the channels are open. Pyrethroids are classified into two types based on their mode of toxic action. Type I pyrethroids (e.g. permethrin) cause hyperactivity and incoordination. Alternatively, type II pyrethroids (e.g. cypermethrin) usually contain an "α-cyano" group and induce nerve depolarization, and subsequently paralysis of the target species [21].

First-generation photo-labile pyrethroids (e.g. allethrin) were synthesized during the 1950s through the early 1970s, and many are still used as active ingredients in mosquito repellents today [22]. Later, photo-stable pyrethroids were introduced to the market. Due to their photo-labile property, first-generation synthetic pyrethroids are mainly used in indoor household, industrial, and commercial settings. In contrast, second-generation photo-stable synthetic pyrethroids are mainly registered for use in agricultural and non-agricultural activities outdoors.

Pyrethroids have been extensively used all over the world. Fig. 1 shows the worldwide annual use of pyrethroid active ingredients from 1990 to 2013 and the data were collected from FAOSTAT [23]. In general, the reported use of pyrethroid active ingredients fluctuated around a mean value of 7000 t, with two peaks in 1997 (13,200 t) and in 2012 (16,800 t) and a sharp decrease in their use in 2002 (1150 t). Geographically, Ukraine, Pakistan, Turkey, Paraguay and India were the top five countries in use

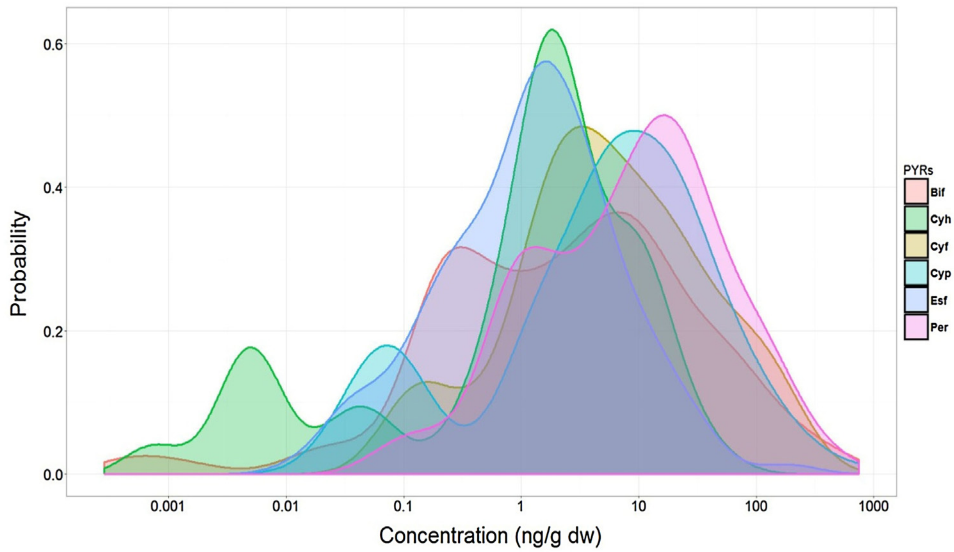

Fig. 2. The frequency distribution of detected pyrethroid concentrations (ng/g dry weight (dw)) in sediments from the current survey dataset. A histogram was established based on the frequency density and concentration, and was smoothed using software R (version 3.2.5, *ggplot2* package). Target pyrethroids (PYRs) included bifenthrin (Bif), *lambda*-cyhalothrin (Cyh), cyfluthrin (Cyf), cypermethrin (Cyp), esfenvalerate (Esf) and permethrin (Per).

of pyrethroid active ingredients. Unfortunately, detailed use data on individual pyrethroids are lacking for most countries and regions. The most complete datasets in terms of use data for pyrethroids in the field are from California in the U.S. As reported in the California Department of Pesticide Regulation Pesticide Sales Database [24], permethrin, cypermethrin, bifenthrin, cyfluthrin, fenpropathrin, *lambda*-cyhalothrin and esfenvalerate were the top seven pyrethroids applied in agricultural, commercial structural and landscape maintenance applications in California [11].

Physicochemical properties of the most commonly used pyrethroids are shown in Table 1 and the values were from literature [25–33]. In general, pyrethroids have relatively low vapor pressures; therefore, they have a limited tendency to volatilize during application or re-volatilize when they are in the environment. Their low water solubility and high octanol-water partition coefficients (log K_{ow}) suggest fast dissipation from water and a high affinity for organic matter, e.g. suspended particles and sediment. In other words, pyrethroids are more likely to be retained at or close to the application sites compared to the more water soluble and volatile insecticides [19]. Although pyrethroids are less toxic to mammals than organophosphate insecticides, they exhibit extremely high toxicity to non-target fish and invertebrate species [34,35] after entering aquatic systems via runoff and/or atmospheric deposition [2,13]. Hence, the occurrence and toxicity of sediment-associated pyrethroids is an emerging concern [1].

3. Evidence of sediment contamination by pyrethroids

The current study provides an overview of the occurrence and toxicity of pyrethroids in sediment, and was conducted using the keywords “pyrethroid” and “sediment” with a literature search on the ISI web of science. In addition, the six pyrethroids, bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin, esfenvalerate and permethrin were individually used as a keyword to replace “pyrethroid” and further searched on the ISI Web of Science. The search was undertaken in March, 2015 and re-checked in August, 2016; thus, the articles published after August, 2016 were not included in the statistical analysis as part of this review.

In total, approximately 400 papers were examined and 58 of these papers reported pyrethroid concentrations in field sediments, which are listed in Table S1 (“S” represents figures and tables in the Supplemental material thereafter). Some papers detailed concentrations of each detected pyrethroid in each sediment, whereas other papers only provided a range of concentrations or mean concentrations plus standard deviations in the text. Only data that included detailed concentrations were used for further analysis as indicated in Table S1. If an individual pyrethroid was detected at a concentration lower than its reporting limit or was not detected, its sediment concentration was considered to be half of the reporting limit or zero, respectively and was included in the data analysis [36]. Significant differences in sediment pyrethroid concentrations among individual pyrethroids, locations, and land use types were evaluated by a non-parametric Kruskal-Wallis analysis for multiple comparisons (one-tailed test, $\alpha = 0.05$) using software R (version 3.2.5, *npmc* package).

3.1. Occurrence of pyrethroid residues in sediment

3.1.1. A summary

A summary of pyrethroid residues in sediment collected in the current data survey is presented in Table S1. Geographically, the most studied area was America (33 and three studies were conducted in North America and South America, respectively), followed by Asia (13 and two studies were conducted in East Asia and South Asia, respectively), Europe (five), Australia (one) and Africa (one). According to the statistical usage data [23], countries from Europe, South America and South Asia consumed the most pyrethroid active ingredients; however, investigations of environmental occurrence and risk of pyrethroids have lagged far behind in these areas of the world.

Pyrethroids were frequently detected in the sediments sampled during 2000 through 2013 in this dataset (Table S1), except for studies in England, which were conducted in the 1990s. Bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin, esfenvalerate and permethrin were the dominant pyrethroid residues in all sediment samples, with detection frequencies of 78%, 37%, 49%, 48%, 43% and 57%, respectively. The frequency distribution of concentrations of these six pyrethroids in sediment is plotted in Fig. 2, with 80% of the detected concentrations being in the range of 0.1 to 100 ng/g dry weight (dw).

Table 1
Physicochemical and environmental properties and sediment benchmarks for selected pyrethroid insecticides.

Property/benchmark	Allethrin	Bifenthrin	Cyfluthrin	*lambda*-Cyhalothrin	Cypermethrin	Deltamethrin	Esfenvalerate	Fenpropathrin	Permethrin
Type	First generation	Second generation type I	Second generation type II	Second generation type II	Second generation type II	Second generation type II	Second generation type II	Second generation type II	Second generation type I
Molecular weight	302.4	422.9	434.3	449.9	416.3	505.2	419.9	347.4	391.3
Solubility ($\mu g\,L^{-1}$)	984 (EPI)[a]	0.014	2.3	5.0	4.0	0.20	6.0	10.3	5.5
Henry's law constant (atm m^3 mol^{-1})	6.12E-07 (EPI)	7.20E-03	3.70E-06	1.90E-07	3.40E-07	3.10E-07	1.40E-07	6.30E-07	1.40E-06
Vapor Pressure (mm Hg)	3.53E-05 (EPI)	1.80E-07	1.50E-08	1.60E-09	2.50E-09	9.30E-11	1.50E-09	1.40E-08	1.50E-08
log K_{ow} [25]	4.78 (EPI)	6.40	5.97	7.00	6.54	4.53	5.62	6.00	6.90
log K_{OC} [25]	3.49 (EPI)	5.37	5.09	5.51	5.49	5.85	–[b]	4.63	5.44
log K_{OC} based on SPME measurements [26]	–	6.34	6.48	5.85	6.20	6.18	6.64	5.70	6.26
log K_{DOC} based on SPME measurements [26]	–	6.26	6.08	6.30	6.00	6.32	6.15	5.85	5.90
log $K_{PDMS\text{-}WATER}$ using 7-μm PDMS fiber [27]	–	4.22	4.24	4.15	4.33	4.14	4.06	4.44	4.50
Soil degradation half life (d, aerobic) [25]	75 (EPI)	96.3	11.5	42.6	27.6	24.6	38.6	22.3	39.5
Soil degradation half life (d, anaerobic) [25]	–	425	33.6	–	55	28.9	90.4	276	197
Sediment degradation half life (d, aerobic) [26]	–	629	30	89	–	–	–	89	–
Sediment LC50 to *Hyalella azteca* (μg/g OC, 10 d)	–	0.11[c]	1.08[d]	0.45[d]	0.38[e]	0.79 [d]	0.89[d]	1.57[f]	10.8[d]
Sediment LC50 to *Chironomus dilutus* (μg/g OC, 10 d)	–	6.2[c]	1.9[g]	2.8[c]	1.34[e]	–	4.8[g]	8.9[f]	24.5[c]
Integrated threshold effect benchmark (μg/g OC) [28]	–	0.17	0.046	0.023	0.049	0.02	0.055	0.11	0.42

[a] Data from Estimation Program Interface (EPI) Suite™ provided by U. S. Environmental Protection Agency.
[b] Data was not available.
[c] Median lethal concentration (LC50) data from Maul et al. [29].
[d] LC50 data from Amweg et al. [30].
[e] LC50 data from Maund et al. [31].
[f] LC50 data from Ding et al. [32].
[g] LC50 data from Mehler et al. [33].

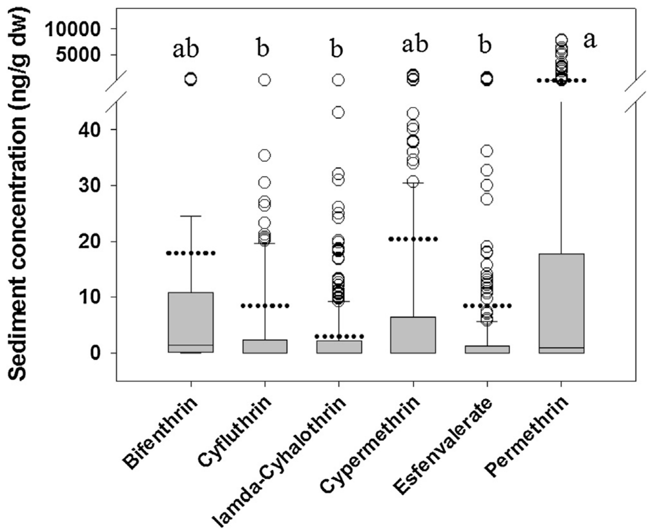

Fig. 3. Box plot of pyrethroid concentrations (ng/g dry weight (dw)) in sediments from the current survey dataset. The open dots represent outliers. The three solid lines in the box represent 25%, 50% and 75% of pyrethroid concentrations. The dashed line represents mean concentration, and the bars represent standard deviations. Different lowercase letters on the top of each box represent significant differences ($p < 0.05$), i.e. sites sharing the same letter are not significantly different from one other, while sites with different letters are significantly different.

Mean (± standard deviation) sediment concentrations for bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin, esfenvalerate and permethrin were 18.0 ± 52.8, 8.41 ± 27.2, 2.92 ± 7.85, 20.4 ± 100, 8.44 ± 50.8 and 138 ± 773 ng/g dw, respectively. Overall, bifenthrin, cypermethrin and permethrin were detected at higher concentrations in sediment than the remaining three pyrethroids, and their concentrations were not significantly different from one another (Fig. 3). Sediment concentrations for permethrin were statistically greater than those for cyfluthrin, *lambda*-cyhalothrin and esfenvalerate, while bifenthrin and cypermethrin concentrations were not significantly greater than cyfluthrin, *lambda*-cyhalothrin and esfenvalerate ($p < 0.05$).

Pyrethroid residues in field sediments were consistent with their use patterns, i.e. bifenthrin, cypermethrin and permethrin were the top three pyrethroids being used [11]. In addition, bifenthrin has a longer half life in sediment (>1 yr) than other pyrethroids (weeks to months) and is more persistent in sediment [25,26], which helps explain its relatively high sediment residues. In addition to the six most frequently detected pyrethroids, fenpropathrin and deltamethrin were also detected in some sediments (Table S1). Fenpropathrin was detected in sediments in the U.S. [16,37,38] and China [39], with a peak concentration at 54.5 ng/g dw in the sediment collected in an urban stream in South China [39]. Deltamethrin was detected in sediments collected in the U.S. [40], Botswana [41], Vietnam [42] and China [43], with a peak concentration of 59,714 ng/g dw in a sediment collected from an urban river in Ha Noi, Vietnam [42]. Since data for fenpropathrin and deltamethrin were limited, they were not included for further discussion in this review.

As a photo-labile first-generation pyrethroid, it was surprising that allethrin was only referenced in one study, which found allethrin in sediments collected from Chao Lake, China. Unfortunately, no detailed concentration data were reported in this paper [44]. A recent study monitored atmospheric pyrethroids in the Pearl River Delta (PRD), China, and found that allethrin was the third most dominant pyrethroid detected in air samples, which implied that the extensive usage of allethrin-based mosquito repellents has caused residues of this insecticide to be present in the environment [22,45]. Thus, allethrin should be included in the target list in the future when monitoring the occurrence of pyrethroids in aquatic system.

3.1.2. Geographical distribution

As mentioned above, monitoring of pyrethroid concentrations in sediment were mostly conducted in the U.S. and China, with a few studies being performed in other countries (Table S1). Therefore, the spatial distribution of individual pyrethroids in different cities and/or regions was evaluated based on the detailed data indicated in Table S1. The results are presented in Fig. 4 and the significance among each location for individual pyrethroids are shown in Table S2.

Bifenthrin was the most frequently detected pyrethroid in sediment, with an overall detection frequency of 78%. Sediment concentrations from the U.S., Australia and China were available to evaluate the spatial distribution of bifenthrin (Fig. 4A). Sediments collected from Florida in the U.S. contained the highest concentration of bifenthrin on average of samples taken, and this concentration was significantly higher than concentrations detected in sediments from Atlanta, Boston, California, Dallas and Texas in the U.S. Bifenthrin concentrations in sediments from Texas were significantly higher than those from Atlanta, Dallas, Milwaukee, Salt Lake City, Seattle in the U.S. and the Pearl River Delta in China. In addition, sediments from Melbourne, Australia had bifenthrin concentrations comparable with those from the U.S. and China. Sediment concentrations of cyfluthrin from California in the U.S. were compared with those from Liao River, Tai Lake and the PRD in China, and the results showed that sediments from California contained significantly higher residues of cyfluthrin than those from China (Fig. 4B). For *lambda*-cyhalothrin, concentrations in sediments from California, Illinois and Texas in the U.S. were comparable, and concentrations from California were significantly higher than those from Liao River and Tai Lake in China, but were significantly lower than those from the PRD, China (Fig. 4C).

In terms of cypermethrin, sediment concentrations from the U.S. (California and Texas), Argentina (Riodela Plata Estuary), England (Humber), Vietnam (Ha Noi) and China (Chao Lake, Liao River, Tai Lake and the PRD) were available to evaluate their spatial distribution (Fig. 4D). Sediments from Humber, England had the highest mean concentration of cypermethrin at 135 ng/g dw and a peak concentration of 1140 ng/g dw [46]. Although certain sediments from Humber contained extremely high residues of cypermethrin, mean sediment concentrations of cypermethrin from Humber were not significantly higher than those from other countries due to the low detection frequency (18%). Apart from sediments from Humber in England, sediments from the PRD, China contained significantly higher concentrations of cypermethrin than those from California in the U.S. Unlike bifenthrin, which was the most abundant sediment-associated pyrethroid in the U.S., cypermethrin was the most prevalent pyrethroid detected in sediments in China. For example, 95% of the sediments ($n = 58$) sampled in the PRD contained cypermethrin concentrations greater than the reporting limit [39,47,48]. Cypermethrin is one of the most commonly used pyrethroids in Asia and its extensive use has caused elevated residues in sediment [49]. Within China, cypermethrin sediment concentrations were significantly greater in the PRD of South China compared with those in Chao Lake in the central eastern portion of China. The warm and humid weather in the PRD enhances pest outbreaks, and thus pesticide applications are more frequent in the PRD compared with Anhui Province where Chao Lake is located [50]. In addition, sediments from Ebro River in Spain [51] contained cypermethrin residues significantly higher than those from California in the U.S. and Chao Lake in China.

For esfenvalerate, sediments from Humber, England had the highest mean concentration of 91.4 ± 169 ng/g dw and a peak concentration of 628 ng/g dw [46]. Similar to cypermethrin; however,

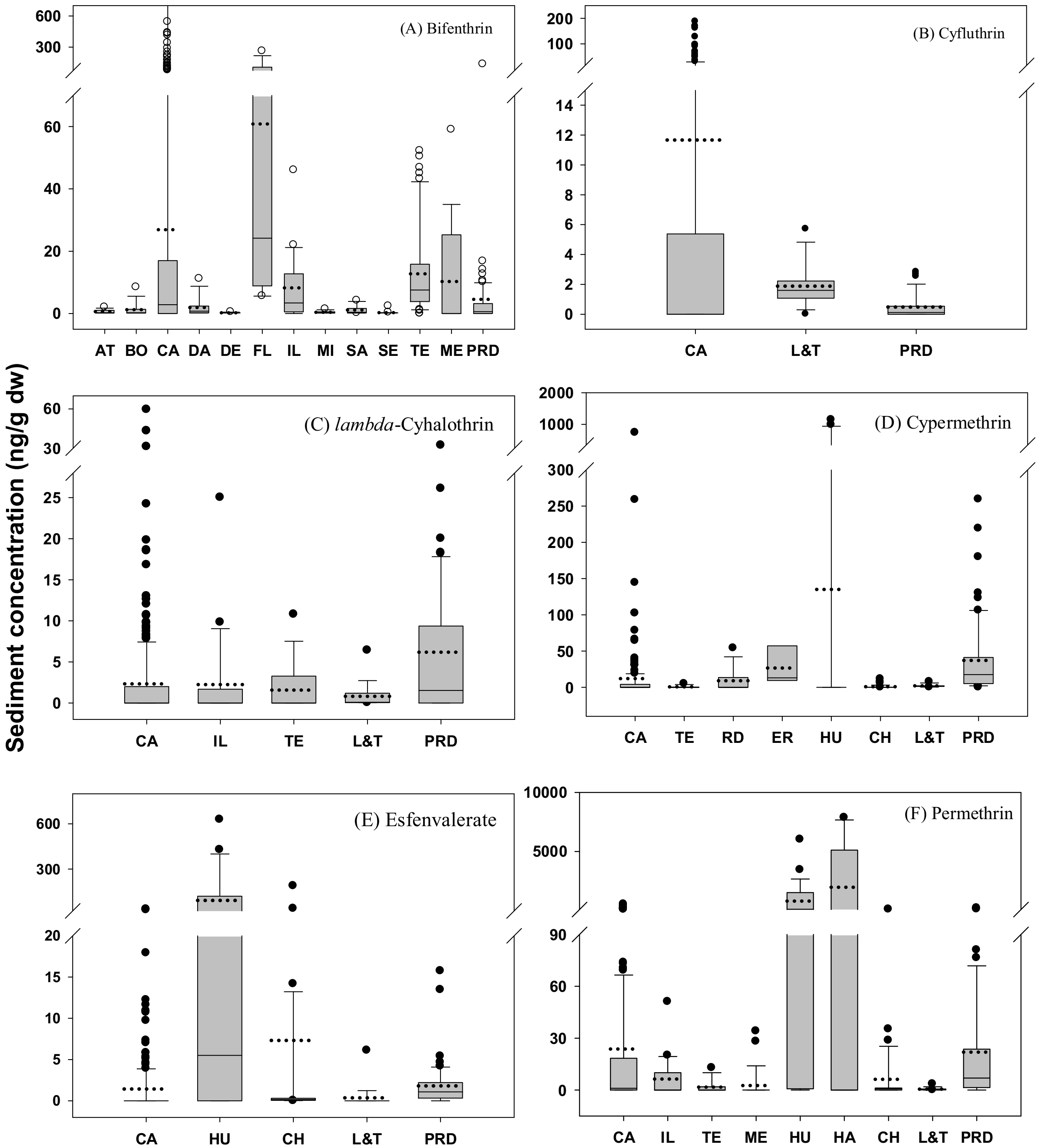

Fig. 4. Box plots of pyrethroid concentrations (ng/g dry weight (dw)) in sediment from different locations. Target pyrethroids included bifenthrin, *lambda*-cyhalothrin, cyfluthrin, cypermethrin, esfenvalerate and permethrin. Sample locations included Atlanta (AT), Boston (BO), California (CA), Dallas (DA), Denver (DE), Illinois (IL), Florida (FL), Milwaukee (MI), Salt Lake City (SA), Seattle (SE), Texas (TE), Tennessee (TEN) in the U.S.; Melbourne (ME) in Australia; Riodela Plata Estuary in Argentina (RD); Ebro River in Spain (ER); Humber in England (HU); Ha Noi in Veitnam (HA); Chao Lake (CH), Liao River and Tai Lake (L&T), Pearl River Delta (PRD) in China. The open dots represent outliers and three solid lines in the box represent 25%, 50% and 75% of pyrethroid concentrations. The dashed line represents mean concentrations, and the bars represent standard deviations. Significant difference among sites are presented in Table S2.

sediment concentrations of esfenvalerate in Humber showed no significant difference compared to other locations according to the statistical analysis (Fig. 4E). Sediments collected from Chao Lake, China contained significantly higher residues of esfenvalerate than those from California in the U.S. and the PRD in China. Finally, sediment concentrations of permethrin from the U.S. (California, Illinois and Texas), Australia (Melbourne), England (Humber), Vietnam (Ha Noi) and China (Chao Lake, Liao River, Tai Lake and the PRD) were compared (Fig. 4F). Sediments from Ha Noi, Vietnam had the highest mean concentration of permethrin at 1876 ± 2939 ng/g dw with a peak concentration of 7854 ng/g dw [42], followed by sediments from Humber, England with mean and peak concentrations of 988 ± 1566 and 6018 ng/g dw, respectively [46]. Statistically, mean sediment concentrations of permethrin from Ha Noi, Vietnam were not significantly higher than those from other locations, probably due to the low detection frequency. Conversely, sediment concentrations of permethrin from Humber, England were significantly higher than those from California in the U.S. and Chao Lake in China.

Overall, certain sediments from Europe (Humber, England) and South Asia (Ha Noi, Vietnam) were severely contaminated with pyrethroids, e.g. cypermethrin, esfenvalerate and permethrin. However, very few studies have been conducted in these areas to evaluate the relevant effects of pyrethroid exposure on benthic organisms. This, calls for more attention to be made to the occurrence and potential toxic effects of pyrethroids in the areas in which pyrethroids have been extensively used. A recent study conducted in Melbourne, Australia found bifenthrin in sediments collected from urban waterways and the levels were similar to those from California in the U.S. and the PRD in China. A similar study conducted in Africa (Botswana) reported that deltamethrin was detected in sediments with concentrations ranging from 13 to 291 ng/g dw [41]. This suggested that pyrethroids were contaminating the local sediments, although more studies are needed to better understand the magnitude of the exposure.

The occurrence and geographic distribution of pyrethroids in sediment can be impacted by a number of factors, including their use patterns, local weather conditions (e.g. temperature and humidity), regional economic conditions, and physicochemical (affinity to organic carbon) and environmental (e.g. half life in sediment) properties of the individual pyrethroids [19]. In the current study, the influence of use patterns on pyrethroid occurrence in sediments was evaluated by classifying sediment-associated pyrethroids with land use type.

3.1.3. Pyrethroids in sediments classified by land use

Pyrethroid insecticides have been widely applied to control pests in agricultural (e.g. crops, vegetables and fruits), urban and residential settings (e.g. professional landscape and structure maintenance as well as home and garden uses). According to the land use patterns, areas where sediments were sampled for pyrethroid analysis were classified into three types of land use, namely agriculture (crops, vegetable and fruit planting areas), urban (urban and residential areas) and mixed (mixture functional zones with agricultural, urban and residential functions). The occurrence of sediment-associated pyrethroids in the three land use areas is summarized in Fig. 5. Concentrations of the six pyrethroids in urban sediments were significantly greater than those in agricultural areas. For bifenthrin and esfenvalerate, sediment concentrations in urban areas were significantly greater than those in mixed land use areas (Fig. 5A and E). Sediment concentrations of *lambda*-cyhalothrin and permethrin were significantly greater in agricultural land use compared with mixed land use (Fig. 5C and F), and the opposite was true for cyfluthrin, cypermethrin and esfenvalerate (Fig. 5B, D and E).

Data on use patterns of pyrethroids are usually not publically available, with the exception being the Pesticide Use Report (PUR) database at the California Department of Pesticide Regulation (CDPR). The reported use of pyrethroids in 2004 in California showed that the majority of bifenthrin, cyfluthrin, cypermethrin and permethrin (70%–95%) was applied to urban and residential areas, whereas approximately 50% of *lambda*-cyhalothrin and esfenvalerate were used in urban and residential settings [11]. The relationship between pyrethroid occurrence and land use type was limited to sediment samples in California only, since data detailing use patterns of pyrethroids are only available from this state. The concentrations of bifenthrin, cyfluthrin and permethrin in urban sediments were significantly greater than their counterparts in agricultural sediments in California, while comparable concentrations of esfenvalerate were detected in sediments regardless of land use type. Conversely, the usage patterns for cypermethrin and *lambda*-cyhalothrin in California were different from the rest of the current datasets, but consistent with their reported land use patterns in California [11]. Cypermethrin had significantly greater sediment concentrations in urban than agricultural areas, while sediment concentrations of *lambda*-cyhalothrin were not significantly different among land use types.

Although studies detailing the occurrence of sediment-associated pyrethroids in various land uses are restricted to California, the available data demonstrated that pyrethroid use patterns (geographic difference and land use type) were the most important factors in loading pyrethroids to surrounding waterways. However, there were some exceptions, suggesting that other factors, like ground type (vegetated or concrete) and rainfall intensity, may also influence the transport and accumulation of pyrethroids in watershed sediments [37,52,53]. For example, Budd et al. [37] detected greater concentrations of bifenthrin, *lambda*-cyhalothrin and cyfluthrin in agricultural sediments compared with sediments collected from residential areas in California. The authors thought that vegetative ground cover in residential areas, e.g. grasses and shrubs, prevented pyrethroids from being transported to nearby waterways, resulting in lower sediment concentrations in the study area [37,54].

3.2. Toxicity of pyrethroids in sediment to benthic invertebrates

Although pyrethroids are considered to have low mammalian and avian toxicity, they exhibit high toxicity to non-target invertebrates and fish [34,35]. Short pulsed exposures of pyrethroids have been shown to cause acute effects to water column species after they enter aquatic systems via runoff and spray drift [55,56]. Pyrethroid residues in sediment were well correlated to acute effects to benthic invertebrates, suggesting their potential contribution to sediment toxicity [16,33,39,57,58]. Furthermore, benthic invertebrates are often chronically exposed to pyrethroids in sediment, raising special concern about pyrethroid contamination in aquatic systems [59,60].

3.2.1. Correlations between pyrethroid residues in sediment and toxicity

In the current survey, 34 of the 58 studies evaluated sediment toxicity to benthic invertebrates in addition to quantifying pyrethroid concentrations in sediment (Table S1). Weston et al. [58] was the first to point out the important contribution of pyrethroids to sediment toxicity in agriculturally dominated watersheds of California. This study was followed up by a similar study by the same authors concentrating this time on pyrethroid use in residential areas of California [10]. Later, studies were conducted to screen the toxicity of sediment-associated pyrethroids in agricultural (e.g. [61–64]) and urban waterways in California and throughout the U.S. (e.g. [30,65–67]). Sediment samples collected from waterways across California exhibited high toxicity to benthic invertebrates, e.g. 88% of the sediments from residential areas showed acute lethality to *Hyalella azteca,* and 25% of the samples were lethal to all of the amphipods in 10-d acute toxicity tests [10]. Furthermore, toxic unit (TU) measurements of pyrethroids in sediment were well correlated to the mortality in *H. azteca*, suggesting that pyrethroids were important contributors to sediment toxicity and specifically, bifenthrin was responsible for the majority of the noted TUs [10,30,64]. For example, Amweg et al. [30] found a good relationship between sum pyrethroid TUs and mortality for *H. azteca* exposed to sediments collected from creeks in California, and found that 21 of the 22 toxic sediments had sum pyrethroid TUs greater than 1. This indicated that pyrethroids played a major role in the observed sediment toxicity. Besides California, toxicity due to sediment-associated pyrethroids has also been evaluated in urban

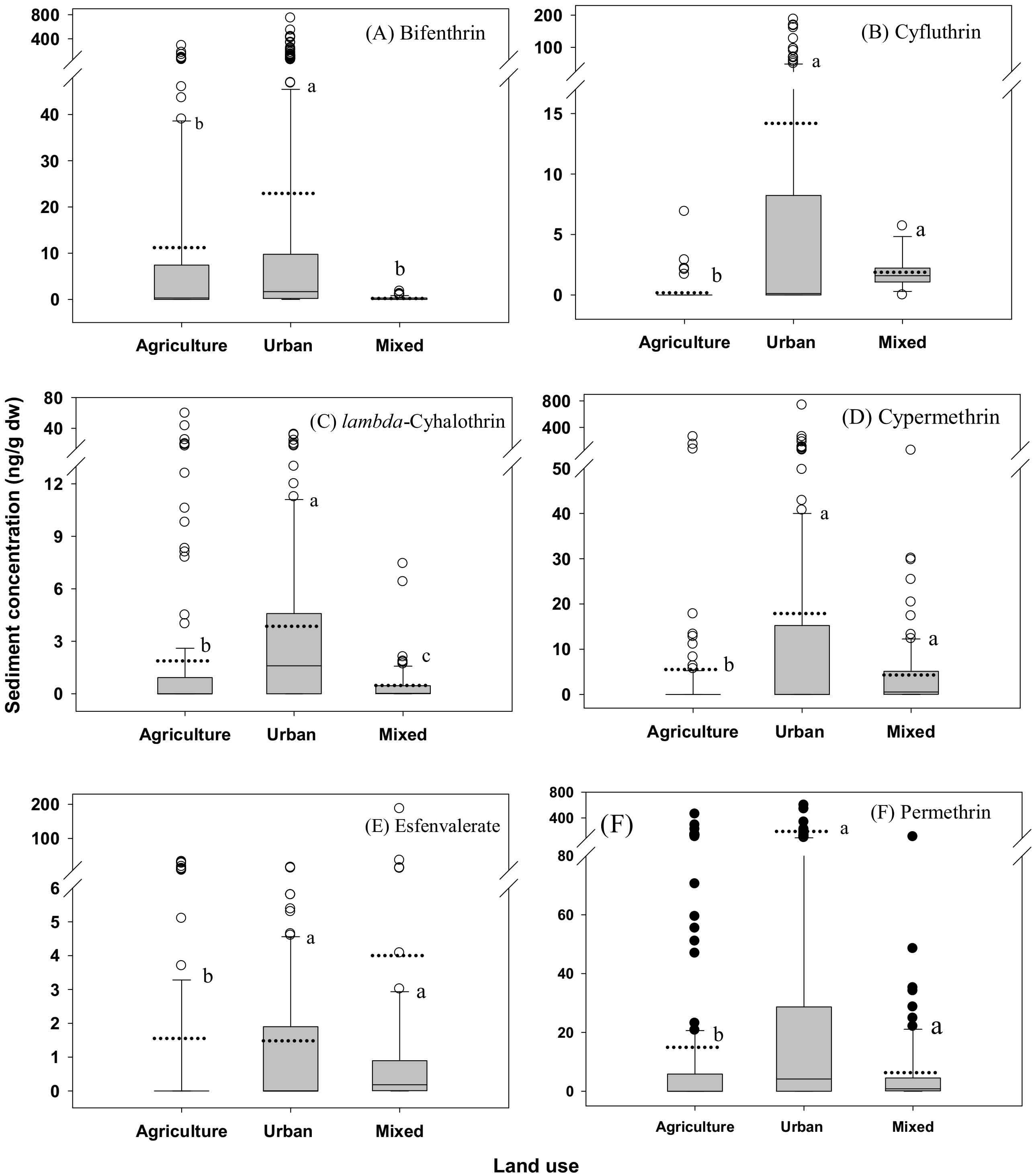

Fig. 5. Box plot of pyrethroid concentrations (ng/g dry weight (dw)) in sediments from different types of land use. Target pyrethroids included bifenthrin, *lambda*-cyhalothrin, cyfluthrin, cypermethrin, esfenvalerate and permethrin. The open dots represent outliers. The three solid lines in the box represent 25%, 50% and 75% of pyrethroid concentrations. The dashed line represents mean concentrations, and the bars represent standard deviations. Different lowercase letters on the top of each box represent significant differences ($p < 0.05$).

waterways in Washington and Oregon [68], Tennessee [30] and Texas [69], as well as in agricultural waterways in Mississippi [70] and Illinois [16].

In 2007, a nationwide assessment was carried out by the U.S. Geological Survey to analyze the occurrence and toxicity of sediment-associated pyrethroids from seven metropolitan areas across the U.S. [57,71]. In total, 26% of the sediments caused a lethal response to *H. azteca* during 28-d toxicity testing. Similar to the studies in California, pyrethroid TUs were significantly correlated to the mortality in *H. azteca*, and bifenthrin contributed the most to the observed toxicity. Although sediments from the seven metropolitan areas exhibited lower toxicity to *H. azteca* than those in California, the contribution of pyrethroids to sediment toxicity across the U.S. was evident and of significant concern [57]. The frequent detection and high toxicity of pyrethroids to benthic organisms have caught the attention of the U.S. Environmental Protection Agency, and prompted reregistration of many formulations as well as limiting their use [72,73].

Concerns about pyrethroid toxicity to non-target aquatic species were not only an important issue in the U.S., but also a problem in China (Table S1). Sediments collected from urban waterways in the PRD, China were highly toxic to benthic invertebrates, e.g. 94% and 81% of sediments collected from an urban stream in Guangzhou were acutely toxic to *Chironomus dilutus* and *H. azteca*, respectively. In fact, some sediments were lethal to all of the test organisms (e.g. midges) even after they were diluted 16 times [39,74]. A good correlation was observed between pyrethroid TUs and sediment mortality for *H. azteca* and *C. dilutus*; thereby, more formally linking sediment-associated pyrethroids to toxicity in this region. In contrast to the U.S. where bifenthrin was the most important contributor to sediment toxicity, cypermethrin dominated the sediment toxicity contribution in the PRD urban waterways [33,39,74]. Finally, sediments collected from watersheds with mixed land use in China exhibited much lower toxicity compared with samples from urban sites in the PRD [47], and none of the sediments collected from Tai Lake (a mixed land use site) were acutely toxic to *C. dilutus* [75].

Pyrethroid-induced sediment toxicity was further validated by toxicity identification evaluation (TIE) techniques, which were applied to identify toxicants in a complex system [76]. Focused TIE tools, e.g. addition of the synergist piperonyl butoxide, changing the testing temperature, and application of an esterase enzyme, were developed to validate if pyrethroids were the cause of toxicity in field-collected sediments [77–79]. A focused TIE approach was then used to assess and validate causality between sediment-associated pyrethroids and sediment toxicity to benthic invertebrates in California [65,67,80,81] and in the PRD [33].

The good correlations found when pyrethroid occurrence was regressed with sediment toxicity and the validation that pyrethroids were the main cause of toxicity strongly suggested potential ecological risk to non-target aquatic species due to exposure to pyrethroids. Geographically, bifenthrin was the major pyrethroid contributing to sediment toxicity in the U.S., while cypermethrin was the main contributor in China. In addition, sediment samples collected from the PRD, China showed much greater mortality to test species than would be expected from pyrethroid exposure alone. This suggests the presence of other toxicants may be playing a role in the noted toxicity besides pyrethroids. This point was confirmed by conducting a whole-sediment TIE study, in which cypermethrin and *lambda*-cyhalothrin were identified as significant contributors to toxicity along with fipronil, a phenylpyrazole insecticide and heavy metals, in urban sediments in the PRD [82].

3.2.2. Assessing risk of sediment-associated pyrethroids on a global scale

The deterministic hazard quotient method has been commonly used in ecological risk assessments for calculating TU and hazard quotient (HQ) values. This method simply provides a conservative screening-level assessment for environmental contaminants and gives basic information for risk management decisions. In the current study, TUs and HQs were calculated for sediment-associated pyrethroids using the following equations:

$$\mathrm{TU} = C_{\text{sed-OC}}/\mathrm{LC50} \quad (1)$$

$$\mathrm{HQ} = C_{\text{sed-OC}}/\mathrm{SQC} \quad (2)$$

Where, $C_{\text{sed-OC}}$ is the organic carbon (OC) normalized concentration of a pyrethroid in field sediment, LC50 is the OC-based median lethal concentration of the pyrethroid to benthic invertebrates, *H. azteca* or *C. dilutus*, and SQC is the OC-based sediment quality criteria for that pyrethroid. The LC50 and SQC values are presented in Table 1. As shown in Table S1, the toxicity data that were available for sediment-associated pyrethroids were mainly focused on two freshwater species, *H. azteca* and *C. dilutus*. Conversely, toxicity of pyrethroids to other non-target species or the potential risk to the water/sediment environment is largely unknown. Therefore, the acute LC50 values for *H. azteca* and *C. dilutus* (Table 1) were used as benchmarks to calculate TUs for individual pyrethroids from the concentrations of sediment-associated pyrethroids in the survey dataset (Table S1). In addition, the available threshold effect benchmarks were applied as SQC to evaluate the possible adverse effects of the pyrethroids on benthic-dwelling organisms by calculating HQs. Furthermore, a Monte Carlo simulation (Crystal Ball v11.1) was applied to evaluate the distribution and uncertainty of TUs and HQs by setting the trials and confidence interval at 20,000 randomizations and 95%, respectively (Table 2).

As shown in Table 2, bifenthrin, cypermethrin and permethrin were the most potent sediment-associated pyrethroids to *H. azteca* worldwide, with respective TUs of 16.3 ± 48.0, 5.37 ± 26.3 and 1.27 ± 7.16, and a percentage of TU values > 1 (greater than 50% of mortality) being 52%, 32% and 8.5%, respectively. The elevated TU values strongly suggest that bifenthrin and cypermethrin concentrations were high enough to cause acute toxicity to *H. azteca* in sediment. Conversely, the average contribution of the remaining three pyrethroids to the acute lethality noted for *H. azteca* was individually lower than 1 TU. Compared with *H. azteca*, *C. dilutus* was relatively less sensitive to pyrethroids, indicated by its smaller mean TU values, which were all less than 1 except for cypermethrin, which had the highest TU value for *C. dilutus* at 1.52 ± 7.45 and the percentage of TU > 1 was 18%, followed by cyfluthrin (10%) and bifenthrin (7.8%) (Table 2).

The hazard concentration affecting 5% of the species (HC5) in a system, and species sensitivity distributions (SSD) are often used to better understand the potential risk of contaminant exposure to aquatic species. The HC5 and SSD measurements are then used to derive water quality criteria as benchmarks for assessing ecological risk of contaminants in surface waters [6,83]. Nevertheless, risk assessments concentrating on sediment-associated pyrethroids have seldom been performed due to the lack of SQC for this class of insecticides. To date, very little sediment toxicity data are available to establish SSD curves and derive benchmarks. Recently, researchers at the U.S. Geological Survey developed freshwater sediment toxicity benchmarks for current-use pesticides based on toxicity data derived from spiked-sediment bioassays [28]. Threshold effect benchmarks (TEB) define a concentration below which adverse effects are unlikely to occur. Therefore, the integrated TEBs developed in Nowell et al. [28] (Table 1) were chosen as benchmarks to calculate the HQs of sediment-associated pyrethroids in the current survey dataset to benthic invertebrates.

The HQs for the six pyrethroids ranged from 10.5 ± 31.1 (bifenthrin) to 41.7 ± 204 (cypermethrin), and the percentages of HQ > 1 and HQ ≥ 10 were from 31% (esfenvalerate) to 49% (bifenthrin) and from 9.8% (esfenvalerate) to 28% (cypermethrin), respectively. In general, a HQ > 1 indicates potential ecological risk, and a HQ ≥ 10 suggests significant risk [84]. Therefore, the six target pyrethroids detected in sediments globally exhibited significant risk to benthic organisms according to the mean HQ calculations.

Even though the Monte Carlo simulation took the distribution of exposure (i.e. environmental concentrations) into consideration, there were still factors introducing uncertainty in the HQ estimates. Sediment concentrations were normally reported on a dry weight basis; however, the total organic carbon (TOC) content for most sediments was not reported, so TEB benchmarks were calculated on a dry weight basis and TOC corrected assuming a sediment TOC content of 1%. Unfortunately, TOC levels in sediments are often variable which adds uncertainty to the estimate, e.g. TOC contents of 16 sediments collected from a same urban stream in Guangzhou,

Table 2
Toxic unit (TU, mean ± standard deviation) and hazard quotient (HQ, mean ± standard deviation) measurements and the percentage of TU and HQ values being greater than 1 estimated by Monte Carlo simulation. The median lethal concentrations (LC50) to *Chironomus dilutus* and *Hyalella azteca* was used to calculate TU values. The integrated threshold effect benchmark was used to calculate HQ values. Benchmark values are presented in Table 1 and sediment total organic carbon was assumed to be 1% for the TU and HQ calculations.

Compound	*H. azteca*		*C. dilutus*		Threshold effect benchmark		
	TU	Percentage of TU > 1	TU	Percentage of TU > 1	HQ	Percentage of HQ > 1	Percentage of HQ ≥ 10
Bifenthrin	16.3 ± 48.0	52	0.29 ± 0.85	7.8	10.5 ± 31.1	49	23
lambda-Cyhalothrin	0.65 ± 1.74	15	0.10 ± 0.28	1.4	12.7 ± 34.1	45	23
Cyfluthrin	0.78 ± 2.52	13	0.44 ± 1.43	10	18.3 ± 59.2	33	20
Cypermethrin	5.37 ± 26.3	32	1.52 ± 7.45	18	41.7 ± 204	40	28
Esfenvalerate	0.95 ± 5.71	8.1	0.18 ± 1.06	2.4	15.3 ± 92.4	31	9.8
Permethrin	1.27 ± 7.16	8.5	0.56 ± 3.16	4.5	32.8 ± 184	39	15

China ranged from 0.6% to 14.7% [39]. In addition, uncertainty in benchmark calculations is an important source of uncertainty in risk assessments. To date, few taxa have been used to determine sediment thresholds, e.g. only two taxa were used to derive toxicity values for pyrethroids [28], so the minimal requirement of five taxa to construct sediment SSD curves was not achieved. Instead, the lowest toxicity data reported in a test (e.g. LC50, median effect concentration, or no-observed effect concentration) was chosen to calculate the TEB values for *H. azteca* or *C. dilutus*, and then the integrated TEB was defined as the lower value of TEB for *H. azteca* and *C. dilutus* [28]. This introduced a lot of uncertainty to the SQC. Even though uncertainties exist in the assessment, the estimated TUs and HQs for pyrethroids worldwide (Table 2) provided strong evidence that sediment-associated pyrethroids posed high acute lethality to the two target benthic invertebrates (*H. azteca* and *C. dilutus*) and significant risk to benthic communities on a global scale.

Recently, researchers found positive relationships between the occurrence of sediment-associated pyrethroids and benthic community metrics, like taxonomic richness, chronic sublethal effects to benthic invertebrates and direct and indirect effects on species at multiple trophic levels, which were ecologically meaningful [85–87]. Those mesocosm studies strongly suggested that sediment-associated pyrethroids posed lethal and sublethal effects on benthic organisms and subsequently influenced ecological risk to benthic community, which supported the HQ results in the current study.

4. Factors affecting the risk assessment of pyrethroids in sediment

It is evident that the worldwide occurrence of pyrethroids in sediment has caused significant risk to benthic invertebrates based on the evaluations presented above. Inconsistencies have been noted; however, in toxicity data when extrapolating toxicity results derived from laboratory bioassays to the effects in the field, demanding a better understanding of factors affecting sediment toxicity, such as sediment-specific bioavailability, joint toxicity, and the selection and developing resistance of test species [59,74,88].

4.1. Bioavailability

Exposure of benthic organisms to sediment-associated contaminants is primarily through the routes of partitioning of freely dissolved molecules into sediment porewater and direct ingestion of contaminant-associated particles [59]. Equilibrium partitioning theory described the partitioning among biota, porewater and sediment phases and proposed the use of OC-normalized concentrations as dose metrics for sediment toxicity of hydrophobic contaminants [89]. This theory served as the basis for developing the TU method, which has been widely used for assessing risk of sediment-associated pyrethroids [10,33]. Nevertheless, an increasing number of studies have found that OC-normalized pyrethroid concentrations overestimated sediment toxicity, because bioavailability of pyrethroids varied by site (e.g. Kuivila et al., [57]; Lao et al., [90]; Li et al., [74]; You et al., [91]).

Sequestration of hydrophobic contaminants in sediment can significantly decrease their bioavailability and ultimately decrease their toxicity. Sequestration is controlled by several factors, such as the content, type and characteristics of the OC present in sediment, and the contact time between the sediment and contaminants [92,93]. It is challenging to theoretically differentiate the partitioning of contaminants to individual OC components, so alternative approaches, e.g. passive sampling and desorption-based extraction techniques have been developed to measure bioavailability and toxicity of contaminants in sediment [94–96].

While bioavailability-based approaches have been mostly used to estimate bioaccumulation of persistent organic contaminants, several studies have been conducted to investigate the partitioning processes of pyrethroids between passive sampler and sediment porewater [27,97–100]. These studies have established a significant correlation between pyrethroid concentrations in passive samplers and body residues. Xu et al. [98] determined LC50s of pyrethroids to *C. dilutus* in spiked sediment based on five concentrations, namely bulk sediment concentration, OC-normalized concentration, porewater concentration, dissolved OC-normalized porewater concentration and freely dissolved concentration in porewater. Results showed that the LC50 values expressed using bulk sediment and porewater exhibited the largest variation among sediment types, while LC50s based on the freely dissolved concentration was independent of sediment type and aging time [98].

The application of bioavailability-based measurements are more limited for pyrethroids in field-collected sediments compared with the studies using spiked sediments, due to the difficulty in quantifying low concentrations of pyrethroids in complicated matrices [74,91,101]. You et al. [91] found that traditional TU measurements based on OC-normalized concentrations significantly overestimated the toxicity of pyrethroids to *H. azteca* in sediments sampled from California. Alternatively, Tenax extraction was applied to measure the rapidly desorbed concentration of sediment-associated pyrethroids, and the correlation of bioavailable TUs based on Tenax extractable concentrations and mortality (expressed in probits) of *H. azteca* was significantly improved [91]. A similar overestimation in toxicity was noted for cypermethrin to *H. azteca* in sediments collected in urban waterways in South China [74]. The authors compared three TU measurements to predict toxicity: TUs based on OC-normalized sediment concentration; Tenax extractable concentration; and, solid-phase microextraction (SPME) measured freely dissolved concentration in porewater. They found that the TU based on SPME measured concentration correlated to mortality (expressed in probit) the best, followed by the TU based on Tenax extractable concentration and finally the OC-normalized sediment concentration [74]. Overall, the freely dissolved concentration of pyrethroids in sediment porewater greatly reduced the variation in toxicity values across sediments, and provided an effective approach to improve sediment toxicity evaluation in the field.

Due to the lack of bioavailable LC50 values for the target pyrethroids, You et al. [91] and Li et al. [74] limited their assessment to a qualitative evaluation of bioavailable TUs by judging the correlation between TU and mortality. Xu et al. [98] reported the freely dissolved concentration-based bioavailable LC50s for bifenthrin, cyfluthrin and esfenvalerate to *C. dilutus* in 10-d bioassays, but bioavailable LC50s for the other pyrethroids to other species have not been measured nor reported yet. Therefore, it is imperative to establish a bioavailability-incorporated approach to improve the accuracy and efficiency in assessing the risk due to pyrethroids.

4.2. Extrapolating from sediment toxicity to ecological risk

The majority of the studies that evaluated pyrethroid-induced sediment toxicity used *H. azteca* as a model species (Table S1). *H. azteca* is an epibenthic species that lives at the sediment-water interface and often seek refuge in macrophtyes or large debris [102]. Therefore, exposure routes for *H. azteca* differ from organisms that have direct contact with sediments, like midges [103,104]. Available data indicate that *H. azteca* are exceptionally sensitive to pyrethroids, e.g. *H. azteca* was in the 2% of affected species (HC2) in a SSD for cypermethrin based on four taxa groups (algae, crustaceans, insects and fish) [83]. In the meantime, micro/mesocosm tests suggest that impacted populations of invertebrates with high reproductive rates, like *H. azteca,* recovered rapidly after short-term exposures to pyrethroids [105–107]. So reductions in a few sensitive species with rapid recovery ability are unlikely to cripple the functionality of an ecosystem. Based on the above concern, Palmquist et al. [59] concluded that bioassays using *H. azteca* was an effective screening tool for sediment-associated pyrethroids, but could not accurately predict sediment toxicity in the field nor risk for larger benthic invertebrate communities.

In addition to *H. azteca*, *C. dilutus* has been used to evaluate toxicity of sediment-associated pyrethroids (e.g. Bouldin et al., [70]; Li et al., [39]; Mehler et al., [33]; Weston et al., [58]). The midge, *C. dilutus* is a sediment-dwelling invertebrate that actively feeds on sediment particles [108] and is less susceptibility to pyrethroids than *H. azteca* (Table 1). Chironomidae are found ubiquitously in freshwater systems throughout the world, and are an important food source for fish [109]. The short life cycle and presence of a non-aquatic life stage for chironomidae help them recover rapidly from pyrethroid exposure. For example, Conrad et al. [110] reported that *C. riparius* experienced rapid recovery after a > 50% decrease in abundance following pyrethroid exposure; however, some sediments collected from the PRD, China showed nearly 100% mortality to *C. dilutus* [33,39], which may cripple a *Chironomus* sp. population and influence fish predation. Therefore, *Chironomus* sp. could be an additional choice for evaluating exposure and toxicity of pyrethroids in freshwater sediments. Even with the inclusion of *C. dilutus* as a sediment bioassay species, SSD measurements cannot be established for pyrethroids with only two species (e.g. *H. azteca* and *C. dilutus*). So, there is an urgent need to develop multi-species sediment toxicity methods so that more accurate SSD-based SQC can be developed.

Another issue is variable sensitivity of laboratory-cultured organisms versus those in the field due to development of resistance. Recently, Weston et al. [88] evaluated the relative sensitivity of 10 populations of laboratory-cultured and wild-collected *H. azteca* to pyrethroids in sediment. The authors observed up to a 55-fold difference in sensitivity to pyrethroids, implying ongoing evolution of resistance in wild-caught *H. azteca* to pyrethroids, which makes the extrapolation from laboratory to field more difficult.

Finally, the presence of other contaminants may alter the toxicity of pyrethroids. Mehler et al. [111] found antagonistic interactions between lead and cypermethrin in sediment to *C. dilutus*. The reduced toxicity of the mixture was because lead induced biotransformation enzymes in *C. dilutus,* thereby, enhancing the biotransformation of cypermethrin to less toxic metabolites [112,113]. On the other hand, the toxic contribution from other pesticides which co-occur with pyrethroids in sediment should also be considered [32], and a simple concentration addition model was considered as a conservative estimation of toxicity for pesticide mixtures [114–116].

5. Conclusions and perspectives

Pyrethroid residues are an emerging threat to aquatic ecosystems globally, due to their frequent detection at high concentrations in sediments from agricultural and non-agricultural (urban and residential) areas. Application patterns, physicochemical and environmental properties and various environmental factors are influencing the distribution of pyrethroids in field sediments. Yet, most of the studies on the fate and toxicity of pyrethroids to date have been conducted in California, the U.S. and the PRD, China, while limited survey/monitoring has been performed in other countries or regions. Some countries in South Asia and South American, like Pakistan, India and Paraguay, use greater amounts of pyrethroids than the U.S. and China [23]; however, little information have been reported on sediment residues of pyrethroids in these countries [117,118]. In addition, studies have concentrated on certain areas within countries. For example, Grung et al. [119] reviewed the pesticide levels in aquatic systems in China and found that the most studied areas were the most populated east and south sections of China, and fewer studies have been conducted in remote areas of the country. Thus, to gain a more complete picture of the global contamination levels of sediment-associated pyrethroids, more studies are needed in different landscapes and locations where pyrethroids are applied.

The total chemically extractable concentration of a contaminant in sediment does not accurately reflect the exposure of organisms in that media; rather, it is the bioavailable concentration that provides a better predictor of toxicity. Pyrethroids are extremely toxic to benthic invertebrates, suggesting small differences in exposure may cause large differences in toxicity. Therefore, accurate measurements of the bioavailable fraction of pyrethroids in a sediment and quality effects data are needed to assure accurate sediment toxicity assessments. We recommend establishment of toxicity thresholds based on the bioavailable portion of sediment-associated pyrethroids [98,120,121]. Moreover, the adverse effects of long-term exposure to pyrethroids in sediment at sublethal levels should also be addressed. While degradation products of pyrethroids have been shown to be less toxic to benthic organisms, they have been shown to have endocrine disrupting effects greater than the parent compounds [122]. This point should not be ignored, since the degradation products are more persistent in the environment compared with the parent pyrethroids [123].

As a type of neurotoxicant, sediment-associated pyrethroids pose a high risk to non-target invertebrate species. Although laboratory toxicity data for sediment-associated pyrethroids to *H. azteca* may not be the best indicator of toxicity in the field or the effects on benthic communities [59,102], lethal and sublethal effects have been linked to benthic invertebrates at an individual level, and plausibly linked to the effects at population and community levels [124]. Therefore, effective SQC and associated risk assessment methodology are needed for pyrethroids in order to protect benthic communities and the broader biodiversity in aquatic ecosystems.

Acknowledgements

This research was supported by the National Science Foundation of China (41503091, 41473106 and 41273120), Guangdong Provincial Department of Science and Technology (2015TX01Z168) and the Natural Science Foundation of Guangdong Province, China (2015A030310219 and 2016A030312009).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2016.10.056.

References

[1] S. Stehle, R. Schulz, Agricultural insecticides threaten surface waters at the global scale, PNAS 112 (2015) 5750–5755.
[2] R. Schulz, Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution, J. Environ. Qual. 33 (2004) 419–448.
[3] E. Malaj, P.C. v. d. Ohe, M. Grote, R. Kühne, C.P. Mondy, P. Usseglio-Polatera, W. Brack, R.B. Schäfer, Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale, PNAS 111 (2014) 9549–9554.
[4] R.B. Schäfer, V. Pettigrove, G. Rose, G. Allinson, A. Wightwick, P.C. v. d. Ohe, J. Shimeta, R. Khne, B.J. Kefford, Effects of pesticides monitored with three sampling methods in 24 sites on macroinvertebrates and microorganisms, Environ. Sci. Technol. 45 (2011) 1665–1672.
[5] W.W. Stone, R.J. Gilliom, K.R. Ryberg, Pesticides in U.S. streams and rivers: occurrence and trends during 1992–2011, Environ. Sci. Technol. 48 (2014) 11025–11030.
[6] C.A. Morrissey, P. Mineau, J.H. Devries, F. Sanchez-Bayo, M. Liess, M.C. Cavallaro, K. Liber, Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review, Environ. Int. 74 (2015) 291–303.
[7] E.T. Rodrigues, I. Lopes, M.Â. Pardal, Occurrence, fate and effects of azoxystrobin in aquatic ecosystems: a review, Environ. Int. 53 (2013) 18–28.
[8] S. Stehle, R. Schulz, Pesticide authorization in the EU-environment unprotected? Environ. Sci. Pollut. Res. 22 (2015) 19632–19647.
[9] I. Denholm, G.J. Devine, M.S. Williamson, Insecticide resistance on the move, Science 297 (2002) 2222–2223.
[10] D.P. Weston, R.W. Holmes, J. You, M.J. Lydy, Aquatic toxicity due to residential use of pyrethroid insecticides, Environ. Sci. Technol. 39 (2005) 9778–9784.
[11] F. Spurlock, M. Lee, Synthetic pyrethroid use patterns, properties, and environmental effects, in: J. Gan, F. Spurlock, P. Hendley, D.P. Weston (Eds.), Synthetic Pyrethroids, 2008, pp. 3–25.
[12] http://www.mordorintelligence.com/industry-reports/pyrethroid-insecticide-market#menu1 and http://www.mordorintelligence.com/industry-reports/global-insecticides-market-industry.
[13] H. Li, Y. Wei, M.J. Lydy, J. You, Inter-compartmental transport of organophosphate and pyrethroid pesticides in South China: implications for a regional risk assessment, Environ. Pollut. 190 (2014) 19–26.
[14] W. Yang, J. Gan, W. Hunter, F. Spurlock, Effect of suspended solids on bioavailability of pyrethroid insecticides, Environ. Toxicol. Chem. 25 (2006) 1585–1591.
[15] T.L. Fojut, T.M. Young, Pyrethroid sorption to Sacramento River suspended solids and bed sediments, Environ. Toxicol. Chem. 30 (2011) 787–792.
[16] Y. Ding, A.D. Harwood, H.M. Foslund, M.J. Lydy, Distribution and toxicity of sediment-associated pesticides in urban and agricultural waterways from Illinois, USA, Environ. Toxicol. Chem. 29 (2010) 149–157.
[17] K. Siegler, B.M. Phillips, B.S. Anderson, J.P. Voorhees, R.S. Tjeerdema, Temporal and spatial trends in sediment contaminants associated with toxicity in California watersheds, Environ. Pollut. 26 (2015) 1–6.
[18] S.J. Maund, P.J. Campbell, J.M. Giddings, M.J. Hamer, K. Henry, E.D. Pilling, J.S. Warinton, J.R. Wheeler, Ecotoxicology of synthetic pyrethroids, Top. Curr. Chem. 314 (2012) 137–165.
[19] K. Palmquist, J. Salatas, A. Fairbrother, Pyrethroid insecticides: use, environmental fate, and ecotoxicology, in: F. Perveen (Ed.), Insecticides Advances in Integrated Pest Management, InTech, 2012, pp. 251–278.
[20] R. Schulz, S., Stehle, Synthetic pyrethroids in agricultural surface waters: Exposure, effects, and risk mitigation, in: J. Gan, F., Spurlock, P., Hendley, D.P. Weston (Eds.) Synthetic Pyrethroids: Occurrence and Behavior in Aquatic Environments (2008) pp. 171–201.
[21] T.J. Shafer, D.A. Meyer, K.M. Crofton, Developmental neurotoxicity of pyrethroid insecticides: critical review and future research needs, Environ. Health Perspect. 113 (2005) 123–136.
[22] H. Li, M.J. Lydy, J. You, Pyrethroids in indoor air during application of various mosquito repellents: occurrence, dissipation and potential exposure risk, Chemosphere 144 (2016) 2427–2435.
[23] http://faostat3.fao.org/search/pyrethroid/E.
[24] http://www.cdpr.ca.gov/docs/per/purmain.htm.
[25] D.A. Laskowski, Physical and chemical properties of pyrethroids, Rev. Environ. Contam. Toxicol. 174 (2002) 49–170.
[26] J. Gan, S., Bondarenko, F. Spurlock, Persistence and phase distribution in sediment, in: J. Gan, F., Spurlock, P., Hendley, D.P. Weston (Eds.) Synthetic Pyrethroids (2008) pp. 203–222.
[27] S. Bondarenko, F. Spurlock, J. Gan, Analysis of pyrethroids in sediment pore water by solid-phase microextraction, Environ. Toxicol. Chem. 26 (2007) 2587–2593.
[28] L.H. Nowell, J.E. Norman, C.G. Ingersoll, P.W. Moran, Development and application of freshwater sediment-toxicity benchmarks for currently used pesticides, Sci. Total Environ. 550 (2016) 835–850.
[29] J.D. Maul, A.A. Brennan, A.D. Harwood, M.J. Lydy, Effect of sediment-associated pyrethroids, fipronil, and metabolites on Chironomus tentans growth rate, body mass, condition index, immobilization, and survival, Environ. Toxicol. Chem. 27 (2008) 2582–2590.
[30] E.L. Amweg, D.P. Weston, J. You, M.J. Lydy, Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee, Environ. Sci. Technol. 40 (2006) 1700–1706.
[31] S.J. Maund, M.J. Hamer, M.C.G. Lane, E. Farrelly, J.H. Rapley, U.M. Goggin, W.E. Gentle, Partitioning, bioavailability, and toxicity of the pyrethroid insecticide cypermethrin in sediments, Environ. Toxicol. Chem. 21 (2002) 9–15.
[32] Y. Ding, D.P. Weston, J. You, A.K. Rothert, M.J. Lydy, Toxicity of sediment-associated pesticides to *Chironomus dilutus* and *Hyalella azteca*, Arch. Environ. Contam. Toxicol. 61 (2011) 83–92.
[33] W.T. Mehler, H. Li, M.J. Lydy, J. You, Identifying the causes of sediment-associated toxicity in urban waterways of the Pearl River Delta, China, Environ. Sci. Technol. 45 (2011) 1812–1819.
[34] USEPA, Reregistration eligibility decision (RED) for permethrin, Case No. 2510, Washington, D.C. (2009).
[35] USEPA, Reregistration eligibility decision (RED) for cypermethrin, Case No. 2130, Washington, D.C. (2006).
[36] D.R. Helsel, More than obvious: better methods for interpreting nondetect data, Environ. Sci. Technol. 39 (2005) 419A–423A.
[37] R. Budd, S. Bondarenko, D. Haver, J. Kabashima, J. Gan, Occurrence and bioavailability of pyrethroids in a mixed land use watershed, J. Environ. Qual. 36 (2007) 1006–1012.
[38] L. Delgado-Moreno, K. Lin, R. Veiga-Nascimento, J. Gan, Occurrence and toxicity of three classes of insecticides in water and sediment in two Southern California coastal watersheds, J. Agric. Food Chem. 59 (2011) 9448–9456.
[39] H. Li, B. Sun, M.J. Lydy, J. You, Sediment-associated pesticides in an urban stream in Guangzhou, China: implication of a shift in pesticide use patterns, Environ. Toxicol. Chem. 32 (2013) 1040–1047.
[40] M.L. Hladik, K.M. Kuivila, Pyrethroid insecticides in bed sediments from urban and agricultural streams across the United States, J. Environ. Monit. 14 (2012) 1838–1845.
[41] P.S. Daka, V.C., Obuseng, N., Torto, P. Huntsman-Mapila, Deltamethrin in sediment samples of the Okavango Delta, Botswana, Water SA, 32 (2006) 483–488.
[42] H.T. Duong, K. Kadokami, S.Y. Pan, N. Matsuura, T.Q. Nguyen, Screening and analysis of 940 organic micro-pollutants in river sediments in Vietnam using an automated identification and quantification database system for GC–MS, Chemosphere 107 (2014) 462–472.
[43] N. Xue, F. Li, H. Hou, B. Li, Occurrence of endocrine-disrupting pesticide residues in wetland sediments from Beijing, China, Environ. Toxicol. Chem. 27 (2008) 1055–1062.
[44] J.-Z. Wang, Y.-S. Bai, Y. Wu, S. Zhang, T.-H. Chen, S.-C. Peng, Y.-W. Xie, X.-W. Zhang, Occurrence, compositional distribution, and toxicity assessment of pyrethroid insecticides in sediments from the fluvial systems of Chaohu Lake, Eastern China, Environ. Sci. Pollut. Res. 23 (2016) 10406–10414.
[45] H. Li, H. Ma, M.J. Lydy, J. You, Occurrence, seasonal variation and inhalation exposure of atmospheric organophosphate and pyrethroid pesticides in an urban community in South China, Chemosphere 95 (2014) 363–369.
[46] J.L.A. Long, W.A. House, A. Parker, J.E. Rae, Micro-organic compounds associated with sediments in the Humber rivers, Sci. Total Environ. 210 (1998) 229–253.
[47] B.-Q. Sun, F. Wang, H.-Z. Li, J. You, Occurrence and toxicity of sediment-associated contaminants in Guangzhou college city and its adjacent areas: the relationship to urbanization, Arch. Environ. Contam. Toxicol. 68 (2015) 124–131.
[48] H. Li, W.T. Mehler, M.J. Lydy, J. You, Occurrence and distribution of sediment-associated insecticides in urban waterways in the Pearl River Delta, China, Chemosphere 82 (2011) 1373–1379.
[49] B. Whittle, Communities in peril: Asian regional report on community monitoring of highly hazardous pesticide use, in, Pesticide action network (PAN) Asia and the Pacific (2010) pp. 150.
[50] H. Li, E.Y. Zeng, J. You, Mitigating pesticide pollution in China requires law enforcement, farmer training, and technological innovation, Environ. Toxicol. Chem. 33 (2014) 963–971.
[51] M.L. Feo, A. Ginebreda, E. Eljarrat, D. Barcelo, Presence of pyrethroid pesticides in water and sediments of Ebro River Delta, J. Hydrol. 393 (2010) 156–162.
[52] D.P. Weston, M.J. Lydy, Stormwater input of pyrethroid insecticides to an urban river, Environ. Toxicol. Chem. 31 (2012) 1579–1586.

[53] W. Jiang, J. Gan, Importance of fine particles in pesticide runoff from concrete surfaces and its prediction, Environ. Sci. Technol. 46 (2012) 6028–6034.
[54] I. Werner, F.G. Zalom, M.N. Oliver, L.A. Deanovic, T.S. Kimball, J.D. Henderson, B.W. Wilson, W. Krueger, W.W. Wallender, Toxicity of storm-water runoff after dormant spray application in a French prune orchard, Glenn County, California, USA: Temporal patterns and the effect of ground covers, Environ. Toxicol. Chem. 23 (2004) 2719–2726.
[55] J.J. Rasmussen, P. Wiberg-Larsen, E.A. Kristensen, N. Cedergreen, N. Friberg, Pyrethroid effects on freshwater invertebrates: a meta-analysis of pulse exposures, Environ. Pollut. 182 (2013) 479–485.
[56] R. Schulz, M. Liess, Toxicity of aqueous-phase and suspended particle-associated fenvalerate: chronic effects after pulse-dosed exposure of *Limnephilus lunatus* (Trichoptera), Environ. Toxicol. Chem. 20 (2001) 185–190.
[57] K.M. Kuivila, M.L. Hladik, C.G. Ingersoll, N.E. Kemble, P.W. Moran, D.L. Calhoun, L.H. Nowell, R.J. Gilliom, Occurrence and potential sources of pyrethroid insecticides in stream sediments from seven U.S. metropolitan areas, Environ. Sci. Technol. 46 (2012) 4297–4303.
[58] D.P. Weston, J. You, M.J. Lydy, Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's Central Valley, Environ. Sci. Technol. 38 (2004) 2752–2759.
[59] K. Palmquist, A. Fairbrother, J. Salatas, P.D. Guiney, Environmental fate of pyrethroids in urban and suburban stream sediments and the appropriateness of *Hyalella azteca* model in determining ecological risk, Integr. Environ. Assess. Manage. 7 (2011) 325–335.
[60] J.J. Schleier III, R.K.D. Peterson, A refined aquatic ecological risk assessment for a pyrethroid insecticide used for adult mosquito management, Environ. Toxicol. Chem. 32 (2013) 948–953.
[61] B.S. Anderson, B.A. Phillips, J.W. Hunt, K. Worcester, M. Adams, N. Kapellas, R.S. Tjeerdema, Evidence of pesticide impacts in the Santa Maria River watershed, California USA, Environ. Toxicol. Chem. 25 (2006) 1160–1170.
[62] J.L. Domagalski, D.P. Weston, M. Zhang, M. Hladik, Pyrethroid insecticide concentrations and toxicity in streambed sediments and loads in surface waters of the San Joaquin Valley, California USA, Environ. Toxicol. Chem. 29 (2010) 813–823.
[63] M. Ensminger, R. Bergin, F. Spurlock, K.S. Goh, Pesticide concentrations in water and sediment and associated invertebrate toxicity in Del Puerto and Orestimba Creeks California, 2007–2008, Environ. Monit. Assess. 175 (2011) 573–587.
[64] D.P. Weston, Y. Ding, M. Zhang, M.J. Lydy, Identifying the cause of sediment toxicity in agricultural sediments: the role of pyrethroids and nine seldom-measured hydrophobic pesticides, Chemosphere 90 (2013) 958–964.
[65] J.S. Brown, M. Sutula, C. Stransky, J. Rudolph, E. Byron, Sediment contaminant chemistry and toxicity of freshwater urban wetlands in Southern California, J. Am. Water Resour. Assoc. 46 (2010) 367–384.
[66] R.W. Holmes, B.S. Anderson, B.M. Phillips, J.W. Hunt, D.B. Crane, A. Mekebri, V. Connor, Statewide investigation of the role of pyrethroid pesticides in sediment toxicity in California's urhan waterways, Environ. Sci. Technol. 42 (2008) 7003–7009.
[67] B.M. Phillips, B.S. Anderson, J.P. Voorhees, J.W. Hunt, R.W. Holmes, A. Mekebri, V. Connor, R.S. Tjeerdema, The contribution of pyrethroid pesticides to sediment toxicity in four urban creeks in California, USA, J. Pest. Sci. 35 (2010) 302–309.
[68] D.P. Weston, A.M. Asbell, S.A. Hecht, N.L. Scholz, M.J. Lydy, Pyrethroid insecticides in urban salmon streams of the Pacific Northwest, Environ. Pollut. 159 (2011) 3051–3056.
[69] E.P. Hintzen, M.J. Lydy, J.B. Belden, Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in Central Texas, Environ. Pollut. 157 (2009) 110–116.
[70] J.L. Bouldin, C.D. Milam, J.L. Farris, M.T. Moore, S. Smith, C.M. Cooper, Evaluating toxicity of Asana XL (R) (esfenvalerate) amendments in agricultural ditch mesocosms, Chemosphere 56 (2004) 677–683.
[71] L.H. Nowell, P.W. Moran, R.J. Gilliom, D.L. Calhoun, C.G. Ingersoll, N.E. Kemble, K.M. Kuivila, P.J. Phillips, Contaminants in stream sediments from seven United States metropolitan areas: part I: distribution in relation to urbanization, Arch. Environ. Contam. Toxicol. 64 (2013) 32–51.
[72] P.D. Thacker, Household pesticides are poisoning city creeks, Environ. Sci. Technol. 39 (2005) 497A–498A.
[73] https://www.epa.gov/ingredients-used-pesticide-products/pyrethrins-and-pyrethroids-reregistration-and-labeling.
[74] H. Li, B. Sun, X. Chen, M.J. Lydy, J. You, Addition of contaminant bioavailability and species susceptibility to a sediment toxicity assessment: application in an urban stream in China, Environ. Pollut. 178 (2013) 135–141.
[75] H. Qi, P. Ma, H. Li, J. You, Assessment of sediment risk in the north end of Tai Lake, China: integrating chemical analysis and chronic toxicity testing with *Chironomus dilutus*, Arch. Environ. Contam. Toxicol. 69 (2015) 461–469.
[76] USEPA, Sediment toxicity identification evaluation (TIE) phases I, II, and III guidance document. EPA 600/R-07/080. Washington, D.C. (2007).
[77] E.L. Amweg, D.P. Weston, Whole-sediment toxicity identification evaluation tools for pyrethroid insecticides: I. Piperonyl butoxide addition, Environ. Toxicol. Chem. 26 (2007) 2389–2396.
[78] D.P. Weston, E.L. Amweg, Whole-sediment toxicity identification evaluation tools for pyrethroid insecticides: II. Esterase addition, Environ. Toxicol. Chem. 26 (2007) 2397–2404.
[79] D.P. Weston, J. You, A.D. Harwood, M.J. Lydy, Whole sediment toxicity identification evaluation tools for pyrethroid insecticides: III. Temperature manipulation, Environ. Toxicol. Chem. 28 (2009) 173–180.
[80] B.M. Philips, B.S. Anderson, J.W. Hunt, S.A. Huntley, R.S. Tjeerdema, N. Kapellas, K. Worcester, Solid-phase sediment toxicity identification evaluation in an agricultural stream, Environ. Toxicol. Chem. 25 (2006) 1671–1676.
[81] B.M. Phillips, B.S. Anderson, J.W. Hunt, K. Siegler, J.P. Voorhees, R.S. Tjeerdema, K. McNeill, Pyrethroid and organophosphate pesticide-associated toxicity in two coastal watersheds (California, USA), Environ. Toxicol. Chem. 31 (2012) 1595–1603.
[82] X. Yi, H. Li, P. Ma, J. You, Identifying the causes of sediment-associated toxicity in urban waterways in South China: incorporating bioavailabillity-based measurements into whole-sediment toxicity identification evaluation, Environ. Toxicol. Chem. 34 (2015) 1744–1750.
[83] H. Li, J. You, Application of species sensitivity distribution in aquatic probabilistic ecological risk assessment of cypermethrin: a case study in an urban stream in South China, Environ. Toxicol. Chem. 34 (2015) 640–648.
[84] B. Wang, G. Yu, J. Huang, Y. Yu, H. Hu, L. Wang, Tiered aquatic ecological risk assessment of organochlorine pesticides and their mixture in Jiangsu reach of Huaihe River, China, Environ. Monit. Assess. 157 (2009) 29–42.
[85] S. Hasenbein, S.P. Lawler, J. Geist, R.E. Connon, A long-term assessment of pesticide mixture effects on aquatic invertebrate communities, Environ. Toxicol. Chem. 35 (2016) 218–232.
[86] L.W. Hall, W.D. Killen, R.D. Anderson, R.W. Alden, The relationship of benthic community metrics to pyrethroids, metals, and sediment characteristics in Cache Slough, California, J. Environ. Sci. Health A 51 (2016) 154–163.
[87] L.W. Hall Jr., R.D. Anderson, Relationship between bifenthrin sediment toxic units and benthic community metrics in Urban California streams, Arch. Environ. Contam. Toxicol. 65 (2013) 173–182.
[88] D.P. Weston, H.C. Poynton, G.A. Wellborn, M.J. Lydy, B.J. Blalock, M.S. Sepulveda, J.K. Colbourne, Multiple origins of pyrethroid insecticide resistance across the species complex of a nontarget aquatic crustacean, *Hyalella azteca*, PNAS 110 (2013) 16532–16537.
[89] D.M. DiToro, C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas, P.R. Paquin, Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equlibrium partitioning, Environ. Toxicol. Chem. 10 (1991) 1541–1583.
[90] W. Lao, L. Tiefenthaler, D.J. Greenstein, K.A. Maruya, S.M. Bay, K. Ritter, K. Schiff, Pyrethroids in Southern California coastal sediments, Environ. Toxicol. Chem. 31 (2012) 1649–1656.
[91] J. You, S. Pehkonen, D.P. Weston, M.J. Lydy, Chemical availability and sediment toxicity of pyrethroid insecticides to *Hyalella azteca*: application to field sediment with unexpectedly low toxicity, Environ. Toxicol. Chem. 27 (2008) 2124–2130.
[92] J.V.K. Kukkonen, S. Mitra, P.F. Landrum, D.C. Gossiaux, J. Gunnarsson, D. Weston, The contrasting roles of sedimentary plant-derived carbon and black carbon on sediment-spiked hydrophobic organic contaminant bioavailability to *Diporeia species* and *Lumbriulus variegatus*, Environ. Toxicol. Chem. 24 (2005) 877–885.
[93] T.L. terLaak, S.O. Agbo, A. Barendregt, J.L.M. Hermens, Freely dissolved concentrations of PAHs in soil pore water: measurements via solid-phase extraction and consequences for soil tests, Environ. Sci. Technol. 40 (2006) 1307–1313.
[94] X. Cui, P. Mayer, J. Gan, Methods to assess bioavailability of hydrophobic organic contaminants: principles, operations, and limitations, Environ. Pollut. 172 (2013) 223–234.
[95] M.J. Lydy, P.F. Landrum, A.M. Oen, M. Allinson, F. Smedes, A.D. Harwood, H. Li, K.A. Maruya, J. Liu, Passive sampling methods for contaminated sediments: state of the science for organic contaminants, Integr. Environ. Assess. Manage. 10 (2014) 167–178.
[96] J. You, A.D. Harwood, H. Li, M.J. Lydy, Chemical techniques for assessing bioavailability of sediment-associated contaminants: SPME versus Tenax extraction, J. Environ. Monit. 13 (2011) 792–800.
[97] A.D. Harwood, P.F. Landrum, M.J. Lydy, Can SPME fiber and Tenax methods predict the bioavailability of biotransformed insecticides? Environ. Sci. Technol. 46 (2012) 2413–2419.
[98] Y. Xu, F. Spurlock, Z. Wang, J. Gan, Comparison of five methods for measuring sediment toxicity of hydrophobic cantaminants, Environ. Sci. Technol. 41 (2007) 8394–8399.
[99] J. You, P.F. Landrum, M.J. Lydy, Comparison of chemical approaches for assessing bioavailability of sediment-associated contaminants, Environ. Sci. Technol. 40 (2006) 6348–6353.
[100] J. You, S. Pehkonen, P.F. Landrum, M.J. Lydy, Desorption of hydrophobic compounds from laboratory-spiked sediments measured by Tenax absorbent and matrix solid-phase microextraction, Environ. Sci. Technol. 41 (2007) 5672–5678.
[101] A.D. Harwood, P.F. Landrum, D.P. Weston, M.J. Lydy, Using SPME fibers and Tenax to predict the bioavailability of pyrethroids and chlorpyrifos in field sediments, Environ. Pollut. 173 (2013) 47–51.
[102] F. Wang, R.R. Goulet, P.M. Chapman, Testing sediment biological effects with the freshwater amphipod *Hyalella azteca*: the gap between laboratory and nature, Chemosphere 57 (2004) 1713–1724.

[103] C. de Perre, A.J. Trimble, J.D. Maul, M.J. Lydy, Ecological bioavailability of permethrin and p,p '-DDT: toxicity depends on type of organic matter resource, Chemosphere 96 (2014) 67–73.
[104] J.D. Maul, A.J. Trimble, M.J. Lydy, Partitioning and matrix-specific toxicity of bifenthrin among sediments and leaf-sourced organic matter, Environ. Toxicol. Chem. 27 (2008) 945–952.
[105] J.M. Giddings, K.R. Solomon, S.J. Maund, Probabilistic risk assessment of cotton pyrethroids: II. Aquatic mesocosm and field studies, Environ. Toxicol. Chem. 20 (2001) 660–668.
[106] F. Heimbach, W. Pflueger, H.T. Ratte, Use of small artificial ponds for assessment of hazards to aquatic ecosystems, Environ. Toxicol. Chem. 11 (1992) 27–34.
[107] J.D. Stark, J.E. Banks, R. Vargas, How risky is risk assessment: the role that life history strategies play in susceptibility of species to stress, PNAS 101 (2004) 732–736.
[108] G.T. Ankley, D.A. Benoit, J.C. Balogh, T.B. Reynoldson, K.E. Day, R.A. Hoke, Evaluation of potential confounding factors in sediment toxicity tests with three freshwater benthic invertebrates, Environ. Toxicol. Chem. 13 (1994) 627–635.
[109] A.P. Goyke, A.E. Hershey, Effects of fish predation on larval chironomid (Diptera: chironomidae) communities in an arctic ecosystem, Hydrobiologia 240 (1992) 203–211.
[110] A.U. Conrad, R.J. Fleming, M. Crane, Laboratory and field response of *Chironomus riparius* to a pyrethroid insecticide, Water Res. 33 (1999) 1603–1610.
[111] W.T. Mehler, J. Du, M.J. Lydy, J. You, Joint toxicity of a pyrethroid insecticide, cypermethrin, and a heavy metal, lead, to the benthic invertebrate *Chironomus dilutus*, Environ. Toxicol. Chem. 30 (2011) 2838–2845.
[112] X. Chen, H. Li, J. You, Joint toxicity of sediment-associated permethrin and cadmium to *Chironomus dilutus*: the role of bioavailability and enzymatic activities, Environ. Pollut. 207 (2015) 138–144.
[113] X. Chen, H. Li, J. Zhang, Y. Ding, J. You, Does cadmium affect the toxicokinetics of permethrin in *Chironomus dilutus* at sublethal level? Evidence of enzymatic activity and gene expression, Environ. Pollut. 218 (2016) 1008–1013.
[114] J.B. Belden, R.J. Gilliom, M.J. Lydy, How well can we predict the toxicity of pesticide mixtures to aquatic life? Integr. Environ. Assess. Manage. 3 (2007) 364–372.
[115] A.J. Trimble, D.P. Weston, J.B. Belden, M.J. Lydy, Identification and evaluation of pyrethroid insecticide mixtures in urban sediments, Environ. Toxicol. Chem. 28 (2009) 1687–1695.
[116] M.J. Lydy, J. Belden, C. Wheelock, B. Hammock, D. Denton, Challenges in regulating pesticide mixtures, Ecol. Soc. 9 (2004) 1–15.
[117] L. Hunt, C. Bonetto, V.H. Resh, D.F. Buss, S. Fanelli, N. Marrochi, M.J. Lydy, Insecticide concentrations in stream sediments of soy production regions of South America, Sci. Total Environ. 547 (2016) 114–124.
[118] L. Peluso, G.B. Rossini, A. Salibián, A. Ronco, Physicochemical and ecotoxicological based assessment of bottom sediments from the Lujan River basin, Buenos Aires Argentina, Environ Monit. Assess. 185 (2013) 5993–6002.
[119] M. Grung, Y. Lin, H. Zhang, A.O. Steen, J. Huang, G. Zhang, T. Larssen, Pesticide levels and environmental risk in aquatic environments in China — a review, Environ. Int. 81 (2015) 87–97.
[120] J. Du, J. Pang, J. You, Bioavailability-based chronic toxicity measurements of permethrin to *Chironomus dilutus*, Environ. Toxicol. Chem. 32 (2013) 1403–1411.
[121] A.D. Harwood, P.F. Landrum, M.J. Lydy, Bioavailability-based toxicity endpoints of bifenthrin for *Hyalella azteca* and *Chironomus dilutus*, Chemosphere 90 (2013) 1117–1122.
[122] C.R. Tyler, N. Beresford, M. v. d. Woning, J.P. Sumpter, K. Tchorpe, Metabolism and environmental degradation of pyrethroid insecticides produce compounds with endocrine activities, Environ. Toxicol. Chem. 19 (2000) 801–809.
[123] G. Yao, X. Jing, W. Peng, X. Liu, Z. Zhou, D. Liu, Chiral insecticide *(*-cypermethrin and its metabolites: stereoselective degradation behavior in soils and the toxicity to earthworm *Eisenia fetida*, J. Agric. Food Chem. 63 (2015) 7714–7720.
[124] H.-R. Köhler, R. Triebskorn, Wildlife ecotoxicology of pesticides: can we track effects to the population level and beyond? Science 341 (2013) 759–765.