Distribution and toxicity of current-use insecticides in sediment of a lake receiving waters from areas in transition to urbanization

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ABSTRACT

Current-use insecticides including organophosphate (OPs) and synthetic pyrethroid (SPs) insecticides were analyzed in 35 sediment samples collected from Chaohu Lake in China, where a transition from a traditional agricultural to a modern urbanized society is ongoing. Total concentrations of five OPs and eight SPs ranged from 0.029 to 0.681 ng/g dry weight and 0.016–301 ng/g dry weight, respectively. Toxic unit analysis showed that 13% of the sediment samples likely produced over 50% of the mortality for benthic invertebrates. Analysis also showed that cypermethrin was the principal contributor to the toxicity. Spatial distribution evaluation implied that OPs were mainly from non-point sources associated with agricultural activities. Conversely, SPs may have been derived from runoff of inflowing rivers through urban regions, as their concentrations were well-correlated with concentrations of other urban-oriented contaminants.

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1. Introduction

Organophosphate (OP) and synthetic pyrethroid (SP) insecticides have been widely used as alternatives to organochlorine insecticides which have been banned for use since the 1980s. As a result of their extensive applications, residues of current-use insecticides have been frequently detected in sediments from both agricultural (Hunt et al., 2008; Weston et al., 2004) and urban areas (Amweg et al., 2006; Ding et al., 2010; Hintzen et al., 2009; Holmes et al., 2008; Lao et al., 2010; Li et al., 2011; Trimble et al., 2009; Weston et al., 2005). Recently, Li et al. (2011) reported detection of sediment-associated current-use insecticides in urban waterways of the Pearl River Delta (PRD) in South China, and SPs were identified as one of the principal causes of sediment toxicity to benthic invertebrates (Mehler et al., 2011). Although those studies showed that SPs, which were widely used in urban areas, can pose great risk to aquatic ecosystems near residential areas (Weston et al., 2005), a direct link between their input sources and distribution in aquatic systems that received waters from both agricultural and urban runoff is limited.

Chaohu Lake is the fifth-largest freshwater lake in China, and its watershed lies between Yangtze River Delta and Huaihe River Watershed with an area of 13,350 km^2, accounting for ∼13% of the total area of Anhui Province in East China. The watershed mainly contains Hefei, Liu'an, and Chaohu cities, and agricultural production remains an important driver of the local economy. Beside traditional agricultural economics, urbanization has occurred during the past two decades in this area (Statistical Bureau of Anhui Province, 2010). Extensive agricultural cultivation, along with rapid urbanization, has led to significant deterioration of the aquatic ecosystems in the region. For example, Chaohu Lake has experienced severe eutrophication and become one of the most polluted lakes in China (State Environmental Protection Administration, 1996). The traditional agriculture-based economy, coupled with recent urbanization in Chaohu Watershed, suggested potential risk from current-use insecticides in this area. In this regard, Chaohu Lake is an ideal candidate to assess the input sources of various classes of insecticides.

The objectives of the current study were to analyze the occurrence and distribution of the current-use insecticides, including OPs and SPs, in sediments collected from Chaohu Lake and to evaluate their ecological risk. Furthermore, possible input sources of the target insecticides in Chaohu Lake were also assessed.

2. Materials and methods

2.1. Study area and sampling strategy

Chaohu Lake has a total area of ∼760 km^2, an average depth of 3.0 m, and a volume of 2.1×10^9 m^3 (Fig. S1). Total annual inflow from 33 rivers to the lake is

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4.8 × 10⁹ m³ with total outflow of 3.4 × 10⁹ m³/yr (Environmental Protection Department of Anhui Province, 2009). The lake is mainly surrounded by farmland, however two large cities (Hefei and Chaohu) are located along the northwestern and eastern shore of the lake, respectively (Fig. S1). Hefei and Chaohu cities held 21% and 5.3% of gross domestic product (GDP) and 7.2% and 6.7% of the population of Anhui province, respectively (Statistical Bureau of Anhui Province, 2010). Because of the rapid urbanization and heavy agricultural cultivation along its watershed, Chaohu Lake is one of the most seriously polluted lakes in China.

As shown in Fig. S1, 35 sampling sites (L1–L35) were designed at a 0.05 × 0.05° latitude/longitude resolution throughout the lake. A global positioning system was employed to determine the geographical coordinates of the sampling sites, and surface sediments were collected at each site using a stainless steel grab in October 2009. The sediments were transported back to the laboratory, homogenized, and stored frozen prior to use.

2.2. Chemicals and reagents

Seven SPs (bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, and permethrin) and four OPs (terbufos, diazinon, tebupirimfos, and malathion) were purchased from ChemService (West Chester, PA, USA). Additionally, tefluthrin (a SP) was obtained from Sigma–Aldrich (St. Louis, MO, USA) and chlorpyrifos (an OP) was supplied by Ultra (Kingstown, RI, USA). All insecticides had purities >97% as indicated by the manufacturers, and their physicochemical properties are presented in Table S1. The surrogates decachlorobiphenyl and 4,4′-dibromooctafluorobiphenyl were purchased from Supelco (Bellefonte, PA, USA). Parathion-d_{10} (Cambridge, Andover, MA, USA) and chlorinated biphenyl-189 (AccuStandard, New Haven, CT, USA) were employed as the internal standards for OPs and SPs, respectively.

Dual-layer solid phase extraction (SPE) cartridges packed with 600 mg primary/secondary amine and 300 mg graphite carbon black were purchased from Supelco. Hexane, dichloromethane, and acetone (pesticide grade) were purchased from Honeywell International Inc (Morristown, New Jersey, USA). Copper sheets were activated with 6 M of HCl, and sequentially washed with tap water, deionized water, and acetone.

2.3. Sample preparation

Sediment samples were extracted and cleaned following a previously developed method (Li et al., 2010) with minor modifications. Briefly, the freeze-dried sediments were sieved and subjected to Soxhlet extraction with a 200 ml of a mixture of hexane and acetone (1:1, v/v) for 48 h after the addition of the surrogates. Activated copper was also added to sediment before extraction to remove elemental sulfur. The extracts were concentrated, solvent-exchanged to hexane, and further reduced to ∼1 ml using a TurboVap (Zymark, Hopkinton, MA, USA). The concentrated extracts were then cleaned with the SPE cartridges and 7 ml of 30% dichloromethane in hexane was used as the elution solvents. The cleaned extract was solvent-exchanged to hexane, evaporated to 0.5 ml, and the internal standards were added before instrumental analysis.

2.4. Instrumental analysis

The target insecticides were analyzed using a Shimadzu QP-2010-plus GC–MS (Shimadzu Corporation, Kyoto, Japan) in negative chemical ionization mode with a Rtx-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) being used for separating the analytes. The column temperature was programmed from 60 °C (2 min) to 180 °C at a rate of 25 °C/min and held for 1 min, to 240 °C at 10 °C/min and held for 5 min, then to 290 °C at 7 °C/min and held for 10 min. Helium was used as the carrier gas at a flow rate of 1 ml/min and methane as the reaction gas. The ion source and interface temperatures were maintained at 250 and 260 °C, respectively. A programmable temperature vaporizing injector was used to introduce 1 μl of extract into the GC/MS and the injector temperature was heated from 50 to 300 °C at a rate of 230 °C/min and held for 5 min. Selective ion monitoring mode was used to monitor the ions, and the most abundant ion in scan mode was selected as the target ion for each analyte. Identification of analytes was based on detection of the target and qualifier ions, while quantification was performed using internal standard calibration. Six standards, ranging from 5 to 200 ng/ml for each analyte, were used to set up the calibration curves and the regression coefficients (r^2) were all >0.99. Concentrations of the internal standards remained constant at 50 ng/ml.

The total organic carbon (TOC) content of sediment was measured using an elemental analyzer (Elementar Vavio EL III, Hanau, Germany) after removing the inorganic carbonates with 1 M HCl.

2.5. Quality assurance/quality control

The GC/MS was checked every 10 samples with a calibration standard, and the relative percent variations between the six-point calibration and the check standard were <20%. A method blank (solvent) and a matrix blank (control sediment), a matrix spike, and a matrix spike duplicate were included for every 20 samples. Moreover, performance of analytical processes for all samples was validated by

checking recoveries of the surrogates which were added before extraction. The measured concentrations were not corrected by the surrogate recoveries.

2.6. Data analysis

The reporting limits (RLs) were calculated from the lowest concentrations of the calibration standards (Wang et al., 2007), and the RLs for the target insecticides were 0.07–0.57 ng/g dry weight (dw). When concentration was below the RL, zero was employed for concentration calculation. The total concentrations of five OPs and eight SPs were defined as Σ_5OPs and Σ_8SPs, respectively, while their respective TOC-normalized concentrations were marked as Σ_5OPs/OC and Σ_8SPs/OC. The detection frequency, mean, standard deviation, minimum, maximum and percentile values of the individual OP and SP were calculated using a SPSS 16.0 software package (Chicago, IL, USA). Moreover, the relative abundances were used to depict the occurrence profiles of the target insecticides and were computed by dividing the concentration of an insecticide to the sum concentrations of the insecticides of the same class.

As shown in Equation (1), toxic unit (TU) was the ratio of environmental concentration of a contaminant and its median lethal concentration (LC50), and used in the current study to estimate potential risk caused by each insecticide.

$$TU_i = \frac{C_m(i)/OC}{LC50(i)} \tag{1}$$

Where, $C_m(i)$/OC represents TOC-normalized sediment concentration of contaminant i, LC50(i) is the median lethal concentration of contaminant i to the benthic organism Hyalella azteca. The LC50 values were acquired from the literature (Amweg et al., 2005; Ding et al., 2010, 2011) and presented in Table S1. The LC50 values for terbufos, tebupirimfos, and malathion were not found, therefore they were excluded from the estimation of TUs. Assuming additivity (Belden and Lydy, 2006), total TU for a sediment was calculated by summing the TU_i of individual insecticide detected in sediment.

The normal distribution of log-transformed Σ_5OPs and Σ_8SPs was checked using Kolmogorov–Smirnov test whereas all two-tailed significance tests of Pearson correlations were processed with SPSS. Furthermore, the spatial distribution of concentrations and TUs of the target insecticides were depicted using Golden Surfer 9.0 (Golden Software, Golden, CO, USA) with the gridding method of Kriging.

3. Results and discussion

3.1. Occurrence and toxicity of sediment-associated insecticides

To ensure quality of analytical procedures, quality control check samples were analyzed along with the sediment samples and no target insecticides were found in the blanks. The recoveries of OPs and SPs in the matrix spike and matrix spike duplicate were from 78 to 122% and 78–101%, respectively. In addition, the recoveries of the surrogates in all samples were 44–118% and 65–161% for 4,4′-dibromooctafluorobiphenyl and decachlorobiphenyl, respectively.

Table S2 showed detection frequencies and concentrations of the sediment-associated insecticides in Chaohu Lake. Total concentrations of five OPs (Σ_5OPs) and eight SPs (Σ_8SPs) ranged from 0.029 to 0.681 and 0.016–301 ng/g dw, respectively, which corresponded to 0.054–0.080 and 0.771–2.47 μg/g OC for Σ_5OPs/OC and Σ_8SPs/OC, respectively. The mean and median values were 0.323 and 0.329 ng/g dw for Σ_5OPs, and 14.2 and 0.981 ng/g dw for Σ_8SPs, respectively. Moreover, concentration distribution of each insecticide in all sediments was also profiled as the percentiles in Table S2. Although terbufos and diazinon were detected in all samples, chlorpyrifos, which was detected in 97% of samples, contributed to 54.3 ± 20.9% of Σ_5OPs, followed by malathion (40% of detection) with the relative abundance of 25.9 ± 23.4% (Fig. S2). Compared to OPs, SPs were detected at higher frequencies and concentrations (Table S2). Tefluthrin was detected in all sediments except one, and λ-cyhalothrin, cypermethrin, and esfenvalerate were found in 33 of the 35 sediments. With a detection frequency of 66%, permethrin was detected at the highest concentration and contributed to 65.2 ± 17.8% to Σ_8SPs, which was followed by esfenvalerate and cypermethrin (20.3 ± 22.3% and 34.4 ± 22.2%, respectively, Fig. S2).

Total concentrations of Σ_8SPs were higher than Σ_5OPs in 25 sediments with the mean SP concentration being about 29 times

higher than the mean OP concentration. The variation in SP concentrations among the sites (~ 18800, maximum value of $\Sigma_8 SPs$ divided by the minimum one) was significantly greater than that for $\Sigma_5 OPs$ (23.5) (Fig. 1). Furthermore, there was no spatial correlation between the concentrations of OPs and SPs ($p > 0.05$). These findings implied that the two classes of insecticides may originate from differing sources and may be explained by their application pattern and the physicochemical properties. On the one hand, OPs were mainly used for agricultural purposes whereas SPs were extensively applied for mosquito control and landscaping maintenance in urban areas (Li et al., 2011; Weston et al., 2005). On the other hand, the SPs generally had less water solubility and slower hydrolysis rates than OPs (Table S1), thus SPs had higher tendency to sorb to sediment and were more persistent. As a result, greater concentrations of SPs were detected in sediment than of OPs.

In aquatic systems, hydrophobic organic contaminants tend to be associated with sediment OC. Surprisingly, either $\Sigma_8 SPs$ or $\Sigma_5 OPs$ poorly correlated to sediment TOC ($p > 0.01$), and it may be explained by the origination of sediment TOC in Chaohu Lake. Chaohu Lake has had a long history of eutrophication and high concentrations of *Chlorophyll a* of approximate 30 and 17 mg/m^3 were detected in western and eastern regions, respectively (Xu et al., 2005). As a result, the internal organic matter from phytoplankton dominated sediment TOC in the lake. Conversely, insecticides entered the lake along with the external organic matter. The internal and external organic matter varied in hydrodynamics, degradation rates, and fine grain contents (Liu et al., 2008a), which violated the relationships between contaminant concentrations and sediment TOC contents.

In addition to their occurrence and distribution, toxicity of current-use insecticides to the amphipod *H. azteca* was also estimated from their concentrations in sediment using a TU approach. As shown in Fig. 2 and Fig. S3, TUs ranged from 0.013 to 13.1 for the 35 sediments, with a median value of 0.98. The TUs of the majority of sediments were around 0.1, but 13% of samples had a TU > 1, which theoretically corresponded to over 50% mortality to *H. azteca*. Of all the target insecticides, cypermethrin contributed the most ($44.0 \pm 20.0\%$) of the total TU of SPs, followed by
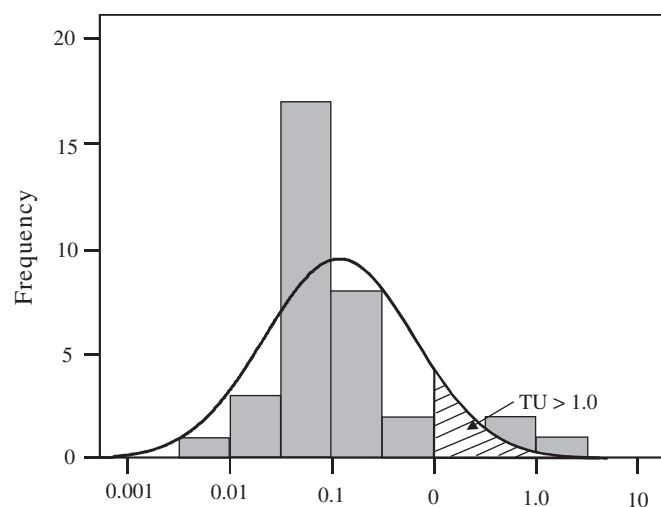

Fig. 2. Frequency distribution of toxicity unit (TU) estimated from concentrations of the target insecticides in sediment from Chaohu Lake and 10-d median lethal concentration to *Hyalella azteca* (Table S1). The shaded area under the curve represents the frequency of a TU value >1.0.

esfenvalerate ($27.8 \pm 18.3\%$) and permethrin ($16.4 \pm 17.2\%$) (Fig. S4). As the least toxic SP (Hintzen et al., 2009), permethrin contributed less to the toxicity than cypermethrin and esfenvalerate, despite permethrin having the highest sediment concentrations. Instead, cypermethrin had the lowest LC50 value and made the greatest contribution to overall TUs.

Overall, current-use insecticides were widespread in sediments from Chaohu Lake. Some sites in the lake were adversely affected, especially by SPs, and may cause acute mortality to benthic organisms.

3.2. Comparison to other studies

Similar to the current study, SPs have been frequently detected in sediments from California (Amweg et al., 2006; Holmes et al., 2008; Trimble et al., 2009; You et al., 2008; Weston et al., 2004, 2005), Texas (Hintzen et al., 2009), and Illinois (Ding et al., 2010) in USA, as well as the PRD in China (Li et al., 2011). The OPs, however, were detected at lower frequencies and concentrations in those studies. For example, chlorpyrifos was the only OP detected at concentrations of 1.33–100 ng/g dw with a detection frequency of 62% in the PRD sediments (Li et al., 2011). In Texas, USA, diazinon and chlorpyrifos were found in 22% and 57% of sediments at concentrations of 0.071–0.95 and 0.039–10 ng/g dw, respectively (Hintzen et al., 2009).

The lower detection frequencies and concentrations of OPs as compared to SPs were also noted in the current study, and differing physicochemical properties of the two classes of insecticides may be one of the reasons. The OPs tended to distribute in water because of their high water solubility (Table S1). If equilibrium of insecticides between water and sediment was attained, the mean concentrations of $\Sigma_5 OPs$ and $\Sigma_8 SPs$ in water were 51 ± 61 and 6.0 ± 21 ng/L, respectively (the calculation was detailed in the SI). As shown in Table S1, both OPs and SPs were quickly degraded in water and their half-lives for photodegradation in water ranged from 1 to 98 d. Kamiya and Kameyama (1998) reported that dissolved humic substances would enhance degradation of OPs in water. Chaohu Lake experienced serious eutrophication and had high occurrence of nitrogen, phosphate, bacterioplankton (Wei et al., 2008), blue-green algae (Liu, 2007), and dissolved OC (Zhang et al., 2004), thus the degradation rates of OPs may be
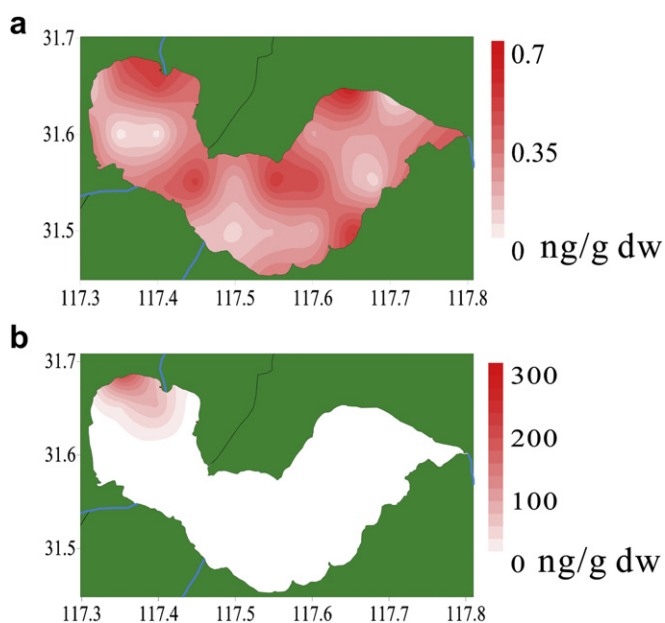

Fig. 1. Spatial distribution of total concentrations of five organophosphate insecticides ($\Sigma_5 OP$) (a) and eight pyrethroid insecticides ($\Sigma_8 SPs$) (b) in sediment from Chaohu Lake.

enhanced. As mentioned earlier, SPs had greater hydrophobicity than OPs, tended to accumulate in solid phase and were more resistant to degradation (Gan et al., 2005), thus it is reasonable that greater amounts of SPs were accumulated in the lake sediment. In addition, the recent restriction of OP usage reduced the input of OPs into the environment. For example, the application of diazinon for agricultural purposes has been limited to the selected crops recently (U.S. Environmental Protection Agency, 2004).

Compared to the other locations, sediment-associated OPs were more frequently detected in Chaohu Lake. Difference in land use of the sampling regions may be one of the reasons. The majority of previous studies focused on urban areas, but Chaohu Lake receives water from both urban and rural areas. Moreover, compared to 80% urbanization in the PRD (Li et al., 2011), the degree of urbanization in Anhui Province was ∼42% (Statistical Bureau of Anhui Province, 2010). Therefore, more OPs are possibly being applied in Chaohu Watershed due to traditional agricultural activities, and it was a feasible explanation for the greater detection frequencies and concentrations of OPs in the current study.

On the other hand, the mean Σ_8SPs concentration in sediment from Chaohu Lake was significantly lower than that in more urbanized areas in previous studies including the PRD in China (Li et al., 2011), and Illinois (Ding et al., 2010) and California (Amweg et al., 2006; Holmes et al., 2008; Weston et al., 2005) in USA, while it was comparable to that in Texas, USA (Hintzen et al., 2009) (Fig. 3a). The highest SP concentration in Chaohu Lake was similar

to that in the PRD, and these concentrations were between the highest SP concentration in California and those in Texas and Illinois in USA. The discovery of lower SP concentrations in sediment from Chaohu Lake than that of other areas was reasonable, since Chaohu Watershed was in transition from a traditional agricultural society to a modern industrialized society and was less urbanized than the other areas.

In addition to sediment concentrations of the insecticides, SP-induced sediment toxicity was also compared among studies. As shown in Fig. 3b, the mean TU value in the current study was the lowest among all studies although the mean SP concentration in sediment from Chaohu Lake was comparable to that in Texas (Fig. 3a). The result implied that not only total sediment concentrations, but also the types of SPs greatly affected the toxicity. Permethrin, esfenvalerate, and cypermethrin were the most frequently detected and the most abundant SPs in sediment from Chaohu Lake, with cypermethrin and permethrin being frequently found at elevated concentrations in the PRD (Li et al., 2011). In USA, the dominated sediment-associated SPs in concentration were bifenthrin, permethrin, and esfenvalerate in Texas (Hintzen et al., 2009), bifenthrin, permethrin, and cypermethrin in California (Amweg et al., 2006; Holmes et al., 2008; Weston et al., 2004, 2005), and permethrin in Illinois (Ding et al., 2010). Permethrin was prevalent in all locations, however, its contribution to sediment toxicity was relatively low as it was the least toxic SP. Instead, bifenthrin and cypermethrin were over 20 times more toxic than permethrin and played important roles in the observed toxicity (Amweg et al., 2005). While bifenthrin was the major contributor to most sediment toxicity in USA (Trimble et al., 2009; Weston et al., 2005), cypermethrin was the principal contributor to sediment toxicity in China (Mehler et al., 2011; the current study). This difference may come from the preference in SP usage in the two countries. Landscape use by homeowners or their gardening services were considered as one of the major input sources of bifenthrin into aquatic ecosystems in USA (Weston et al., 2005). In contrast, few Chinese homeowners have their private lawns, thus the input source of bifenthrin due to homeowners' lawn care is limited in this country. Alternatively, cypermethrin was reported as one of the most commonly used SPs in Asia due to its relatively low price (Whittle, 2010).

Besides cypermethrin, esfenvalerate also greatly contributed to sediment toxicity in Chaohu Lake, although the toxicity contribution from esfenvalerate was negligible in the PRD sediment (Fig. S4). This disparity in patterns of SP residues in differing regions in China may originate from their application patterns. Bifenthrin, permethrin and cypermethrin were the major components in sediment receiving urban runoff, whereas esfenvalerate was mainly related to rural usage (Trimble et al., 2009). Therefore, the high detections of esfenvalerate along with the OPs in Chaohu Lake implied the possible agricultural input of insecticides into the lake.

3.3. Spatial distribution and input sources of sediment-associated insecticides

Spatial distribution of the sediment-associated insecticides in Chaohu Lake was presented in Fig. 1. The highest concentration of Σ_5OPs was observed at site L29, and it was located at the estuary of Zhigao River which flows through the northward farmland (Fig. S1). It suggested that the riverine input of Zhigao River is an important source of OPs, and it was consistent to a previous finding which reported elevated concentrations of dichlorodiphenyltrichloroethane and its metabolites in water adjacent to Zhigao River and claimed Zhigao River played a key role in insecticides' transport to Chaohu Lake (Zhang et al., 2010). Generally higher OP concentrations were detected in sediment near the lake shore, and the lowest
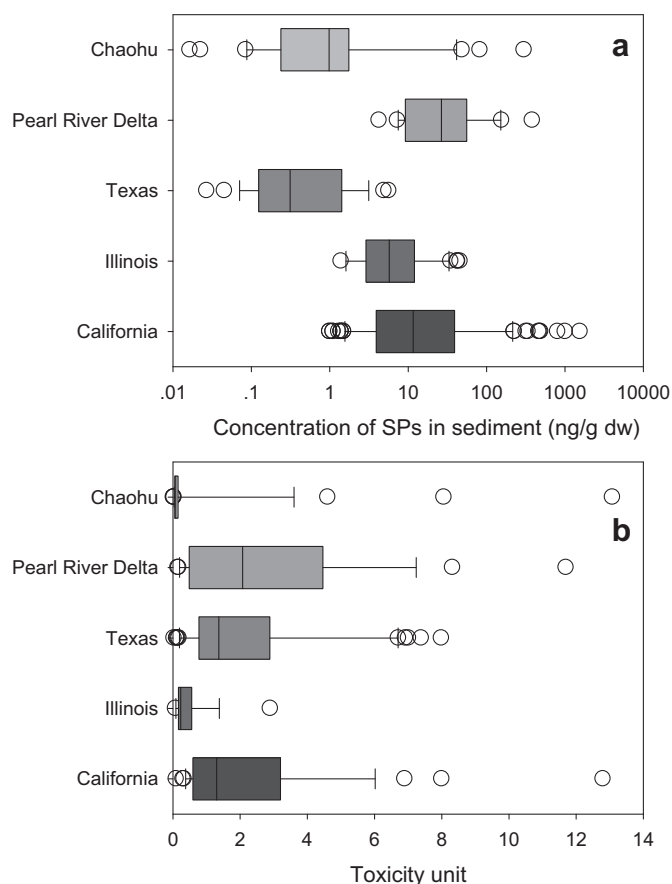

Fig. 3. Comparisons of concentrations and toxicity of synthetic pyrethroid insecticide (SP) in sediments from California (Weston et al., 2005; Holmes et al., 2008; Trimble et al., 2009), Illinois (Ding et al., 2010), and Texas (Hintzen et al., 2009) in USA, the Pearl River Delta (Li et al., 2011; Mehler et al., 2011), and Chaohu Lake (the current study) in China.

Σ_5OPs were determined in samples L5 to L10 which were collected in the center of the western region (Fig. 1a). Tang et al. (2010) suggested that soil erosion and water discharge were the main reasons for accumulation of heavy metal in sediment adjacent to inflowing rivers in Chaohu Lake from local agricultural cultivation. In the same way, insecticides may enter the lake and deposit in sediment near the inflowing rivers.

No significance was noted for sediment OP concentrations in the western region (L1−L11, L14, and L15, with an average of 0.33 ng/g dw) and the eastern region (0.32 ng/g dw) of the lake. This was dissimilar to other contaminants studied before including nitrogen and phosphorus (Pang et al., 2007), TOC (Liu et al., 2008a), heavy metals (Cheng et al., 2008), polycyclic aromatic hydrocarbons (PAHs), and linear alkylbenzenes (LABs) (Table S3). Those contaminants mainly originated from urban sewage discharge, and significantly greater concentrations were detected in the western region compared to the eastern region. As shown in Fig. 4a, OPs in sediment from Chaohu Lake were poorly correlated to 28 PAHs and 19 LABs measured in sediment samples collected from the same sampling sites ($p = 0.18$ and 0.41, respectively). The PAHs were mainly derived from the anthropogenic sources in modern environment and frequently detected at elevated concentrations in urban areas (Liu et al., 2008b; Wang et al., 2007). Meanwhile, LABs were the raw materials of the linear alkylbenzensulfonate anionic surfactants in commercial detergents (de Almeida et al., 1994) and used as molecular markers for urban sewage discharge (Takada and Ishiwatari, 1987). The poor correlations suggested that OPs had different input sources from PAHs and LABs, and OPs may derive

from non-point sources associated with the agricultural activities around the lake.

On the contrary, distinct spatial distribution was noted for SPs in sediment across Chaohu Lake. The mean SP concentration in the western region (36.8 ng/g dw) was significantly higher than that in the eastern region (0.89 ng/g dw) and the highest Σ_8SPs concentration was at the estuary of Wushili River (site L7, 301 ng/g dw) (Fig. 1b). High levels of Σ_8SPs of 36.8, 48.7, and 82.6 ng/g dw were also monitored at sites L6, L8, and L9, located at the estuary of Nanfei River, respectively. Both Wushili River and Nanfei River are in the northwest of Chaohu Lake and receive runoff from Hefei, the largest city in Anhui Province. Furthermore, as shown in Fig. 4b, there were significant relationships between concentrations of SPs and the representative contaminants discharged from urban runoff (PAHs and LABs) in sediments collected from the same sites (both $p < 0.01$). So the riverine input of Wushili River and Nanfei River significantly contributed to sediment-associated SPs in Chaohu Lake, and urban anthropogenic activities may be the major SP source.

Previous studies in California (Amweg et al., 2006) and Texas in USA (Hintzen et al., 2009) reported greater SP concentrations in sediment in urbanized areas. Recently, a study in the PRD in South China (Li et al., 2011) reported that rapid urbanization resulted in widespread distribution of SPs in urban waterways, and greater levels of SPs were detected in sediment from more populous and urbanized areas than those from less developed areas. Weston et al. (2005) suggested that permethrin residues were mainly from professional landscape treatments, whereas structural pest control was the primary source of bifenthrin and cypermethrin in California, USA. Additionally, home garden maintenance was considered as another major source of bifenthrin residues in sediment (Hintzen et al., 2009; Weston et al., 2005). Information of the SP usage in Chaohu Watershed was scarce, however, similar to other urban areas, structural pest control and landscape maintenance may be the primary sources for SPs in the cities of this watershed (Li et al., 2011; Weston et al., 2005). Furthermore, three factories of mosquito-control products were located in the upper reaches of Nanfei River and Wushili River, thus their discharge may also be a probable input source for SPs in Chaohu Lake. However, it is impossible to specify the sources of individual SPs in Chaohu Lake due to a lack of information on their usage.

Overall, spatial distribution of current-use insecticides in sediment from Chaohu Lake implied that OPs originated from non-point agricultural runoff, whereas SPs were mainly from urban discharge. Although previous studies reported detections of SPs at higher concentrations in urban waterways, the current study provided strong support to the hypothesis that SPs mainly originated from urban runoff by establishing direct correlations between sediment-associated SPs and other urban-oriented contaminants (e.g. PAHs and LABs) for the first time.

4. Conclusions

Current-use insecticides including five OPs and eight SPs were widespread in sediment from Chaohu Lake in East China, and SP concentrations were high enough to cause acute toxicity to benthic invertebrates at some sites. Additionally, Chaohu Lake received water from the watershed in transition from traditional agricultural to modern industrialized economics, and it is an ideal candidate for evaluating input sources of various classes of insecticides. Distinct spatial distribution and good correlations between concentrations of SPs and other urban-originated contaminants, e.g. PAHs and LABs, suggested urban runoff was the primary source of SPs into the lake. On the contrary, OPs mainly originated from non-point sources associated with agricultural activities.
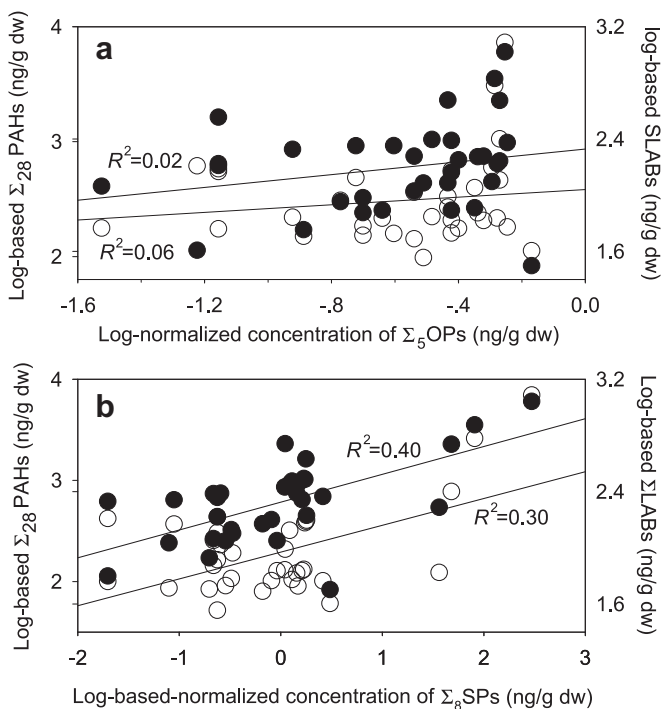

Fig. 4. Relationships of total concentrations of 28 polycyclic aromatic hydrocarbons (Σ_{28}PAHs, black circle) and 19 linear alkylbenzenes (ΣLABs, blank circle) to total concentrations of five organophosphate insecticides (Σ_5OP) (a) and eight pyrethroid insecticides (Σ_8SPs) (b) in sediment from Chaohu Lake. No significant correlations between log-based Σ_5OPs and log-based Σ_{28}PAHs or log-based ΣLABs (LogΣ_{28}PAHs $= 0.278$ logΣ_5OP $+ 2.94$, $r^2 = 0.06$, $p = 0.18$; LogΣLABs $= 0.136$ logΣ_5OP $+ 2.04$, $r^2 = 0.02$, $p = 0.41$), but the correlations between log-based Σ_8SPs and log-based Σ_{28}PAHs or log-based Σ_8SPs and ΣLABs were significant (LogΣ_{28}PAHs $= 0.275$ logΣ_8SPs $+ 2.79$, $r^2 = 0.40$, $p < 0.01$; LogΣLABs $= 0.191$ logΣ_8SPs $+ 1.97$, $r^2 = 0.30$, $p < 0.01$). Two-tailed significance tests of Pearson correlations were processed with SPSS 16.0.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.envpol.2011.10.020.

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