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Polyhalogenated carbazoles in sediments from Lake Tai (China): Distribution, congener composition, and toxic equivalent evaluation☆

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ABSTRACT

Polyhalogenated carbazoles (PHCZs) have attracted mounting environmental concerns since they were recently discovered in sediments and soil. Current knowledge on their occurrence, environmental behavior and fate remains very limited in general. In the present study, 11 PHCZ congeners were screened in surface sediments of Lake Tai, an important freshwater system located in the Yangtze River Delta, China. Total concentrations of PHCZs (∑PHCZs) ranged up to 15.8 ng/g dry weight (median: 1.54 ng/g dw), rivaling those of polybrominated diphenyl ethers (∑PBDEs, 0.07–15.9 ng/g dw) in the same sediments. The PHCZ congener composition profiles revealed a dominance of 3,6-dichlorocarbazole and 3,6-dibromocarbazole with comparable concentrations. These two dominant congeners differed in spatial distribution patterns in Lake Tai, indicating different sources or origins. Potential toxic effects associated with the levels of PHCZs in the sediments were evaluated via the toxic equivalent (TEQ) approach. The TEQs of PHCZs in Lake Tai sediments ranged up to 1.36 pg TEQ/g dw. As the first report on the occurrence of PHCZs in an Asian waterbody, our findings suggest that PHCZs should be given more attention during environmental monitoring and risk assessments of hazardous chemicals, as they may represent another group of persistent organic pollutants with dioxin-like effects and wide distributions.

1. Introduction

Polyhalogenated carbazoles (PHCZs) are a group of chemicals with a common base structure of carbazole and a complexity of halogen atom substitutions, including chlorine, bromine, iodine, or a combination thereof (Parette et al., 2015). Recent studies, while limited in number, have suggested the persistence and toxicity of some PHCZ substances. A variety of PHCZs have been qualitatively or quantitatively determined in aquatic sediments from Lake Michigan (USA) (Guo et al., 2014; Peng et al., 2015, 2016; Zhu and Hites, 2005), the Saginaw River system (USA) (Wu et al., 2016), Ontario (Canada) (Pena-Abaurrea et al., 2014), the Lippe River (Germany) (Heim et al., 2004; Kronimus et al., 2004), the North Sea (Germany) (Chen et al., 2016), and the industrial coastal area of Kavala City (Greece) (Grigoriadou and Schwarzbauer, 2010), demonstrating a wide distribution and substantial level of persistence in aquatic benthic environments. Chlorinated carbazoles, including 3-chlorocarbazole (3-CCZ) and 3,6-dichlorocarbazole (36-CCZ), were also detected in soil from Europe with concentrations up to 3500 ng/g dw (Grigoriadou and Schwarzbauer, 2010; Reischl et al., 2005; Trobs et al., 2011). In addition to their environmental occurrence and persistence, PHCZs also exhibited toxic effects. Due to their structure similarity with polyhalogenated dibenzo-*p*-dioxin, dioxin-like effects on organisms have been reported for PHCZs (Fang et al., 2016; Mumbo et al., 2015; Riddell et al., 2015). Acute developmental toxicity similar to dioxin-induced cardio-toxicity was observed in zebrafish *(Danio rerio)* exposed to 2,7-dibromocarbzole (27-BCZ) and 2,3,6,7-tetrachlorocarbazole (2367-CCZ) (Fang et al., 2016), while 3-CCZ and 36-CCZ induced ethoxyresorufin-*O*-deethylase (EROD) in H4IIA rat hepatoma cells assay (Mumbo et al., 2015).

Despite the environmental occurrence and potential toxicity of PHCZs, knowledge on their origins and environmental behavior

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(e.g. bioavailability and degradation) remains limited. Halogenated indigo dyes were suspected as potential origins of some brominated carbazoles, such as 1,3,6,8-tetrabromocarbazole (1368-BCZ) and 1,8-dibromo-3,6-dichlorocarbazole (18-B-36-CCZ), which may be formed during the indigo manufacturing processes and thus present as impurities in the final products (Parette et al., 2015). However, a general lack of known emission sources (Mumbo et al., 2013; Reischl et al., 2005), as well as possible formation of PHCZs via laboratory-based enzymatic synthesis (Mumbo et al., 2013), may also suggest the likelihood of natural occurrence of at least some, if not all, of the known PHCZ congeners or their precursors. In addition, little is known about the bioavailability of PHCZs and their resistance to environmental or biological degradation, as well as their ecotoxic risks to exposed organisms. Therefore, more studies, including environmental monitoring and laboratory-based investigations, are essentially needed to elucidate the sources, environmental behavior and fate of these emerging chemicals. Particularly, data from additional aquatic systems are needed to reveal the abundance, distribution patterns, and associations with environmental or anthropogenic factors, on a regional or global scale.

In light of the knowledge gaps and research needs identified above, the present study aimed to investigate the abundance and distributions of PHCZs in Lake Tai, the third largest freshwater lake in China, located in the Yangtze River Delta (YRD). Lake Tai serves as a drinking water resource to more than 34 million residents in its waterbody (Wang et al., 2016) and is one of the most extensively studied aquatic systems worldwide for anthropogenic impacts and pollution (Duan et al., 2009; Wilhelm et al., 2011; Yu et al., 2015; Zhang et al., 2012). Specific objectives of this study were to: (1) elucidate composition patterns and abundances of a variety of PHCZ congeners; (2) compare PHCZ concentrations with those of other well-known halogenated pollutants; and, (3) perform a preliminary risk assessment for sediment-associated PHCZs using pre-existing toxicity information. To the best of our knowledge, this is the first study investigating PHCZs in a large waterbody from Asia.

2. Materials and methods

2.1. Chemicals and reagents

The reference standards of 3-bromocarbazole (3-BCZ), 27-BCZ, and 3,6-dibromocarbazole (36-BCZ) were purchased from Sigma-Aldrich (St. Louis, Missouri). The standard of 1368-BCZ was purchase from the Florida Center for Heterocyclic Compounds of the University of Florida (Gainesville, FL). Reference standards of 3-CCZ, 36-CCZ, 1368-CCZ, 2367-CCZ, 1,3,6-tribromocarbazole (136-BCZ), 1-bromo-3,6-dichlorocarbazole (1-B-36-CCZ), and 18-B-36-CCZ were purchased from Wellington Laboratories (Guelph, ON, Canada). Table S1 summarizes the list of PHCZs determined in the present study. Reference standards of 20 polybrominated diphenyl ether (PBDE) congeners (Table S2) were purchased from AccuStandard (New Haven, CT). Surrogate standards, including 4′-fluoro-2,3′,4,6-tetrabromodiphenyl ether (F-BDE-69), 4′-fluoro-2,3,3′,4,5,6-hexabromodiphenyl ether (F-BDE-160), 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl (PCB-204), and 2,2′,3,3′,4,5,5′,6,6′-nonabromo-4′-chlorodiphenyl ether (4PC-BDE-208, surrogate standard for BDE-209), as well as internal standards, including 3′-Fluoro-2,2′,4,4′,5,6′-hexabromodiphenyl ether (F-BDE-154) and decachlorodiphenyl ether (DCDE), were purchased from AccuStandard or Wellington Laboratories. Diatomaceous earth (DE), sodium sulfate (10–60 mesh), copper (50 mesh, granular, reagent grade), and high-performance liquid chromatography (HPLC) grade solvents were purchased from Fisher Scientific (Hanover Park, IL). The Isolute® silica sorbent (average pore size: 60 Å) was purchased from Biotage Inc. (Charlotte, NC, USA) and baked at 130 °C (>6 h) prior to use.

2.2. Sample collection and preparation

Lake Tai was geographically divided into five regions (E-East, W-West, S-South, N-North and C-Central). Sediment samples were collected from 22 locations in 2013–2014 (Fig. 1), covering the entire lake system. Surface sediments, approximately 10 cm in depth from the top, were sampled with a stainless steel core sampler and stored in pre-cleaned sampling bags. Four subsamples, approximately 50 cm away from each other, were collected at each location and mixed into a composite. All sediments were freeze-dried for 48 h and sieved through a 250-μm stainless cloth sieve (Hogentogler & Co., Inc., Columbia, MD). The dried sediments were stored at −20 °C prior to further treatment.

Analyses of PHCZs in sediments were performed following the analytical methodology previously reported with slight modifications (Wu et al., 2016). The extraction and cleanup procedures also applied to the analysis of flame retardants in sediments. Briefly, 5 g of freeze-dried sediments were spiked with 50 ng each of surrogate standards, and then subjected to accelerated solvent extraction (Dionex ASE 350, Sunnyvale, CA, USA) with dichloromethane (DCM). After sulfur removal by activated copper, the extract was purified through a Phenogel gel permeation chromatography (GPC) column (300 × 21.2 mm, 5 μ, 100 Å; Phenomenex, Inc., Torrance, CA) coupled to a Phenogel guard column (50 × 21.2 mm, 10 μ, 100 Å), installed on a Shimadzu Prominence Semi-Prep HPLC (Shimadzu America Inc., Columbia, MD). The purified extract was further cleaned up on a solid phase extraction (SPE) cartridge packed with 2 g of Isolute® silica sorbent, which was pre-conditioned with 10 mL of hexane (HEX). After the sample was loaded, a first fraction was eluted with 3 mL HEX and discarded. A second fraction, containing target PHCZs as well as PBDEs, was eluted with 11 mL of a mixture of HEX and DCM (60:40, v/v). The latter fraction was concentrated and spiked with internal standards (i.e.100 ng each of F-BDE-154 and DCDE) prior to instrumental analysis.

The determination of PHCZs was conducted on an Agilent 7890B gas chromatography (GC; Agilent Technologies, Palo Alto, CA) interfaced with a single quadrupole mass analyzer (Agilent 5977A MS). The GC was equipped with a 30 m HP-5MS column (0.25 mm i.d., 0.25 μm, J&W Scientific, Agilent Tech.) and an injector operated in pulsed-splitless mode (held at 240 °C). Initial oven temperature was set at 50 °C (held for 3 min) and then ramped to 150 °C at 10 °C/min, followed by an increase to 300 °C at 5 °C/min (held for 10 min). The concentrations of 3-CCZ, 3-BCZ and 36-CCZ were determined via selected ion monitoring (SIM) in electron impact (EI) ionization mode, whereas the other PHCZs were quantified in the electron-capture negative ionization (ECNI)-SIM mode. The SIM ions of each analyte are listed in Table S1 (Supplementary data). PBDEs were analyzed by GC-MS equipped with a 15 m DB-5HT column (0.25 mm i.d., 0.1 μm, J&W Scientific). Detailed information on the instrumental analysis of flame retardants, as well as their characteristic SIM ions and concentrations in sediments, is summarized in Supplementary data (Tables S2 and S3).

2.3. Quality control and quality assurance

Sediment samples were analyzed using the QA/QC procedures previously established with minor modifications (Wu et al., 2016). A procedural blank was processed along with every seven samples. None of the target PHCZs was detected in any blank. The recoveries of surrogate standards were 91.3 ± 6.8%, 88.8 ± 4.7% and 100.1 ± 4.0% for PCB-204, F-BDE-69 and F-BDE-160, respectively. Concentrations of analytes were adjusted based on the recoveries of F-BDE-160 or PCB-204 for PHCZs determined under the ECNI or

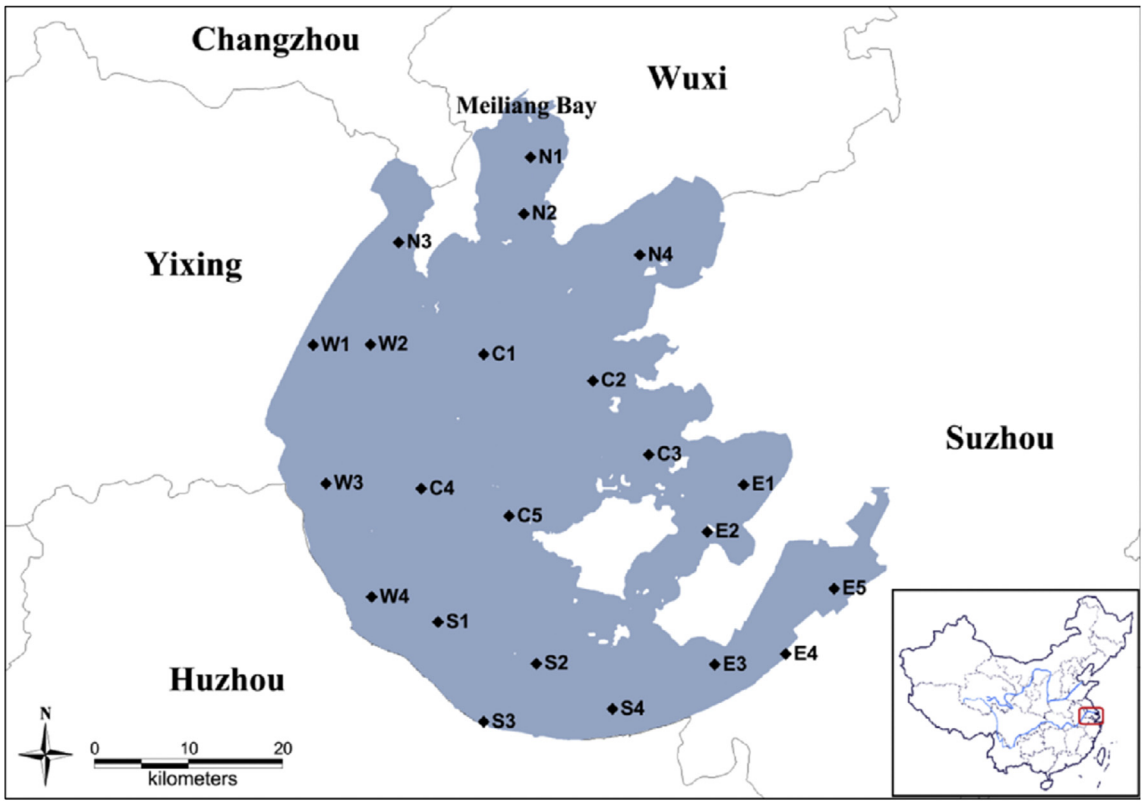

Fig. 1. Location of Lake Tai and sampling sites.

EI mode, respectively (Wu et al., 2016). The instrumental detection limit (IDL) was defined as a concentration of each analyte yielding a signal-to-noise ratio (S/N) of five. Analytes having responses below IDLs were considered non-detectable (nd). The method limits of quantification (MLOQs) were assessed by replicate analyses (n = 8) of 5 g reference sediment (collected from Au Sable River (Michigan, USA; 45°12′21″N, 84°05′20″W)) spiked with 2 ng each of target PHCZs. The MLOQs (Table S1; Supplementary data) were calculated by multiplying a Student's t-value designated for a 99% confidence level with standard deviations in the replicate analyses (Chen et al., 2012). For measurements below MLOQs or non-detectable, a regression plotting method was applied to assign values for statistical analysis (Newman, 1995). The analyses of the National Institute of Standards Technology Standard Reference Material (SRM) 1944 Sediment revealed mean recovery efficiencies of PBDE congeners ranging from 88.2 ± 3.5% to 94.4 ± 7.0% (Table S2). The SRM for PHCZs has not been available.

2.4. Data analysis

Statistical analyses were performed using the Student's t-test, principal component analysis (PCA), the Kruskal-Wallis one-way analysis of variance (ANOVA), Fisher's test for mean comparison, or Pearson's correlation analysis (OriginPro 9.0, OriginLab Corporation), wherever applicable. Data were subject to logarithmic transformation prior to statistical analysis in order to achieve a normal distribution. A significance level of $\alpha = 0.05$ was applied.

3. Results and discussion

3.1. Concentrations of PHCZs in Lake Tai sediments

The PHCZs were quantifiable in 21 out of 22 Lake Tai sediments, revealing a wide distribution in the studied waterbody. The detection frequency of individual PHCZ congeners ranged from 41% for 2367-CCZ to 100% for 36-, 136-, and 1368-BCZ, while the quantification frequency ranged from 0% for 2367-CCZ to 91% for 36-BCZ. The only site with none of the PHCZ congeners quantifiable was located in the north lake (N2). The summed concentrations of all detectable PHCZs (∑PHCZs) ranged from <MLOQ to 15.8 ng/g dry weight (dw), with a median value of 1.54 ng/g dw (Table 1). Comparison with global studies on the PHCZ abundances in aquatic sediments is limited by the very small number of investigations so far. Most available sediment studies only qualitatively determined a selected number of congeners, whereas only two very recent reports quantified a list of PHCZ congeners comparable to our list (Chen et al., 2016; Wu et al., 2016). The sediments of Lake Tai contained significantly lower concentrations of PHCZs than the levels (<MLOQ – 46.3 ng/g dw, median: 20.3 ng/g dw) reported in the Saginaw River system (USA) (Wu et al., 2016), but higher than those (0.004–22.0 ng/g dw, median: 0.23 ng/g dw) reported in the sediments collected from the rivers and coastal water of the North Sea estuary (Germany) (Chen et al., 2016). Brominated carbazoles, including 36-BCZ and 1368-BCZ, were also determined in sediment cores from Lake Michigan (USA). Some other PHCZ congeners were qualitatively or semi-quantitatively determined in Lake Michigan and Ontario (Canada) river sediments (Guo et al., 2014; Pena-Abaurrea et al., 2014; Zhu and Hites, 2005).

Concentrations of PHCZs were compared with those of polybrominated diphenyl ethers (collectively referred to ∑PBDEs) in the same sediments determined in the present work (data given in Table S3), as well as the literature data of other groups of organic compounds in Lake Tai sediments. Comparable concentrations were determined between ∑PHCZs (<MLOQ – 15.8 ng g dw) and ∑PBDEs (0.07–15.9 ng/g dw) in Lake Tai sediments. It is noted that our PBDE data were lower compared to the concentrations in Lake

Table 1
Concentrations (ng/g dry weight) of polyhalogenated carbazoles (PHCZs) in sediments collected from Lake Tai, China.

Sampling site	3-CCZ	36-CCZ	1368-CCZ	2367-CCZ	3-BCZ	27-BCZ	36-BCZ	136-BCZ	1368-BCZ	1-B-36-CCZ	18-B-36-CCZ
C1	nd[a]	<MLOQ[b]	nd	nd	nd	<MLOQ	0.11	<MLOQ	<MLOQ	<MLOQ	<MLOQ
C2	nd	<MLOQ	nd	nd	nd	nd	0.26	<MLOQ	<MLOQ	<MLOQ	nd
C3	<MLOQ	3.35	<MLOQ	<MLOQ	<MLOQ	<MLOQ	0.65	<MLOQ	0.13	<MLOQ	<MLOQ
C4	0.32	7.73	0.19	<MLOQ	<MLOQ	<MLOQ	0.73	0.18	0.37	0.18	0.23
C5	0.31	7.43	0.20	<MLOQ	<MLOQ	<MLOQ	1.24	0.22	0.42	0.17	0.25
E1	nd	<MLOQ	nd	nd	nd	nd	0.16	<MLOQ	<MLOQ	<MLOQ	nd
E2	nd	<MLOQ	nd	nd	nd	nd	0.19	<MLOQ	<MLOQ	<MLOQ	<MLOQ
E3	nd	<MLOQ	<MLOQ	nd	nd	nd	0.23	<MLOQ	<MLOQ	<MLOQ	<MLOQ
E4	nd	0.27	<MLOQ	nd	nd	<MLOQ	0.97	0.12	<MLOQ	<MLOQ	<MLOQ
E5	nd	0.34	<MLOQ	nd	nd	nd	0.29	<MLOQ	<MLOQ	<MLOQ	<MLOQ
N1	<MLOQ	4.48	<MLOQ	nd	<MLOQ	<MLOQ	1.45	<MLOQ	0.14	<MLOQ	<MLOQ
N2	nd	<MLOQ	nd	nd	nd	nd	<MLOQ	<MLOQ	<MLOQ	<MLOQ	<MLOQ
N3	nd	1.19	nd	nd	nd	nd	<MLOQ	<MLOQ	<MLOQ	<MLOQ	<MLOQ
N4	nd	0.51	nd	nd	nd	nd	0.16	<MLOQ	<MLOQ	<MLOQ	<MLOQ
S1	nd	0.92	<MLOQ	<MLOQ	nd	nd	0.81	<MLOQ	<MLOQ	<MLOQ	<MLOQ
S2	<MLOQ	1.61	<MLOQ	nd	<MLOQ	<MLOQ	1.53	<MLOQ	<MLOQ	<MLOQ	<MLOQ
S3	<MLOQ	1.70	<MLOQ	<MLOQ	0.74	<MLOQ	12.90	0.37	0.12	<MLOQ	<MLOQ
S4	0.39	9.23	0.17	<MLOQ	<MLOQ	0.06	0.76	0.17	0.40	0.23	0.19
W1	nd	1.50	<MLOQ	<MLOQ	nd	nd	1.20	<MLOQ	<MLOQ	<MLOQ	<MLOQ
W2	<MLOQ	5.22	<MLOQ	<MLOQ	nd	<MLOQ	0.37	<MLOQ	0.19	0.10	0.11
W3	<MLOQ	1.82	<MLOQ	<MLOQ	<MLOQ	<MLOQ	1.81	<MLOQ	<MLOQ	<MLOQ	<MLOQ
W4	<MLOQ	nd	<MLOQ	nd	0.27	nd	0.48	<MLOQ	<MLOQ	<MLOQ	<MLOQ

[a] Non-detectable (S/N < 5).
[b] Below method limit of quantification (MLOQ).

Tai sediments from earlier studies (Wang et al., 2016; Zhou et al., 2012). The discrepancy may be due to the differences in collection sites and years among various studies. The remediation project implemented in the mid-to late 2000's in the Meiliang Bay may also result in decreasing contamination over time (Qiao et al., 2009; Xu et al., 2015). The concentrations of ∑PHCZs were also greater than or comparable with those of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexane (HCH), and perfluorinated chemicals (PFCs), but two orders of magnitude lower than that of polycyclic aromatic hydrocarbons (PAHs) (Fig. 2). These different groups of halogenated pollutants, including PBDEs, PCBs, DDTs, and HCH, have been subjected to extensive studies worldwide. They are widely distributed in global sediments, revealing substantial persistence in aquatic environments and a tendency to absorb on organic particles (Tang et al., 2014; Zhu et al., 2014). The comparable concentrations between PHCZs and the abovementioned halogenated pollutants implied the relative abundance and persistence of the former group of chemicals and raised concerns on their potential exposure risk for benthic organisms in Lake Tai.

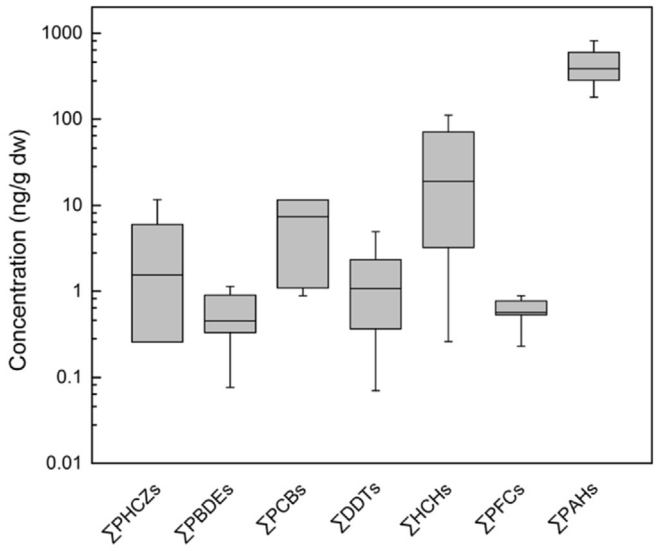

Fig. 2. Comparison of ∑PHCZ concentrations with those of ∑PBDEs (data from this study) and other groups of organic contaminants in Lake Tai sediments (data from Lei et al., 2014; Yang et al., 2011; Zhang and Jiang, 2005; Zhao et al., 2009).

3.2. PHCZ congener composition profile

Among the variety of PHCZ congeners detected in Lake Tai sediments, 36-CCZ and 36-BCZ dominated the composition profile, showing comparable relative abundances on average (Table 1; Fig. S1). Other congeners in total accounted for 0–36.2% of the concentrations of ∑PHCZs. This composite pattern differed from what has been reported in the Saginaw Bay River system and the coastal North Sea waterbodies, where 36-CCZ was generally the predominant congener but 36-BCZ had much lower contributions (Chen et al., 2016; Wu et al., 2016). The 36-CCZ had a mean contribution of 83% to the ∑PHCZs concentrations in the Saginaw Bay River sediments, followed by 3-CCZ (11%), whereas 36-BCZ accounted for only 0.2% on average. The river and marine sediments from the North Sea system contained 36-CCZ at levels over 55% of ∑PHCZs, but 36-BCZ was present at less than 10% of ∑PHCZs. Slight differences in congener compositions were also observed between river and marine sediments of the North Sea. The 36-BCZ was at higher concentrations in marine versus river sediments, while the concentrations of 1-B-36-CCZ were much greater in river sediments. The consistency in the abundance of 36-CCZ or 36-BCZ in various aquatic systems may agree with an electrophilic aromatic substitution pattern which favors halogen substitution at the *ortho* and *para* positions relative to nitrogen on the carbazole (Bonesi and Erra-Balsells, 1997). This may be true for both chemical and enzymatic synthesis of polyhalogenated carbazoles (Mumbo et al., 2013). The dominance of *para*-over *ortho*-substituted substances in environmental samples is likely attributed to the high charge density at the *para* relative to the *ortho* positions and the enhanced stability of *para*-substituted products by the lone pair of electrons in NH_2 moiety (Effenberger and Maier, 2001; Mumbo et al., 2013). Indeed, enzymatic synthesis of polyhalogenated carbazoles resulted in a dominance of products with

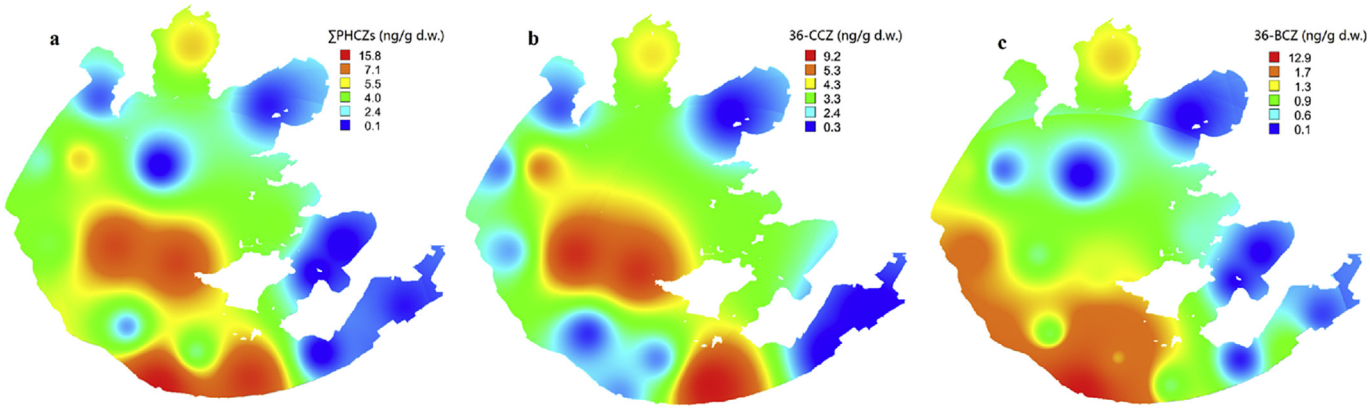

Fig. 3. Spatial distributions of ∑PHCZs (a), 3,6-dichlorocarbazole or 36-CCZ (b), and 3,6-dibromocarbazole or 36-BCZ (c) in Lake Tai sediments.

halide substitution at the 3- and 3,6- positions (Mumbo et al., 2013), while 36-CCZ demonstrated a greater thermal stability than 3-CCZ (Mumbo et al., 2013). In contrast with the consistency of the abundance of 36-CCZ, other congeners, including 3-CCZ, 36-BCZ, 3-BCZ, 1368-CCZ and 1368-BCZ, differed in detection frequencies and relative abundances among different waterbodies, which may reflect varying origins of PHCZs and/or a complexity of anthropogenic influences and natural processes.

3.3. Distribution pattern and potential sources of PHCZs

Spatial distribution patterns of ∑PHCZs, as well as the two most abundant congeners (i.e. 36-CCZ and 36-BCZ), are shown in Fig. 3. Elevated concentrations of ∑PHCZs were found in the central and southern parts of Lake Tai. The non-parametric ANOVA suggested marginally significant differences in concentrations among five regions ($p = 0.043$). Concentrations of ∑PHCZs in sediments from eastern Lake Tai were significantly lower than those from the central ($p = 0.018$) and southern ($p < 0.01$) regions according to the Fisher post-hoc test. The spatial distribution pattern of 36-CCZ resembled that of ∑PHCZs, but differed from that of 36-BCZ. Peak concentrations of 36-BCZ were generally observed in the sediments collected from the southwestern part of Lake Tai. Data structure of PHCZs in the sediments was also interpreted using standardized principal component analysis (PCA). Two main components accounting for 84.48% of total variance in the dataset were extracted. The score plot (Fig. 4) shows that the sampling sites could be separated into three groups in terms of their data structures: 1) S3 with a peak concentration of 36-BCZ; 2) C4, C5 and S4 which contained the highest concentrations of 36-CCZ; and, 3) all of the other locations. Sampling sites that were not grouped together might indicate they were influenced by different contamination sources.

The spatial distribution pattern of ∑PHCZs in Lake Tai sediments differed from those of other halogenated pollutants such as PCBs, PBDEs, hexabromocyclododecane (HBCD), and PFCs. Previous studies have reported a general distribution pattern of these industrially-derived pollutants, i.e. northern > southern > central part of the Lake (Wang et al., 2016; Yang et al., 2011; Zhang et al., 2011; Zhao et al., 2009). Highest concentrations of these well known substances were usually found at offshore sites of the Meiliang Bay, where a human-populated metropolitan region (Wuxi) is located. Municipal and industrial input apparently elevated contamination along the shoreline, leading to a significant signature of urban influence. For example, concentrations of ∑PBDEs were reported to be as high as 347 ng/g dw in offshore

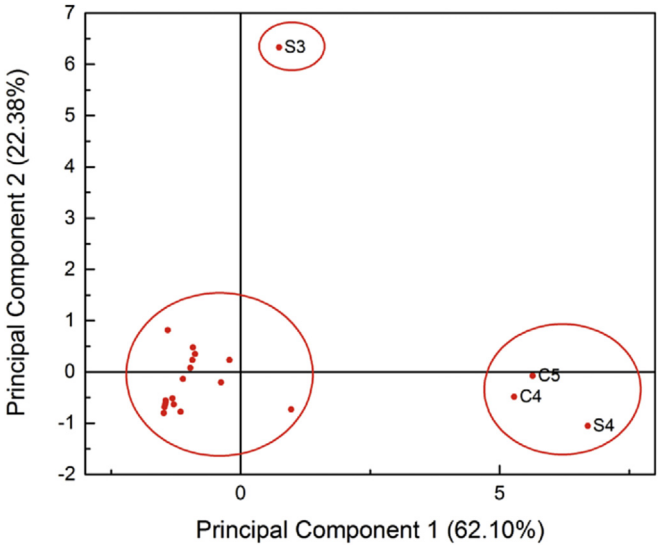

Fig. 4. Score plot of the principal component analysis of PHCZ concentrations in Lake Tai sediments.

sediments of Meiliang Bay (Wang et al., 2016). The southern Lake also receives direct input from another metropolitan area (Huzhou) which has a lower population density compared to Wuxi (Yu et al., 2015). The central part of the lake has been documented for the lowest concentrations of the most investigated organic pollutants (Yu et al., 2015; Wang et al., 2016; Xu et al., 2013). By contrast, the distribution of 36-BCZ exhibited a gradient of southern > northern > central part of the Lake. It is noteworthy to point out that the present work had very few sites from the Meiliang Bay and none from the Meiliang lakeshore sites. The small number of sites may not represent, and possibly underestimate, the overall contamination scenario in the Meiliang Bay. Nonetheless, the relatively more abundance of 36-BCZ in the southern lake and a much lower abundance in the central part may reflect a typical industrial/urban input. This may explain the peak 36-BCZ concentration at S3 which was located offshore of the southern lake. Additionally, the concentration of 36-BCZ positively correlated with that of ∑PBDEs in the same sediments of Lake Tai ($p < 0.05$). A significant, positive correlation between two contaminants or groups of contaminants may indicate some common origins or sources, whereas weak associations may suggest different environmental sources or fate (Fu et al., 2014; Liu et al., 2003, 2016; Nam et al., 2008; Tokalıoğlu and Kartal, 2006). Flame retardants

are primarily from anthropogenic origins (Hale et al., 2012; Xian et al., 2011; Yu et al., 2016). Therefore, we hypothesized that 36-BCZ in the Lake Tai sediments or at least a major portion of its abundance may originate from anthropogenic input. Parette et al. have suggested that some polyhalogenated carbazoles (e.g. 1368-BCZ and 18-B-36-CCZ) may be formed during the manufacturing process of halogenated indigo dye such as 5,5′,7,7′-tetrachloroindigo or 7,7′-dibromo-5,5′-dichloroindigo (Parette et al., 2015). The change of the production volume of tetrabromoindigo over time in the United States was found to resemble the temporal trend of 1368-BCZ concentrations in the Lake Michigan core sediments (Parette et al., 2015). Elevated concentration of 1368-BCZ was also reported near the outfall of a former dye manufacturer (Kuehl et al., 1984). These studies pointed to anthropogenic sources of brominated carbazoles through direct or indirect evidence. Although 36-BCZ was not suggested as a by-product from halogenated indigo dye production (Parette et al., 2015), it could also be a potential product from other relevant industrial processes, given that the *para* positions on the carbazole ring are mostly preferred by electrophilic substitutions (Altarawneh and Dlugogorski, 2015). Both 36-BCZ and 27-BCZ were reported to be used as raw materials in light emitting applications (Gong et al., 2012). Additionally, 36-BCZ may originate from potential degradation of 1368-BCZ or other brominated carbazoles originating from anthropogenic sources. However, natural origins cannot be ruled out for 36-BCZ. Mumbo et al. have reported an enzymatic synthesis of bromo- and chloro-carbazoles by chloroperoxidase from *Caldariomyces fumago* in water (Mumbo et al., 2013). The 36-BCZ was one of the most abundant brominated products from the enzymatic synthesis, suggesting the likelihood of natural origins. However, it should be noted that most naturally produced brominated substances are generally found in marine versus freshwater environment (Zhu and Hites, 2005).

The spatial distribution of 36-CCZ differed from that of 36-BCZ. In addition to few southern sites, central part of the lake (i.e. sites C3 and C4) also revealed some of the highest concentrations. This pattern is different from what has been observed for most halogenated contaminants in Lake Tai as discussed above. The reason for a high abundance of 36-CCZ in the central lake remains unknown. A possible explanation is that the central lake has a sediment depositional zone due to a counter-clockwise water current generated by prevailing winds from the southeast or southwest in the summer (Qin et al., 2007). The occurrence of high levels of organic contaminants in a depositional zone has been reported in other aquatic systems, such as the Great Lakes of North America (Gewurtz et al., 2008). Concentrations of 36-CCZ also had a weak association with those of $\sum$PBDEs ($p = 0.66$). This may indicate that 36-CCZ in Lake Tai sediments might be from sources different from those of 36-BCZ, flame retardants, or other traditional halogenated pollutants (e.g. PCBs, DDTs, and HCH). Natural origins cannot be excluded as well. The 36-CCZ was among the most abundant chlorinated carbazoles produced from enzymatic synthesis (Mumbo et al., 2013). Previous studies have suggested natural origins as the likely source of 36-CCZ in soil and sediments (Grigoriadou and Schwarzbauer, 2010; Reischl et al., 2005). Eutrophication of Lake Tai has caused severe algal blooms nearly every year in recent decades (Huang et al., 2013; Le et al., 2010), which might enhance enzymatic synthesis of chlorinated organic substances. However, current evidence is apparently insufficient for drawing any conclusion of the possible sources of PHCZs.

Overall, despite the increasing number of reports on polyhalogenated carbazoles in the environment, their origins or sources remain generally unidentified and controversial in some cases. In order to better elucidate plausible sources, further research is required to seek additional evidence from laboratory-based experiments and field-derived environmental samples. Laboratory studies are needed to investigate the pathways involved in, and products of, the synthesis of polyhalogenated carbazoles via natural-mimicking or industrial processes, as well as the mechanisms and products of biotransformation or degradation of PHCZs or their potential precursors under natural or near natural conditions. It is recommended that environmental samples, including wastewater influents, effluents and sludge, should be screened for PHCZs. This might provide more direct evidence for the likelihood of anthropogenic sources for polyhalogenated carbazoles.

3.4. Toxic equivalent of PHCZs (TEQ^{PHCZs}) in Lake Tai sediments

Polyhalogenated carbazoles have been reported to exhibit a variety of toxic effects, among which dioxin-like toxicity has been confirmed by several studies and drawn mounting concerns (Fang et al., 2016; Mumbo et al., 2015; Riddell et al., 2015). Relative effect potencies (REP) of PHCZs (compared to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin or TCDD) were estimated based on the structure-dependent induction of cytochrome P450 1A1 mRNAs in MDA-MB-468 breast cancer cells (Riddell et al., 2015). Riddell et al. reported that the structure-dependent induction by PHCZs was similar to that observed for dibenzo-*p*-dioxin (Riddell et al., 2015). The estimated REPs ranged between 0.000013 and 0.00066 for mono-to tetra- PHCZs (Riddell et al., 2015). These REPs can be used to represent toxic equivalency factors (TEFs) of PHCZs, as they were evaluated following an extensively used approach for TEF estimations (Van den Berg et al., 1998). Thus, to understand potential toxic effects of sediment-associated PHCZs on benthic organisms, the toxic equivalent (TEQ) of PHCZs was determined based on the estimated REPs and using Equation (1).

$$TEQ^{PHCZs} = \sum C_i \times REP_i \quad (1)$$

where C_i and REP_i are the concentration and REP of individual PHCZ congeners, respectively.

The estimated TEQ^{PHCZs} of the Lake Tai sediments ranged from 0 to 1.36 pg TEQ/g dw, lower than the safe sediment TEQ value of 20 pg TEQ/g dw, which was derived from a no-observed-effect-concentration (NOEC) of 200 pg TEQ/g dw in sediment divided by a safety factor of 10 when chronic toxicity data are rare (Colombo et al., 2006; Eljarrat et al., 2001, 2005). Relatively higher TEQ^{PHCZs} values were determined in sediments from sites S4, C4 and C5, where elevated concentrations of 36-CCZ were detected. The TEQs of PHCZs in Lake Tai sediments were lower than those of well-known dioxin-like substances in the same waterbody, such as polychlorinated dibenzo-*p*-dioxins, dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), ranging from 0.83 to 17.72 pg TEQ/g dw (Zhang and Jiang, 2005). However, synergistic or additive effects induced by the coexistence of PHCZs and other dioxin-like compounds cannot be ruled out. For example, rats exposed to a combination of TCDD and 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB-153) tended to accumulate higher levels of hepatic porphyrin than when exposed to individual substances, due to enhanced induction of CYP1A2 (van Birgelen et al., 1996). Synergistic induction of AhR regulated genes in developmental toxicity was also discovered when zebrafish were exposed to two model PAHs simultaneously (Timme-Laragy et al., 2007). Additionally, resembling many other halogenated organic compounds (e.g. BDE-47 and mutagenic polycyclic aromatic hydrocarbons), PHCZs may also possess AhR-independent effects (Machala et al., 2001; Nebert et al., 2004; Wahl et al., 2008), inducing additional toxic risks. Thus, the presence of PHCZs in aquatic sediments and associated adverse effects on aquatic organisms should be given sufficient attention during

the assessment of persistent and toxic substances in aquatic environments.

4. Conclusions

The present study provides the first report on the occurrence of PHCZs in a waterbody from Asia. These emerging halogenated substances revealed a wide distribution across the studied waterbody and their concentrations rivaled those of other extensively studied halogenated contaminants such as PBDEs. The congener composition profiles of PHCZs in Lake Tai sediments suggested a possible combination of natural and anthropogenic origins. Further studies are critically needed to investigate the sources and fate of PHCZs in the environment, given the limitation of current knowledge and the contradictory information in some cases. The potential toxic effect of sediment-associated PHCZs was assessed via TEQ estimation. Although the contribution of PHCZs to sediment TEQs was less than those of PCDDs/Fs and PCBs in Lake Tai sediments, additional effects other than dioxin-like activities, as well as the likely synergistic or additive effects due to the coexistence of PHCZs and other dioxin-like substances, should not be neglected in future research. Overall, as suggested by the findings of the present study, along with a few other reports, polyhalogenated carbazoles should be given more attentions during environmental monitoring and risk assessment of hazardous chemicals, as they may represent another group of persistent organic pollutants with dioxin-like effects and global distributions.

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Appendix A. Supplementary data

Supplementary information includes Tables S1–S3, Figure S1, as well as a description of the analytical methodology for the determination of polybrominated diphenyl ethers.

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.09.032.

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