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PAPER

Chlorinated and brominated dibenzo-*p*-dioxins and dibenzofurans in surface sediment from Taihu Lake, China†

Lin Zhou,[ab] Huiru Li,[a] Zhiqiang Yu,*[a] Man Ren,[a] Xiangying Zeng,[a] Ping'an Peng,*[a] Guoying Sheng[a] and Jiamo Fu[a]

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Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) in surface sediment samples from Taihu Lake—an important water supply of the Yangtze River Delta, China—were investigated in the present study. Concentrations of PCDD/Fs ranged from 0.91 to 4.8 pg TEQ g^{-1} dw (mean: 2.9 pg TEQ g^{-1} dw, TEQ: Toxic Equivalent), which were all higher than the threshold effect level established by interim sediment quality guidelines in Canada (0.85 pg TEQ g^{-1} dw). The levels of PBDD/Fs ranged from 0.16 to 1.6 pg TEQ g^{-1} dw (mean: 0.52 pg TEQ g^{-1} dw) and accounted for 5–33% (mean: 14%) of the total PCDD/Fs and PBDD/Fs TEQ. Comparatively, the abundance of sedimentary PCDD/Fs in the three regions (Meiliang Bay, Gonghu Bay, and Xukou Bay) showed a decreasing trend from the inflow region to the outflow region, while no significant difference was observed among their 2,3,7,8-PBDD/Fs levels, which suggested that the sources of PCDD/Fs and PBDD/Fs differed in this area. Principal component analysis suggested that the historical production/usage of pentachlorophenol and sodium pentachlorophenate was the dominant source of PCDD/Fs in the sediment of these regions. Although the specific sources of PBDD/Fs in the sediment of Taihu Lake were unclear, it was suspected to be due to atmospheric deposition; however, an additional study is needed to confirm this.

1 Introduction

Taihu Lake, which is the third largest freshwater lake in China, is located in the Yangtze River Delta. This region is one of the most rapidly developing regions in China. Owing to the agricultural use and industrial development of this area, the water quality of Taihu Lake has greatly deteriorated. Some regions have suffered from serious blue-green algal blooms, which have the potential to threaten ecological safety and health.[1–4] Because Taihu Lake is the most important drinking water source for surrounding cities such as Wuxi and Suzhou, its pollution status has elicited a high degree of concern from the government. Accordingly, more than one billion US dollars have been provided for environmental investigation, clean up, and mitigation of the lake, and the total annual costs for its water pollution control accounted for 5.97% of the gross domestic product of this area in 1998.[5] These studies focused on prevention and control of the blue-green algal bloom, as well as development of water quality criteria and ecological and human health risk assessment of toxic contaminants.

[a]*State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environment and Resources, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. E-mail: zhiqiang@gig.ac.cn; Fax: +86 (20) 85290288/0117; Tel: +86 (20) 85292391/0163*
[b]*Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*

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Environmental impact

Chlorinated and brominated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs and PBDD/Fs) have great potential risk to ecosystems and human health. In this study, we focused on the drinking water sources area of Taihu Lake, and 26 surface composite sediments were sampled and investigated. The results indicated that the sedimentary concentrations of PCDD/Fs and PBDD/Fs in the study areas were at background levels internationally. Principal component analysis suggested that the historical production/usage of pentachlorophenol and sodium pentachlorophenate was the dominant source of PCDD/Fs in the sediment of these regions. Although the specific sources of PBDD/Fs in the sediment of Taihu Lake were unclear, it was suspected to be atmospheric deposition.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are typical persistent organic pollutants (POPs) covered by the Stockholm Convention, which China signed in 2001. Since then, many studies of PCDD/Fs in environmental media and biota in China have been conducted and the results have indicated that the highly contaminated areas of PCDD/Fs in China are primarily associated with e-waste recycling areas, surrounding areas of some chemical facilities which have utilized or produced chlorinated organics and schistosomiasis affected areas.[6] Sodium pentachlorophenol salt (PCP-Na), which contains PCDD/Fs as an impurity (92 ng I-TEQ g^{-1} PCP-Na),[7] has been used to control the snail-borne schistosomiasis in China since the 1960s.[8,9] This may have resulted in high amounts of PCDD/Fs in the sediments and soils in the disease areas.[6] The concentrations of PCDD/Fs (245–33 660 pg g^{-1} dw) in the sediment and soil of snail-borne schistosomiasis areas were about 10–400 times higher than the background values.[10] Taihu Lake Basin is also a typical schistosomiasis affected area; however, PCDD/Fs have only been investigated in the sediment of Meiliang Bay in Taihu Lake.[4,11] The results of a sediment core sample collected in that study showed an increasing trend of PCDD/Fs from the bottom to the top.

Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are analogues of PCDD/Fs that exhibit similar physicochemical properties, toxicity and geochemical behavior to PCDD/Fs in the environment.[12–14] Manufacturing, usage and recycling of brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and BFRs-containing products are the main sources of PBDD/Fs in the environment.[14] In general, the levels of PBDD/Fs in environmental media and biota samples are lower than those of PCDD/Fs.[15,16] However, in some places, the concentrations of PBDD/Fs were comparable to or even higher than their chlorinated analogues.[17–19] In the general population of Sweden, TEQ contributed by PBDD/Fs accounted for up to 15% of the total dioxin TEQ (PCDD/Fs and PBDD/Fs).[20] Actually, PBDD/Fs showed an increasing trend in some environment matrices in response to the excessive usage of BFRs in recent years.[21,22] A high concentration of PBDEs (220 pg m^{-3}, 33 congeners), which was nearly double that in US urban regions, has been found in ambient air around Taihu Lake.[23] However, no studies have been conducted to investigate the occurrence of PBDD/Fs in Taihu Lake.

As part of the national basic research program of China known as the Water Environmental Quality Evolution and Water Quality Criteria in Lakes, the present study was conducted to assess the contamination status, congener profiles, spatial distribution and possible sources of PCDD/Fs and PBDD/Fs in surface sediments from three typical drinking water sources of Taihu Lake. These results should facilitate further ecological and health risk assessments of Taihu Lake.

2 Materials and methods

2.1 Sample collection

Taihu Lake is a large shallow freshwater lake with a surface area of 2338 km^2, an average water depth of 1.9 m and a drainage area of 36 500 km^2. The lake is the main drinking water source for approximately 45 million residents in this basin. Three typical water supply regions; two inflow regions, Meiliang (ML) Bay and Gonghu (GH) Bay; and one outflow region, Xukou (XK) Bay, of Taihu Lake were investigated in this study. Surface sediment samples were collected from a depth of about 5 cm in June of 2009 using grab samplers (Ekmangrab, Wildlife Supply Company, Buffalo, USA). Overall, a total of 26 composite sediment samples were collected from ML ($n = 9$), GH ($n = 10$) and XK ($n = 7$). All sampling locations were located with a global positioning system (Magellan, San Dimas, CA, USA) and are shown in detail in Fig. 1. After collection, samples were freeze-dried and homogenized, sieved through 80 mesh, and finally stored at −20 °C until analysis.

2.2 Standards and reagents

All standards of PCDD/Fs and PBDD/Fs were obtained from Cambridge Isotope Laboratories (Andover, MA, USA), including $^{13}C_{12}$-labeled PCDD/Fs surrogate standards (EDF-8999), PCDD/Fs recovery standards (EDF-5999), PCDD/Fs window defining and isomer specificity mixture (EDF-4147), $^{13}C_{12}$-labeled PBDD/F surrogate standards (EDF-5071) and PBDD/Fs recovery standards (EDF-5073). All solvents used in the analytical procedure were of pesticide residue grade and were purchased from Merck (Germany). The silica gel (70–230 mesh, Aldrich, USA) and Florisil (60–100 mesh, Merck, Germany) were Soxhlet extracted with dichloromethane (DCM) for 24 h, vacuum-dried and then activated at 180 °C for 5 h and 135 °C for 24 h, respectively prior to use.

2.3 Sample clean-up and analysis

The analysis of PCDD/Fs and PBDD/Fs was conducted according to US EPA Method 1613B. Detailed descriptions of the sample extraction and clean-up procedures have been previously reported.[24] Briefly, sediment samples were freeze-dried, after which the pebbles and twigs were removed and the samples were homogenized and passed through a 80 mesh sieve. Next, 10–30 g dry samples were weighed and spiked with $^{13}C_{12}$-labeled surrogate standards (EDF-8999 and EDF-5071, CIL) before Soxhlet extraction with toluene for 48 h. All extracts were concentrated to 1 ml using a rotary evaporator and then successively cleansed with acid silica gel slurry, a multi-layer silica gel column and a Florisil column. The Florisil column was rinsed with 100 ml *n*-hexane to remove the ethers, after which the dioxins were eluted with 80 ml 60 : 40 (v/v) DCM : *n*-hexane and 80 ml DCM. The latter eluent was concentrated to 20 μl under gentle nitrogen flow, and injection standards (EDF-5999 and EDF-5073, CIL) were then added for instrumental analysis. Seventeen 2,3,7,8-PCDD/Fs congeners and eight 2,3,7,8-PBDD/Fs congeners (including 2,3,7,8-TBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 2,3,7,8-TBDD, 1,2,3,7,8-PeBDD, 1,2,3,4/6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD) were quantified based on the response factors obtained from the corresponding standards. Other non-2,3,7,8-PCDD/Fs congeners were quantified with the average response factors of the isomers with the same degree of chlorination.

2.4 Instrumental analysis

The target compounds analysis was conducted using high-resolution gas chromatography combined with high-resolution mass

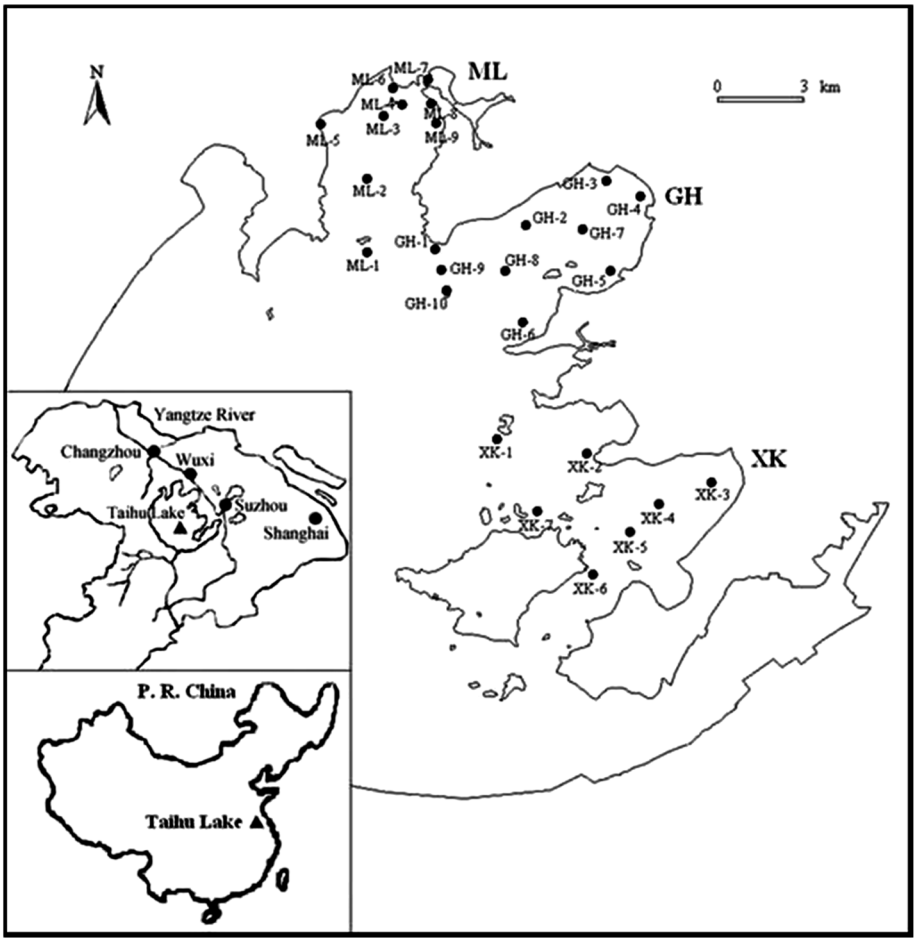

Fig. 1 The detailed locations of sampling sites in Taihu Lake.

spectrometry (HRGC-HRMS, Trace GC 2000 and Thermo Finnigan MAT95 XP, Germany) running in positive electron impact (EI+) and selected ion monitoring (SIM) mode with a resolution >10 000.

PCDD/Fs: Samples were analyzed using a DB-5 MS fused silica capillary column (J&W Scientific, CA, 60 m × 0.25 mm i.d., 0.25 μm). The temperature program of the GC was as follows: 120–160 °C at 20 °C min^{-1}, 160–220 °C at 7.5 °C min^{-1}, held at 220 °C for 16 min, 220–235 °C at 5 °C min^{-1}, held at 235 °C for 7 min, 235–320 °C at 5 °C min^{-1}, held at 320 °C for 7 min. Carrier gas: helium (0.8 ml min^{-1}).

PBDD/Fs: Samples were analyzed using a DB-5 MS fused silica capillary column (J&W Scientific, CA, 30 m × 0.25 mm i.d., 0.1 μm). The oven temperature program was as follows: 120–160 °C at 40 °C min^{-1}, 160–235 °C at 25 °C min^{-1}, held at 235 °C for 2 min, 235–250 °C at 15 °C min^{-1}, 250–315 °C at 10 °C min^{-1}, held at 315 °C for 4 min. Carrier gas: helium (0.8 ml min^{-1}).

2.5 Total organic carbon (TOC) analysis

Sediment samples were digested with 5% (w/w) hydrochloric acid at 80 °C for 2 h in a crucible to remove the inorganic carbonates. Next, the residues were washed with deionized water six times and then dried at 105 °C. Finally, the samples were analyzed for TOC using an elemental analyzer (LECOCELII C230, USA).

2.6 Quality assurance and quality control (QA/QC)

Each sample was spiked with $^{13}C_{12}$-labeled internal standards of PCDD/Fs and PBDD/Fs to evaluate the cleanup procedures. Recovery of the spiked internal standards ranged from 41 to 104% for PCDD/Fs and 38 to 124% for PBDD/Fs, respectively, which all meet the limits of US EPA 1613B. A standard reference soil material (EDF-2513, CIL) sample, method blank and ongoing precision and recovery sample (OPR, EPA 1613B) were analyzed for each batch of twelve samples for quality control. No target compounds were detected in the method blanks, except for OCDD, which was present in negligible levels when compared with sediment samples from Taihu Lake. The detection limits were quantified as three times the standard deviations for the mean concentration in the blanks, which were 0.5–5 pg per sample for PCDD/Fs, and 0.25–1.5 pg per sample for PBDD/Fs, respectively.

2.7 Statistical analysis

The statistical analysis, including *t*-test for significant difference, Pearson correlation analysis and principal component analysis (PCA), were all performed using SPSS 13.0. Prior to the PCA, the seventeen 2,3,7,8-substituted PCDD/Fs congener datasets were normalized towards their own total values. Concentrations

that were below the detection limit were assigned a value zero when processing normalization. The principal components were considered if their eigenvalues were >1. The method of varimax was selected for rotation in the PCA and 25 iterations were performed.

3 Results and discussion

3.1 Concentration levels of PCDD/Fs and PBDD/Fs

The toxic equivalents (TEQs) for PCDD/Fs were estimated using WHO_{1998}-TEFs (toxic equivalence factors). Because the toxic equivalency factors (TEFs) have not been determined for PBDD/Fs, the TEQs of PBDD/Fs were calculated using the WHO_{1998}-TEFs of their corresponding chlorinated counterparts according to the suggestion of the World Health Organization (WHO).[14] Fig. 2 summarized the values of PCDD/Fs and PBDD/Fs in sediment samples from the three regions of Taihu Lake. In general, the concentrations and TEQs of Σ_{17}2,3,7,8-PCDD/Fs were 55.5–351.2 pg g^{-1} dw (mean: 161.7 pg g^{-1} dw) and 0.91–4.8 pg TEQ g^{-1} dw (mean: 2.9 pg TEQ g^{-1} dw), respectively. The ranges (means) of the eight 2,3,7,8-PBDD/Fs were 0.48–5.7 pg g^{-1} dw (1.7 pg g^{-1} dw) and 0.16–1.6 pg TEQ g^{-1} dw (0.52 pg TEQ g^{-1} dw), respectively, which are about 1–2 orders of magnitude lower than those of the PCDD/Fs. These findings were similar to those reported for sediments from coastal areas of Hong Kong, Korea and Japan.[15,16] In accordance with the concentrations, PCDD/Fs were the dominant TEQ contributor at all sampling sites in Taihu Lake, whereas 5–33% (mean: 14%) of the total TEQs were contributed by PBDD/Fs (Fig. 3). Zhang and Jiang[4] also collected and analyzed sediment samples from ML Bay of Taihu Lake in 2005, and found that the concentrations of Σ_{17}2,3,7,8-PCDD/Fs were 134.4–284.9 pg g^{-1} dw (mean 206.6 pg g^{-1} dw, $n = 10$), which were comparable to the results of our study for the same area (79.7–351.2 pg g^{-1} dw, mean 193.7 pg g^{-1} dw, $n = 9$).

In recent years, studies of sedimentary PCDD/Fs have been conducted in some rivers, estuaries and lakes in China (Table 1). In general, sediment samples from e-waste recycling areas—or areas surrounding chemical facilities which have utilized or produced chlorinated organics and schistosomiasis affected areas in China—have much higher levels of PCDD/Fs.[6] Concentrations of PCDD/Fs in the sediment of Ya-Er Lake[25] and Dagu Drainage River,[26] which were severely polluted by the pentachlorophenol manufacturing industry, reached 177 000 and 556 961 pg g^{-1}, respectively. However, the sedimentary PCDD/Fs levels of general rivers in China, such as the Haihe River,[26] Yangtze River Estuary,[27] Pearl River[28] and Liaohe River,[29] were all lower than 10 TEQ pg g^{-1} dw, and were similar to those of rivers in comparable areas of the USA,[30] Finland,[31] the UK[32] and Italy[33] (Table 1). Comparatively, sedimentary concentrations of PCDD/Fs in Taihu Lake were at background levels internationally.

There are little data regarding PBDD/Fs in sediment available for comparison (Table 1); however, previous studies indicate an increasing trend of PBDD/Fs over time. Choi *et al.*[21] found that the sedimentary levels of PBDD/Fs in Tokyo Bay increased significantly from the late 1960s to the mid-1990s. Surface sediment from Lake Djulösjön, Sweden held a higher level of PBDD/Fs (540 pg g^{-1} dw) than that taken at lower depths (440 pg g^{-1} dw).[34] The highest concentrations of PBDD/Fs reported in sediment to date were found in an e-waste recycling area of China (mean: 1132 pg g^{-1} dw).[35] Comparatively higher concentrations of PBDD/Fs (110 pg g^{-1} dw) were also observed in the sediment of Dongguan Reach in East River, an area focusing on electrical and electronic industries, while values of other parts of the East River (0.32–2.7 pg g^{-1} dw) were about 2-orders of magnitude lower than this.[36] Comparatively, PBDD/Fs in Taihu Lake were similar to those of general parts of the East River, and were much lower than those of other reported areas (Table 1).

The summed TEQs of PCDD/Fs and PBDD/Fs ranged from 1.1 to 5.7 pg TEQ g^{-1} dw for all sediment samples from Taihu Lake (Fig. 3). There are still no guidelines for dioxin contaminated sediments in China. However, the threshold effect level (TEL), an interim sediment quality guideline (ISQG) in Canada, and the low risk concentrations defined by the USA for dioxins in sediment based on TCDD toxicity equivalents, are 0.85 and 2.5 pg TEQ g^{-1} dw, respectively.[37,38] The total TEQs of all sediment samples collected from Taihu Lake were higher than the TEL of the ISQG of Canada, and about 77% of the values were above the low risk concentrations of the US EPA. However, all of the values of Taihu Lake were lower than the probable effect

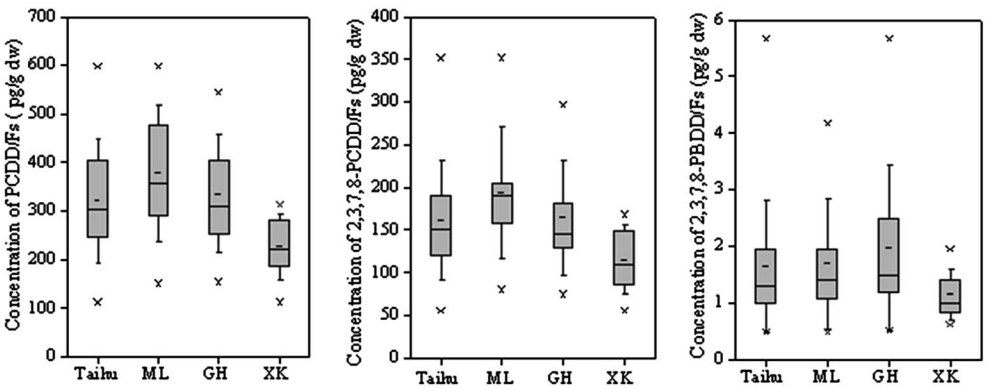

Fig. 2 Concentrations of PCDD/Fs and PBDD/Fs in the sediments from Taihu Lake, China. The box represents the 25–75 percentiles, and the whiskers represent the standard deviation. The crosses represent the min and max values. The short horizontal line represents the mean.

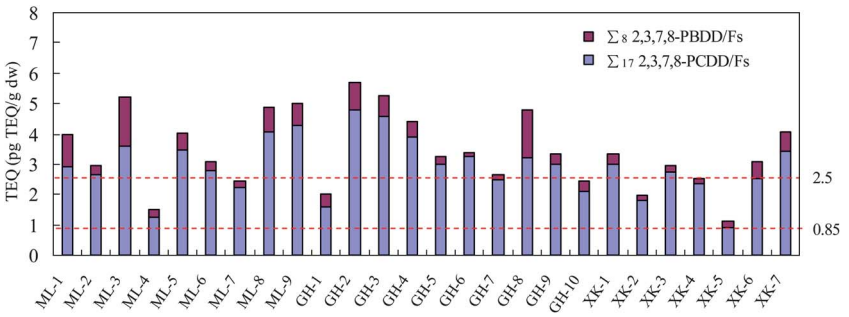

Fig. 3 Total TEQ of $\sum_{17}$ 2,3,7,8-PCDD/Fs and $\sum_{8}$ 2,3,7,8-PBDD/Fs in all sediment samples of Taihu Lake.

level (21.5 pg TEQ g^{-1} dw) defined by Canada for fish and the value indicating high risk to sensitive species (25 pg TEQ g^{-1} dw) for mammalian wildlife specified by the USA.

3.2 Congener profiles of PCDD/Fs, PBDD/Fs and possible source analyses

Similar homologue profiles of 2,3,7,8-PCDD/Fs and PCDD/Fs were found in sediment samples from the three regions of Taihu Lake (Fig. 4). The relative percentages of 2,3,7,8-PCDD/Fs homologues increase as the degree of chlorination increases, and higher chlorinated congeners dominated all sediment samples. Additionally, a trend of decreasing PCDF and increasing PCDD concentrations with increasing chlorine substitution levels was observed for the total PCDD/Fs homologues. OCDD was the most common 2,3,7,8-PCDD/Fs congener in all samples, contributing between 59 and 76% of the total (mean: 70%). This was followed by OCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF. Overall, these four higher chlorinated congeners accounted for 90% of $\sum_{17}$ 2,3,7,8-PCDD/Fs. This congener profile was similar to the profiles of 2,3,7,8-PCDD/Fs impurities in commercial PCP-Na of China,[7] as well as the typical 2,3,7,8-PCDD/Fs patterns in the sediment of schistosomiasis areas in China.[39,40]

Principal component analysis (PCA) of the 2,3,7,8-PCDD/Fs congeners was conducted to identify their main sources in the surface sediment of Taihu Lake. According to the local industrial and agricultural activities of Taihu Lake Basin, the following eight possible emission sources of PCDD/Fs were selected: automobiles exhaust,[41] flue gas and fly ash from municipal solid waste incineration,[42] agricultural straw open burning,[43] pentachlorophenol (PCP) and PCP-Na,[7] waste water from pulp mills,[44] emission gas from cement production,[29] emission gases from secondary Al and Cu metallurgy,[45] and emission gas from iron ore sintering.[46] PCA revealed that the first two PCs (Eigenvalue >1) already accounted for 71.7% of the total

Table 1 Comparison of PCDD/Fs and PBDD/Fs concentrations (pg g^{-1} dw) in sediments from different areas

Country	Location	PCDD/Fs concentration range (mean)	PCDD/Fs TEQ range (mean)	PBDD/Fs concentration range (mean)	PBDD/Fs TEQ range (mean)	References
China	Meiliang Bay of Taihu Lake	134.4–284.9 (206.6)	0.84–3.7 (2.2)[a]	—	—	4
	Ya-Er Lake	72.1–177 000	0.16–797[b]	—	—	25
	Yangtze River Estuary	23.0–375.4	0.35–1.4[a]	—	—	27
	East River	2100–5400 (3600)	2.1–9.8 (4.5)[a]	0.32–110[e]	0.09–18	36 and 51
	Liaohe	13.7–458.5 (121.9)	0.24–27.5 (3.0)[c]	—	—	29
	Daliao River	29.1–3039.1 (864.5)	0.28–29.0 (7.5)[b]	—	—	52
	River in Guiyu	—	—	(1132)[g]	(171)	35
	Haihe River	151–11 546 (2013)	1.4–19 (8.3)[a]	—	—	26
	Dagu Drainage River	1962–556 961(201 290)	21–893 (314)[a]	—	—	26
	Pearl River Delta	2003–4314 (2794)	1.5–6.2 (3.3)[a]	—	—	28
	Hong Kong Coast	2471–6300	6.1–13.1	11–216[h]	2.9–5.5	16
	Taihu Lake	111.9–597.1 (319.7)	0.91–4.8 (2.9)[a]	0.48–5.7 (1.7)[e]	0.16–1.6 (0.52)	This study
Japan	Freshwater lake area	377–15 893	0.4–37.2[b]	—	—	53
	Industrialized areas	—	—	2.1–25.5[f]	—	54
	Tokyo Bay	—	—	(46.9)[h]	—	21
	Osaka	2180–10 500	—	30–370[h]	—	15
Korea	Korea Coast	232–5900	2.3–90	n.d.-460[h]	n.d.-5.6	16
USA	Kentucky Lake	120–2400[d]	0.07–2.6[a]	—	—	30
Finland	Lake Valkjarvi	(220)	(1.1)[b]	—	—	55
	Lake Pahtajarvivi	132–387	1.8–10.8[b]	—	—	31
Sweden	Lake Stensjön & Lake Djulösjön	970–2395	7.3–45	440–540[h]	—	34
Italy	Lake Maggiore	(435)	0.1–32[a]	—	—	33
UK	Eleven Acres Lake	(590)	(6)[b]	—	—	32

[a] TEQ calculated by WHO_{1998}-TEQ.[56] [b] TEQ calculated by I-TEQ. [c] TEQ calculated by WHO_{2005}-TEQ.[57] [d] Sum of seventeen 2,3,7,8-substituted PCDD/Fs congeners. [e] Eight 2,3,7,8-substituted PBDD/Fs congeners. [f] Seven 2,3,7,8-substituted PBDD/Fs congeners. [g] Ten 2,3,7,8-substituted PBDD/Fs congeners. [h] Total PBDD/Fs; n.d.: not detected.

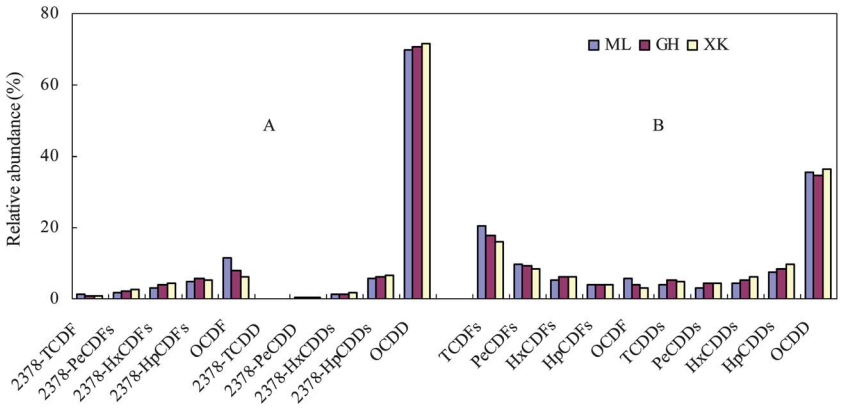

Fig. 4 Homologue profiles of sedimental PCDD/Fs in the three regions of Taihu Lake, China. (A) Homologue profiles of the total 2,3,7,8-PCDD/Fs; (B) Homologue profiles of the total PCDD/Fs.

variability among samples (52.2% for PC1, 19.5% for PC2). As shown in Fig. 5, all sediments were clustered together with PCP, PCP-Na, and close to automobile exhaust, and emission gases from secondary Al and Cu metallurgy. These results indicated that PCP-Na and PCP were likely the principal contamination sources of PCDD/Fs in Taihu Lake, while automobile exhausts, and secondary Al and Cu metallurgy were likely the minor sources of PCDD/Fs in the sediment of Taihu Lake. In this area, PCP-Na has been widely applied since the 1960s to control the spread of snail-borne schistosomiasis. However, in recent years, the number of vehicles has also largely increased with the rapid development of the local and national economy and urbanization in the cities surrounding Taihu Lake. In addition, there are many Al and Cu metallurgy plants concentrated in the Taihu Lake area. Furthermore, a number of municipal solid waste incineration plants have been established around Taihu Lake to gradually replace landfill waste disposal. Therefore, the relative contribution of PCDD/Fs from other emission sources except for PCP will increase in the near future.

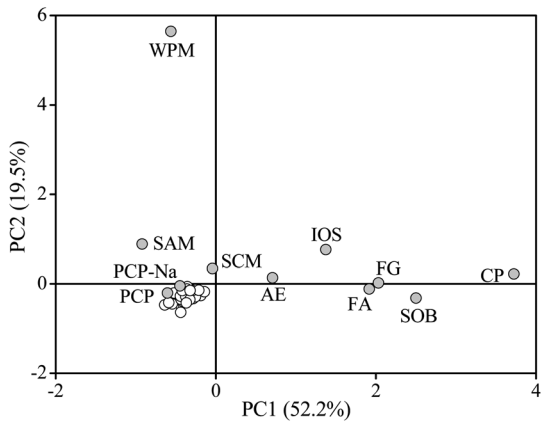

Fig. 5 PCA score plot of 2,3,7,8-PCDD/Fs congeners of suspected PCDD/Fs sources (solid circle) and sediment samples from Taihu Lake (hollow circle). AE: automobiles exhaust; FG: flue gas from MSWI; FA: fly ash from MSWI; PCP: pentachlorophenol; PCP-Na: sodium pentachlorophenate; CP: cement production; SAM: secondary Al metallurgy; SCM: secondary Cu metallurgy; IOS: iron ore sintering; WPM: waste water from pulp mill; SOB: agricultural straw open burning.

When compared with PCDD/Fs, the congener profile of sedimentary PBDD/Fs in Taihu Lake had greater variety among the three regions (Fig. 6). As shown in Fig. 6, PBDFs dominated all sediment samples from Taihu Lake and accounted for approximately 80% of $\Sigma_8$2,3,7,8-PBDD/Fs with 2,3,7,8-TBDF, 1,2,3,7,8-PeBDF and 2,3,4,7,8-PeBDF being the most abundant congeners. This pattern is similar to those of sediment in the East River of the Pearl River Delta.[36] PBDD/Fs have been reported as by-products of PBDEs and the production and use of PBDEs is the most important source of PBDD/Fs. The historical trends of PBDD/Fs in sediment cores from Tokyo Bay have been found to be similar to those of PBDEs.[21] The average atmospheric $\sum_{33}$PBDEs concentration of Taihu Lake was found to be 220 pg m^{-3}, which is nearly double that of urban regions in the US, with BDE-209 being the most abundant congener (average percentage = 41%).[23] High levels of PBDD/Fs (mean 7.8 μg g^{-1}) were also recently found in some commercial deca-BDE from China.[47] Therefore, we suspected that the use of deca-BDE might play an important role in its sedimentary PBDD/Fs. Furthermore, pyrolysis of PBDEs, municipal solid waste incinerators and industrial waste incinerators were also a potential contamination source of PBDD/Fs.[48,49] However, it is difficult to clarify the sources of sedimentary PBDD/Fs of Taihu Lake because of the limited congeners analyzed in this study, the scarcity of data regarding the congener patterns of PBDD/Fs emission sources, and the drastic changes in the profiles of PBDD/Fs during various environmental processes including volatilization, adsorption, photolytic debromination, and biodegradation.[16,48,50] Thus, more research into the environmental behavior of PBDD/Fs and possible sources are necessary.

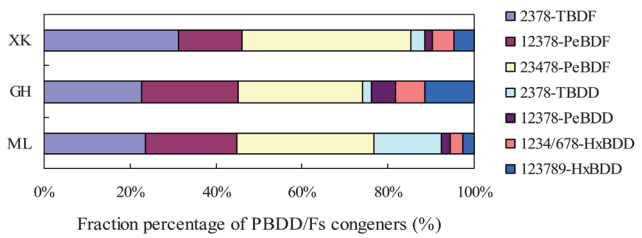

Fig. 6 Relative concentration percentages of 2,3,7,8-PBDD/Fs congeners in the three sediment regions of Taihu Lake, China.

Unlike the concentration profiles, 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the major TEQ contributors of PCDD/Fs, and 2,3,4,7,8-PeBDF was the most important TEQ contributor of PBDD/Fs, accounting for about half of the TEQ value of PBDD/Fs in surface sediment from Taihu Lake. Similar results were also found in sediment from the East River, China.[36]

3.3 Spatial trends of PCDD/Fs and PBDD/Fs in sediments

Three representative regions of Taihu Lake (ML, GH and XK) were investigated in this study. The ranges (means) of PCDD/Fs and 2,3,7,8-PBDD/Fs were 149.8–597.1 (378.2), and 0.48–4.2 (1.7) pg g^{-1} dw for ML; 153.6–543.4 (336.6) and 0.52–5.7 (2.0) pg g^{-1} dw for GH; and 111.9–314.1 (226.9) and 0.63–2.0 (1.2) pg g^{-1} dw for XK, respectively (Fig. 2). Comparatively, the concentrations did not differ significantly between ML and GH ($p > 0.05$), while, with the exception of 2,3,7,8-PBDD/Fs, the values of XK were significantly lower than those of ML ($p < 0.05$). These results suggested a decreasing trend of PCDD/Fs from the inflow region to the outflow region of Taihu Lake. However, no significant difference was observed among the 2,3,7,8-PBDD/Fs concentrations of ML, GH and XK ($p > 0.05$), which indicated that some non-point and unrelated run-off sources of PBDD/Fs existed around Taihu Lake (*e.g.* atmospheric deposition).

The results of correlation analysis between TOC and PCDD/Fs and PBDD/Fs were consistent with these findings. In this study, TOC contents in sediment samples ranged from 0.39 to 1.54%, and they were significantly correlated with PCDD/Fs (correlation coefficient = 0.62, $p < 0.01$), which might suggest they shared the similar sources and TOC could act as an important factor affected the distribution of PCDD/Fs in Taihu Lake. However, PBDD/Fs were independent of TOC (correlation coefficient = 0.20, $p > 0.05$) and this was in accordance with their possible atmospheric deposition source, which contributes very little to TOC in the sediment of a lake.

Two factors might affect the spatial distribution of PCDD/Fs. Firstly, the total flow direction of Taihu Lake is from north-west to south-east and the PCDD/Fs levels were found to be ML $\approx$ GH > XK. XK is one of the major outflow regions of the Taihu Lake, approximately 25% of the total outflow water runs out from this bay per annum, therefore, it is reasonable for the levels of PCDD/Fs in XK Bay to be relatively lower than those in ML and GH.

Secondly, the runoff near the study areas might affect the spatial PCDD/Fs levels. The inflow rivers around ML Bay that flow through some industrial cities including Wuxi and Changzhou, as well as agricultural areas, contribute roughly 10% of the total water intake of Taihu Lake. The concentration of 2,3,7,8-PCDD/Fs in sediment from one inflow river around ML Bay was reported to be 1315.1 pg g^{-1} dw,[4] which is about four times greater than the highest concentration observed in ML Bay (351.2 pg g^{-1} dw) in our study. It seems implied that there are inflow runoff sources of PCDD/Fs in this region. For GH, it is a semi-closed U-shaped bay near ML (Fig. 1) and inflow rivers around this bay contribute approximately 9% of the total water intake of Taihu Lake. The major inflow river of GH is the Yangtze River, and sediment samples from the Yangtze River Estuary were shown to have comparable 2,3,7,8-PCDD/Fs concentrations (21.9–343.1 pg g^{-1} dw)[27] to our results for GH (74.4–296.4 pg g^{-1} dw). However, for XK, there are no inflow rivers which contribute to the total water intake of Taihu Lake.

4 Conclusions

This study investigated PCDD/Fs and PBDD/Fs levels in the surface sediments from three typical drinking water sources of Taihu Lake. The results indicated that sedimentary concentrations of PCDD/Fs and PBDD/Fs in study areas were at background levels internationally. Additionally, inflow runoff and total water direction seems to significantly affect the concentration and spatial distribution of PCDD/Fs. Historical production and usage of pentachlorophenol and sodium pentachlorophenate was the dominant source of PCDD/Fs, whereas the specific sources of PBDD/Fs are still unclear due to limited information. Greater attention is needed because the production and usage of brominated flame retardants such as PBDEs and TBBPA, which were the precursors of PBDD/Fs, are produced in large volumes in the Yangtze River Delta.

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