

LEVELS AND DISTRIBUTIONS OF ORGANOPHOSPHATE FLAME RETARDANTS AND PLASTICIZERS IN SEDIMENT FROM TAIHU LAKE, CHINA

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Abstract—The concentrations and distribution of seven organophosphate flame retardants and plasticizers (OPs) were investigated in 28 sediment samples collected from Taihu Lake. The analytes were ultrasonically extracted, enriched using solid-phase extraction, and determined by gas chromatography-mass spectrometry. The results indicated that the analytes were all detected in the sediments. The total concentrations of seven OPs ranged from 3.38 to 14.25 $\mu\text{g}/\text{kg}$, and tris (2-chloroiso-propyl) phosphate (TCPP), tris (2-chloroethyl) phosphate (TCEP), and tris (2-butoxyethyl) phosphate (TBEP) were the dominant compounds, with concentrations ranging from $<$ limit of quantification to 2.27 $\mu\text{g}/\text{kg}$, 0.62 to 3.17 $\mu\text{g}/\text{kg}$, and 1.03 to 5.00 $\mu\text{g}/\text{kg}$, respectively. The highest concentration of total assessed OPs (14.25 $\mu\text{g}/\text{kg}$) was found at GH-5, with tris (1,3-dichloro-2-propyl) phosphate (TDCPP) as the main component at the sampling site. This result implied that there is an obvious emission source nearby at Suzhou City; in addition, human activities also play an important role in the concentration of OPs in the sediment. Environ. Toxicol. Chem. 2012;31:1478–1484. © 2012 SETAC

Keywords—Organophosphate esters Flame retardant Plasticizer Sediment Taihu Lake

INTRODUCTION

Organophosphate esters (OPs) are a group of important chemicals widely used as flame retardants and plasticizers in a variety of products, such as varnishes, polyurethane foams, electronics equipment, upholstery, and textiles. Generally, chlorinated OPs, such as tris (2-chloroethyl) phosphate (TCEP), tris (2-chloroiso-propyl) phosphate (TCPP), and tris (1,3-dichloro-2-propyl) phosphate (TDCPP), are preferentially used as flame retardants, while nonchlorinated OPs, such as tris (2-butoxyethyl) phosphate (TBEP), tributyl phosphate (TBP), and triphenyl phosphate (TPhP), are applied as plasticizer additives and also as extreme pressure additives and antiwear agents in hydraulic fluids, lubricants, transmission fluids, motor oils, and similar products [1–3]. Detailed information about their applications has been summarized previously [4]. Due to the ban on or phase-out of penta- and octabrominated diphenyl ethers (PBDEs), the use of OPs as flame retardants (OPFRs) increased gradually to meet the commercial need, and these compounds are now listed as high production-volume chemicals [5–7]. Usually, the OPs are directly mixed into the materials and are not chemically bonded; therefore, they can be easily released or leached into the surrounding environment from the OP-containing products during manufacture, application, or disposal [4]. Their widespread application has resulted in extensive diffusion and ubiquitous distribution in the environment, for example, in air [8–11], wastewater and sludge [12–14], surface water [6,13,15–17], groundwater [1], sediment [18–20], soil [7], and even the human body [21–23].

A number of studies have shown their toxicities to animals and humans; for example, TBP, TPhP, and tritolyol phosphate (TTP) are neurotoxic after chronic exposure, and TCEP and

TBEP are suspected to be carcinogenic, with observed tumor growth in tissues. More information about the toxicity has been published elsewhere [24,25]. Additional adverse effects on humans have been disclosed; for example, TBP is strongly related to sick house syndrome [26], and TPhP and TDCPP were associated with altered hormone levels and a decline of semen quality in 50 male patients [27].

Previous studies have demonstrated that some OPs, especially chlorinated OPs, are highly persistent in the environment [16,21], and they can even persist in drinking water after conventional treatment, indicating that these compounds can reach the human body via drinking water [28,29]. Considering their toxicity, much more attention should be paid to human exposure and the potential human health risk.

Taihu Lake, the third largest freshwater lake in China, lies in the Yangtze River delta and is a drinking water source for millions of people inhabiting the most developed cities around the lake, such as Shanghai, Wuxi, Suzhou, and Jiaxing. In addition, Taihu Lake serves as a site for aquaculture and as a shipping route [30]. In recent years, Taihu Lake has been subjected to increasing and more serious contamination due to rapid urbanization and industrial and agricultural development. It has been found that Taihu Lake has suffered from accelerated eutrophication resulting from overloading of nitrogen and phosphorus, thereby posing a health risk to the population surrounding the lake [31–34]. Extensive studies have disclosed a serious deterioration of water quality due to pollutants derived from household, industrial, and agricultural discharge, and several kinds of persistent organic pollutants (POPs) have been detected in air, water, sediment, and even biota in the region. Among the POPs detected are polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), PBDEs, 1,2-bis(2,4,6-tribromophenoxy) ethane, decabromodiphenylethane, dechlorane plus (DP), and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) [30–33,35]. Until now, there has been no information about the pollution status of OPs in this region.

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In the present study, the occurrence and distribution of seven organophosphate flame retardants and plasticizers in 28 sediments from Taihu Lake were investigated, and their possible origins were also preliminarily assessed. The structures of the seven OPs are shown in Figure 1, and their information is listed in Table 1.

MATERIALS AND METHODS

Chemicals and materials

Seven organophosphate flame retardant and plasticizer standards were purchased from Sigma-Aldrich: TBP (99%), TPhP (99%), TCEP (97%), TBEP (94%), TTP (90%), TDCPP (97%), and TCPP (99.5%). Surrogate standard tri-*n*-butyl- d_{27}

phosphate (d_{27} -TBP; 98%) was purchased from C/D/N Isotopes Inc. All solvents used were of chromatographic grade; acetonitrile was from Merck, ethyl acetate was from CNW Technologies, and methanol was from J&K Scientific. Oasis HLB Extraction Cartridges (200 mg, 6 ml) were purchased from Waters Corporation. Internal standard hexamethylbenzene (HMB, 99.5%) was acquired from the laboratories of Ehrenstofer-Schäfer Bgm-Schlosser.

Sample collection

Pollutants derived from domestic, industrial, and agricultural activities are discharged mainly into Meiliang Bay, Zhushan Bay, and the western district of Taihu Lake through several inflows, causing a decline in water quality, harmful algal

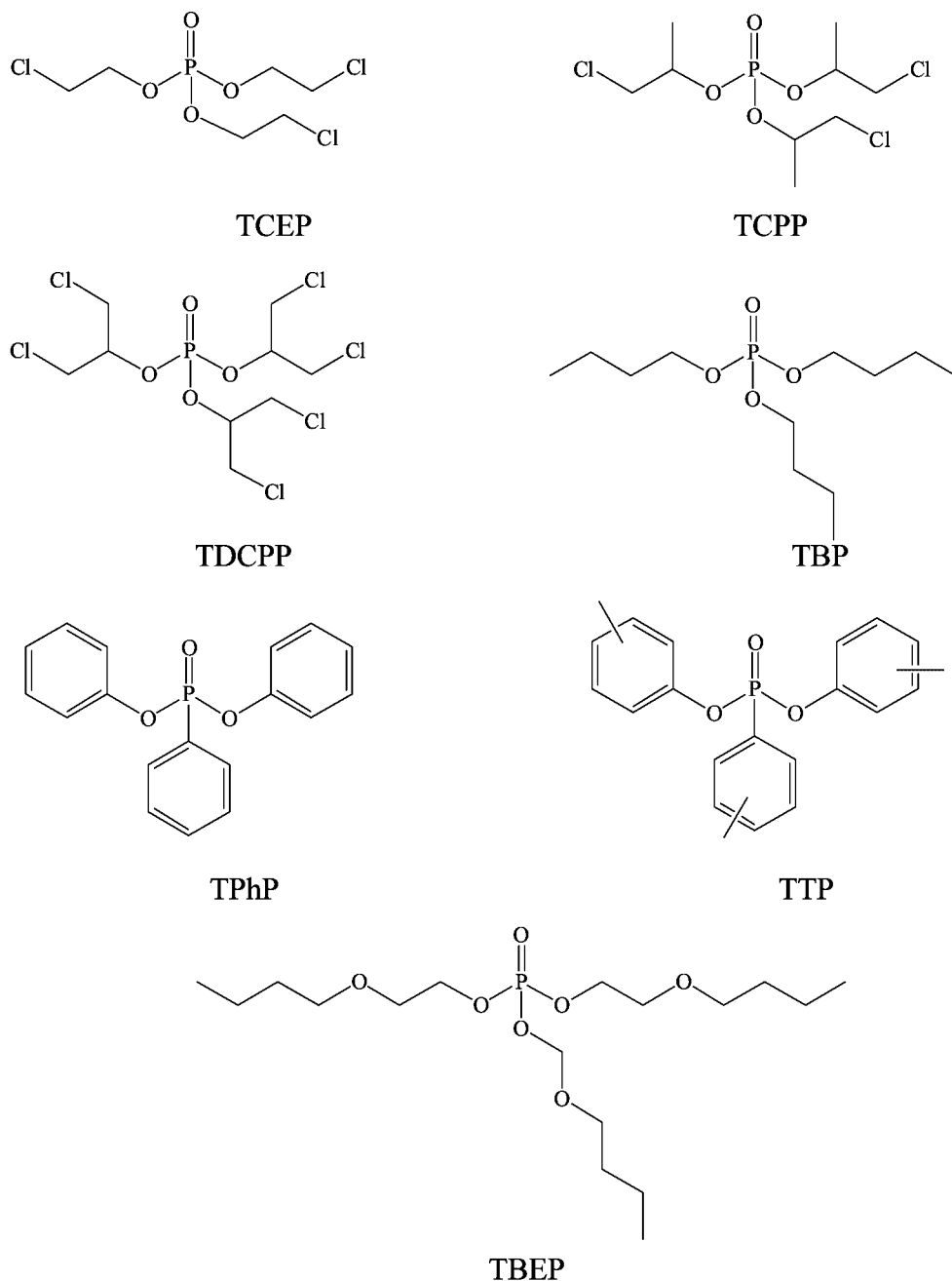


Fig. 1. Structures of seven organophosphates assessed in this work. TCEP = tris (2-chloroethyl) phosphate; TCPP = tris (2-chloroisopropyl) phosphate; TDCPP = tris (1,3-dichloro-2-propyl) phosphate; TBP = tributyl phosphate; TPhP = triphenyl phosphate; TTP = tritolyl phosphate; TBEP = tris (2-butoxyethyl) phosphate.

Table 1. Information about seven organophosphate flame retardant and plasticizer compounds

Compound	Abbreviation	CAS No.	Log K_{ow} ^a	Water solubility ^a
Tributyl phosphate	TBP	126-73-8	4.0	280 mg/l
Tris (2-butoxyethyl) phosphate	TBEP	78-51-3	3.75	1100 mg/l
Tris (2-chloroethyl) phosphate	TCEP	115-96-8	1.44	7000 mg/l
Tris (2-chloroiso-propyl) phosphate	TCPP	13674-84-5	2.59	1200 mg/l
Tris (1,3-dichloro-2-propyl) phosphate	TDCPP	13674-87-8	3.65	7 mg/l
Triphenyl phosphate	TPhP	115-86-6	4.59	1.9 mg/l
Tritolyl phosphate	TTP	1330-78-5	5.11	0.36 mg/l

^a Data from Syracuse Research Corporation database of physicochemical properties (<http://www.syrres.com/what-we-do/databaseforms.aspx?id=386>).

blooms, and ecosystem degradation [33,34,36]. Most of the water intakes for the surrounding population and the main water source protection zone are located in the northern and eastern parts of the lake, including Meiliang Bay, Gonghu Bay, and Xukou Bay. The composite sediment sampling sites were chosen according to the current locations of the water source protection zone and water intakes. Nine composite sediment samples (ML-1-9) were collected in Meiliang Bay, 10 samples were collected in Gonghu Bay (GH-1-10), and seven were from Xukou Bay (XK-1-7). In addition, two samples were from the central section of the lake (HX-1 and HX-2). The top 5 cm of surface sediment was collected using grab samplers (Ekmangrab, Wildlife Supply), then transported on ice to the laboratory where they were kept in a refrigerator at -20°C until

analysis. The sediment samples were freeze-dried, ground fine, sieved through 80 mesh, and kept in amber glass bottles until extraction. The locations of these sampling sites are shown in Figure 2.

Extraction and analysis

The analytes were extracted using ultrasonic assistance according to published procedures with modifications [13,19]. A brief description is given here. Approximately 5 g dry sediment for each sample was spiked with 5 μl of d_{27} -TBP at 10 mg/L as surrogate standard and then extracted by ultrasonic assistance with 20 ml of acetonitrile/water (25:75, v/v) at 20°C for 30 min. The extract was centrifuged at 4,500 rpm for 10 min, and the supernatant was decanted into a flask. The

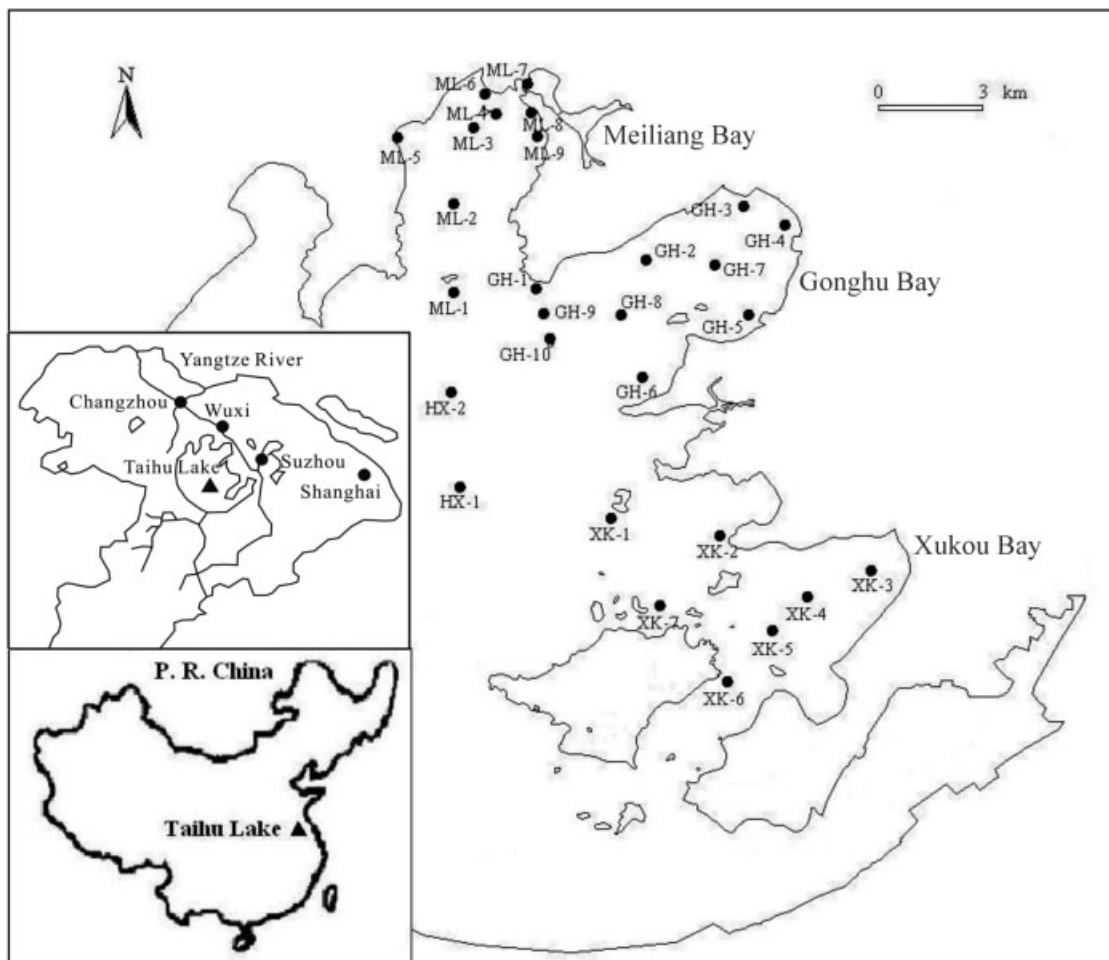


Fig. 2. Sampling sites in Taihu Lake.

residual sediment was extracted again following the same procedure. The combined extract was diluted to 500 ml using ultrapure water and subjected to solid-phase extraction for further separation and concentration. An Oasis HLB cartridge (200 mg, 6 ml) was employed, which was preconditioned with 4-ml ethyl acetate, 4-ml methanol, and 4-ml ultrapure water. After loading, the cartridge was dried under a gentle flow of N₂, and the enriched analytes were eluted twice with 8 ml of ethyl acetate. The eluate was concentrated under a gentle stream of N₂ almost to dryness, and the resulting extract was redissolved in 100 μ l of *n*-hexane. A total of 5 ml of hexamethylbenzene at concentration 20 mg/L (HMB) was added as internal standard before gas chromatography-mass spectrometry.

Identification and quantification of the analytes in the samples were carried out using a Shimadzu 2010 gas chromatograph equipped with a mass spectra detector and a TG-5ms column (30 m \times 0.25 mm I.D \times 0.25 μ m film) (Thermo Technology). The oven temperature was programmed at a rate of 10°C/min from 70°C (held for 2 min) to 160°C and then at 5°C/min to the final temperature of 295°C (held for 15 min). The temperatures of injector and transfer line were set to 290°C and 300°C, respectively. The mass spectrometer was operated in selected ions mode with EI-mode, the source temperature was set at 220°C, and a 1- μ l sample was injected with splitless mode (0.75 min). Helium was used as gas carrier with the column flow rate at 1 ml/min. The quantification and verification ions for each compound are shown in Table 2. Concentrations were calculated using a six-point calibration standard curve with a concentration range of 50 to 5,000 μ g/L. Good correlation coefficients (r^2) between 0.9975 and 0.9997 were obtained. The limits of detection (LODs) for specific chemicals were in the range 0.07 to 0.3 ng/g in 5-g sediment, which is calculated as $3 \times (SD/S)$, where SD is the standard deviation of the response acquired for seven replicate injections of standard at concentrations as low as possible, which was established using a dilution series of stock solution for each compound. The limits of quantification (LOQs) were defined as twice the maximum defined as concentration in blank value for the three OPs detected in blanks, for example, TBEP, TCEP, and TCPP. As for the four OPs not detected in blank samples (TBP, TDCPP, TPhP, and TTP), the LOQs were calculated as two times the LODs.

Quality control and quality assurance

Method blanks ($n = 3$), spiked blanks (standards spiked into solvent, $n = 3$), spiked matrix (standards spiked into pre-extracted sediment, $n = 3$), and replicate samples ($n = 3$) were analyzed with real samples in every batch. In each spiked

sample, a 5- μ l mixture of standards containing 10-mg/L 7OPs was added; meanwhile, 5- μ l d27-TBP at a concentration of 10 mg/L was spiked as surrogate in each sample. Tris (2-butoxyethyl) phosphate, TCEP, and TCPP were found in every method blank at the LOD level, and quantification of these compounds was background corrected. Acceptable recoveries were achieved with ranges from 81 ± 11 to $108 \pm 5\%$ and 66 ± 8 to $112 \pm 7\%$ for spiked blanks and spiked matrix, respectively, depending on the compound (see Table 2).

RESULTS AND DISCUSSION

Levels of OPs in sediment from Taihu Lake

The concentrations and distribution of 7 OPs in 28 sediment samples are listed in Table 3. It can be seen from Table 3 that the 7 OPs were detected in all the sediments, with chlorinated OPs as the main components. The total concentration of the 7 OPs (Σ 7OPs) ranged from 3.38 to 14.25 μ g/kg.

Until now, limited data have been available on levels and distribution of OPs in sediments worldwide. It is shown that the levels of OPs in Taihu Lake sediments were close to those detected in marine sediment and river sediment from Taiwan, Spain, the United States, and Austria [13,18–20], but significantly lower than those found in sediments from highly industrialized areas in Germany [37] and from a sea-based waste disposal site [38]. In 1999, Kawagoshi et al. investigated the occurrence of nine OPs (including the seven analytes in the present study, triethyl phosphate [TEP], and tri-2-ethylhexyl phosphate [TEHP]) in sediments collected from a sea-based solid waste disposal site located at the Osaka North port and found that all the studied OPs were detected, with TCEP (LOD \sim 7,395 μ g/kg) and TBEP (LOD \sim 1,969 μ g/kg) as the main components, and that the total concentrations of the nine OPs in sediments from the disposal site (484–12,081 μ g/kg) were significantly higher than those in the surrounding sea [38]. Stachel et al. measured five OPs (including TBP, TCEP, TCPP, TDCPP, and TBEP) in 37 sediment samples collected from the highly industrialized area along the Elbe River and at the mouths of its main tributaries; all of the OPs were detected in the sediments, and among them, TCPP was the dominant compound with levels ranging from 5.9 to 311 μ g/kg [37].

Distribution profile of individual OPs and possible source in sediment

From Table 3, it also can be seen that the concentration of TBEP varied from 1.03 to 5.00 μ g/kg, with the highest level found at GH-4. The levels of the three chlorinated OPs, TCEP, TCPP, and TDCPP, were in the range of 0.62 to

Table 2. Quantification ion, verification ions, limits of detection, and limit of quantitation of specific organophosphate flame retardants and plasticizers^a

Compound	Quantification ion (<i>m/z</i>)	Qualification ions (<i>m/z</i>)	LOD (ng/g)	LOQ (ng/g)	Recovery (%)		RSD (%)	
					Spiked blanks	Spiked matrix	Spiked blanks	Spiked matrix
TBP	99	155/211	0.2	0.4	108	109	5	3
TBEP	199	299	0.07	0.13	81	99	11	9
TDCPP	379	191/381	0.3	0.6	107	112	8	7
TCEP	249	143	0.2	0.38	108	110	6	7
TCPP	277	279	0.2	0.4	108	109	8	3
TPhP	325	326	0.2	0.4	102	105	8	4
TTP	368	368	0.2	0.4	84	66	11	8

^aFor compound abbreviations see Table 1.

LOD = limits of detection; LOQ = limit of quantitation; RSD = relative standard deviations.

Table 3. Concentrations and distribution of organophosphate flame retardants and plasticizers in sediments from Taihu Lake ($\mu\text{g}/\text{kg}$)

	TBP	TBEP	TCEP	TCPP	TDCPP	TPhP	TTP	$\Sigma 7\text{OPs}$
HX-1	0.65	2.32	2.12	1.48	1.11	1.01	LOQ	8.70
HX-2	0.91	1.65	1.01	1.55	1.02	0.41	<LOD	6.55
ML-1	0.79	1.95	2.67	1.91	1.30	0.40	<LOD	9.01
ML-2	0.50	1.65	1.41	1.35	1.01	0.46	<LOD	6.37
ML-3	1.09	2.13	2.40	2.08	1.23	0.85	<LOD	9.79
ML-4	0.76	1.76	2.00	1.17	1.03	LOQ	<LOD	6.72
ML-5	1.96	1.37	1.18	LOQ	0.86	0.95	0.65	6.97
ML-6	2.65	1.34	1.69	1.82	1.38	0.49	0.43	9.80
ML-7	1.37	1.11	0.89	0.57	0.74	LOQ	<LOD	4.69
ML-8	1.40	1.42	2.11	1.47	1.48	0.49	LOQ	8.38
ML-9	1.03	1.53	1.65	1.69	2.26	0.43	<LOD	8.58
GH-1	1.25	1.03	0.62	0.48	<LOD	LOQ	<LOD	3.38
GH-2	1.53	1.84	1.09	0.71	LOQ	0.51	<LOD	5.68
GH-3	1.46	4.67	3.03	1.65	0.96	1.07	<LOD	12.84
GH-4	1.32	5.00	1.65	1.13	LOQ	0.64	0.46	10.19
GH-5	0.68	3.01	2.05	2.27	5.54	0.71	<LOD	14.25
GH-6	0.72	2.36	1.96	1.54	1.94	1.19	<LOD	9.72
GH-7	0.82	3.04	2.73	1.09	0.80	LOQ	LOQ	8.49
GH-8	2.06	1.66	1.00	0.74	0.62	LOQ	0.63	6.70
GH-9	0.80	1.61	1.35	2.16	1.64	0.57	<LOD	8.13
GH-10	0.91	2.26	2.36	1.46	1.23	0.46	<LOD	8.67
XK-1	0.76	1.53	3.17	1.51	1.23	0.64	<LOD	8.84
XK-2	0.51	1.78	1.02	1.12	0.81	LOQ	<LOD	5.23
XK-3	1.59	1.91	1.67	1.60	1.07	LOQ	<LOD	7.84
XK-4	0.60	1.48	2.35	1.77	0.89	0.71	<LOD	7.80
XK-5	LOQ	1.58	1.14	1.07	0.75	0.74	<LOD	5.29
XK-6	0.50	1.55	1.40	1.33	0.81	0.50	<LOD	6.08
XK-7	0.51	1.38	1.21	1.32	0.92	0.48	<LOD	5.82
Mean	1.04	2.00	1.75	1.36	1.16	0.49		

^a For compound abbreviations see Table 1.

LOD = limits of detection; LOQ = limit of quantitation.

3.17 $\mu\text{g}/\text{kg}$ (mean, 1.75 $\mu\text{g}/\text{kg}$), <LOQ to 2.27 $\mu\text{g}/\text{kg}$ (mean, 1.36 $\mu\text{g}/\text{kg}$), <LOD to 5.54 $\mu\text{g}/\text{kg}$ (mean, 1.30 $\mu\text{g}/\text{kg}$), respectively. Because of the considerable carcinogenic and mutagenic effects of TCEP, it has gradually been replaced by the structurally similar TCPP [37]. However, in the present work, we found concentrations of TCEP ranging from 0.62 to 3.17 $\mu\text{g}/\text{kg}$ in all the sediment samples, implying that TCEP was still in use in the region. Tri-butyl phosphate and TPhP were also found in Taihu Lake, with concentrations ranging from <LOQ to 2.65 $\mu\text{g}/\text{kg}$

(mean, 1.04 $\mu\text{g}/\text{kg}$) and <LOQ to 1.19 $\mu\text{g}/\text{kg}$ (mean, 0.49 $\mu\text{g}/\text{kg}$), respectively, whereas TTP was detected at the LOD level.

The distribution pattern of individual OPs is plotted in Figure 3. In about half of the sediment, TBEP was the most abundant chemical, followed by the chlorinated OPs TCEP and TCPP. The individual OP profiles might be associated with their application in this region [4,36–38]. Sjödin et al. have reported, based on their research in an electronic recycling plant, that TBEP was the most prevalent compound added in electronic goods, followed by TCEP and TCPP [38]. Marklund et al. studied 15 dust samples collected from varied environments and found that TBEP was the most abundant in most of the samples, followed by TCEP, TCPP, and TDCPP. The authors also reported that their distribution was associated with the materials used in the corresponding environment, and their potential source included floor polish, polyvinylchloride floor covering, and upholstery and plastic products [4]. An exceptional distribution, with TCPP as the dominant compound, was also found in river sediments collected in Taiwan, which were strongly affected by the presence of electric parts and plastic goods, and by manufacturing operations [20].

It is well known that OPs are important flame retardants and plasticizers added to diverse products, such as computers, televisions, and mobile phones [3]. Tris (2-butoxyethyl) phosphate is used not only as a flame retardant and plasticizer, but also as a leveling agent in products such as waxes, floor polishes, and paper coatings [4]. Therefore, production and usage of OPs in the Taihu Lake region would significantly affect their congener profiles in environmental media. In addition, several factors might affect the congener profiles of OPs in sediment, for example, significantly different physicochemical properties of individual OPs, their degradation, and complex sources (municipal and industrial effluents). Therefore, further study should be carried out to determine the occurrence and levels of OPs and their degradation products in water, but also the investigation of OPs in different typical sources such as municipal and industrial effluents, and dry/wet deposition.

Spatial distribution of OPs in Taihu Lake

Three districts (Meiliang Bay, Gonghu Bay, and Xukou Bay) were investigated in the present study, and two samples from the

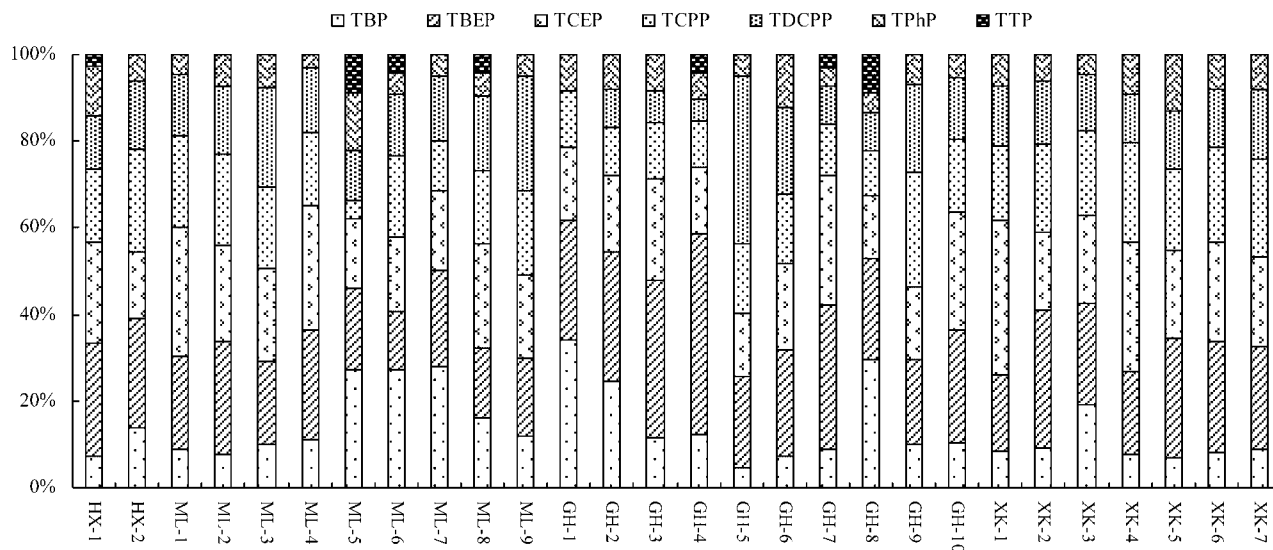


Fig. 3. Distribution of individual organophosphate flame retardants and plasticizers in sediment from Taihu Lake. For compound abbreviations see Figure 1.

center of the lake (HX-1 and HX-2) were also analyzed for comparison. The results indicated that similar levels of Σ 7OPs were found in nine sediments in Meiliang Bay (4.69–9.80 $\mu\text{g}/\text{kg}$) and seven sediments from Xukou Bay (5.23–8.84 $\mu\text{g}/\text{kg}$). In addition, 3.38 to 14.25 $\mu\text{g}/\text{kg}$ of Σ 7OPs were found in Gonghu Bay. Gonghu Bay is an important drinking water source for Suzhou City, and several intakes of waterworks are located there. Similar levels of OPs (6.55 $\mu\text{g}/\text{kg}$ and 8.70 $\mu\text{g}/\text{kg}$) were also found in two sediments collected from the central part of the lake. The highest level of Σ 7OPs was detected at the GH-5 sampling site, among which TDCPP (5.54 $\mu\text{g}/\text{kg}$) accounts for approximate 39% of the Σ 7OPs, and it is noteworthy that this is the highest level of TDCPP found in the present study. It seems that an unknown emission occurs nearby.

It has been reported that Meiliang Bay is heavily polluted by nutrients originating from domestic sewage from the Liangxi River and from nearby Wuxi City, resulting in intense algal blooms in recent years, whereas the water quality in Gonghu Bay and Xukou Bay is much better [34,36]. In the present work, the concentrations of Σ 7OPs from different regions exhibited no significant differences ($p > 0.05$) between districts based on statistical analysis using SPSS 18.0. The results might imply that a diffusive source, such as dry and wet deposition, also plays a role in the extensive distribution of OPs in the lake sediment [39–41].

Concerning the individual compounds, different spatial trends were found in Taihu Lake. For TBP, a significantly higher concentration was found at ML-6 ($p < 0.01$) than at other locations, disclosing an obvious emission spot. It was also found that concentrations of TBP in several alongshore sediments (ML-5-9, GH-1-4, GH-8, XK-3) were significantly higher than that in other sediments, suggesting that, to some extent, TBP in these sampling sites originated from human activities. As for the chlorinated OPs, a considerably higher concentration of TDCPP ($p < 0.05$) was detected at GH-5 (5.54 $\mu\text{g}/\text{kg}$), indicating an obvious and unknown discharge adjacent to the sampling site. The second highest level of TDCPP (2.26 $\mu\text{g}/\text{kg}$) was found at ML-9, a site that is in the heavily polluted region of Meiliang Bay. Further study should be carried out to determine whether there is an exceptional emission source. The highest concentration of TBEP was detected at GH-4, followed by GH-3, GH-7, and GH-5. It can be speculated that there is a noteworthy emission source, nearby but unknown, from which TBEP is discharged, followed by diffusion to circumambient water and settling to the sediment.

The distribution of hydrophobic organic contaminants is strongly related to their water solubility. For example, monochlorinated biphenyl was distributed in the dissolved phase to more than 95%, with low water solubility of 4.3 $\mu\text{mol}/\text{L}$ [38]. The water solubility of TBEP and chlorinated organophosphates in the present study is quite high, as listed in Table 1. It might be assumed that most of the studied compounds tended to be distributed in the water phase. In other words, high concentration of TBEP and TDCPP in sediments suggests much higher concentrations of these compounds in water. As stated, Taihu Lake serves as a source of water for the surrounding population, and the fact that these compounds can remain in drinking water after treatment is of great concern for human exposure and human health risk.

CONCLUSION

Seven organophosphate flame retardants and plasticizers were investigated in 28 sediment samples collected from three

districts and the central part of Taihu Lake. The total concentrations of Σ 7OPs ranged from 3.38 to 14.25 $\mu\text{g}/\text{kg}$, with TBP, TBEP, and chlorinated OPs as the main components. Industrial wastewater discharge and domestic sewage, and dry/wet deposition might be the possible source for OPs in sediments, while a few samples exhibited specific sources such as TDCPP in GH-5 and TBP in ML-6. Further study is needed to monitor the comprehensive contamination status, their sources, and environmental fate.

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