



The occurrence, composition and partitioning of phthalate esters (PAEs) in the water-suspended particulate matter (SPM) system of Lake Chaohu, China

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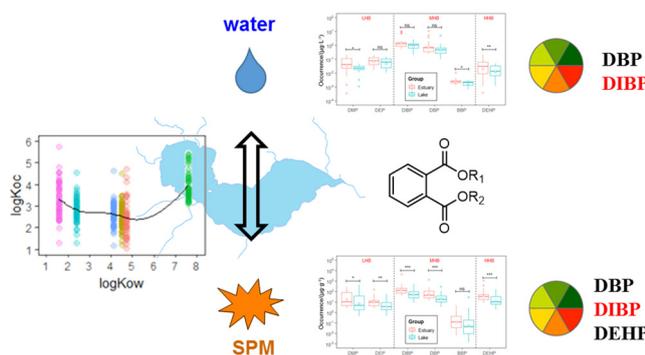
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HIGHLIGHTS

- Σ_6 PAEs in water and SPM phases exhibited different seasonal trend.
- The occurrence of PAEs exists significant spatial difference between lake and estuary.
- DIBP and DBP were the abundant PAEs in Lake Chaohu.
- DIBP should attract more attention in the future.
- The Kow model may be inappropriate to predict the partitioning of PAEs in natural large lakes.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence, composition, and partitioning of six phthalate esters (PAEs) (dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP) and di(2-ethylhexyl) phthalate (DEHP)) in the water-suspended particulate matter (SPM) system of Lake Chaohu were investigated in this study. Our results showed that PAEs were ubiquitous contaminants in Lake Chaohu. The concentration of the Σ_6 PAEs in dissolved and particulate phases ranged from 0.370 to 13.2 $\mu\text{g}\cdot\text{L}^{-1}$ and from 14.4 to 7129 $\mu\text{g}\cdot\text{L}^{-1}$, respectively. The Σ_6 PAEs in water and SPM phases exhibited different seasonal trends. PAEs with different degrees of hydrophobicity demonstrated different temporal distributions in the dissolved phase. In particulate phase, all PAEs exhibited the same temporal distribution. Regarding the occurrence of PAEs, significant spatial differences exist between lake and estuary. However, there were no specific differences in PAEs across lake zones and river types of Lake Chaohu. River input should be considered an important source of PAEs in Lake Chaohu. DIBP and DBP were the most abundant PAEs in Lake Chaohu, and DIBP should attract more attention in the future. The organic carbon normalized partitioning coefficient ($\log K_{oc}$) ranged from an average of 2.38 \pm 0.86 $\text{L}\cdot\text{g}^{-1}$ for BBP to 3.98 \pm 0.66 $\text{L}\cdot\text{g}^{-1}$ for DEHP, and approximately 2 to 3 unit variations of $\log K_{oc}$ existed for the individual PAEs. It was difficult to ascertain whether the partitioning of PAEs was in, near or far from the

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equilibrium. No linear relationship was found between $\log K_{oc}$ and the octanol-water partitioning coefficient ($\log K_{ow}$) for PAEs. K_{oc} might not be suitable for describing the partitioning of PAEs in the water-SPM system. The hydrophobicity of PAEs may have little impact on their partitioning in the complex environmental system, and the K_{ow} model may be inappropriate to predict the partitioning of PAEs in natural large lakes.

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1. Introduction

Phthalate esters (PAEs) are a class of chemical compounds that can increase the flexibility, pliability and elasticity of plastics, simplifying plastic production (Wang et al., 2013). The excellent performance of PAEs has popularized them in the plastic production industry as plasticizers and additives for several decades (Zhu et al., 2018). As the “world factory”, China has become the largest producer and consumer of PAEs in the world (Sun et al., 2013; Wang et al., 2014). PAEs have been widely added to various products, such as toys, food packages, rubber pipes, wallpapers, cleansers, lubricants and cosmetics, and the extensive use of PAEs has greatly enhanced the living conditions of human beings (Gao and Wen, 2016). However, the estrogenic activities of PAEs can disturb the normal endocrine function of organisms (Harris et al., 1997; Moore, 2000). Besides, PAEs can bind to the human hemoglobin molecule and may influence erythrocytic function (Tan et al., 2017). Furthermore, it was reported that PAEs can lead to DNA damage in an experimental in vitro assay (Al-Saleh et al., 2017). In addition, a prospective cohort study found that pregnancy loss was related to PAE metabolites (Toft et al., 2012). Widespread use of PAEs led to their ubiquitous occurrence in environmental matrices such as water (Paluselli et al., 2018; Selvaraj et al., 2015; Dominguez-Moruco et al., 2014), air (Peijnenburg and Struijs, 2006; Teil et al., 2006; Kong et al., 2013), soil (Wang et al., 2017; Kong et al., 2012; Plaza-Bolanos et al., 2012), sediment (Liu et al., 2008a; Chen et al., 2013; Kang et al., 2016), suspended particulate matter (SPM) (Zheng et al., 2014; Net et al., 2015), landfills (He et al., 2015; Kalmykova et al., 2014), vegetables (Wang et al., 2015) and fish (Li et al., 2008). Therefore, PAEs are considered a class of toxic organic pollutants (TOPs) and endocrine disturbing compounds (EDCs) (Chang et al., 2007). To this end, the United States Environmental Protection Agency (USEPA) listed di-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP), dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and butyl benzyl phthalate (BBP) as priority pollutants (Keith and Telliard, 1979). In 2005, the European Parliament and the Council of

the Europe Union promulgated a decree to restrict the use of PAEs in toys and childcare articles (EU, 2005).

In a lake ecosystem, PAEs were transported via several pathways such as deposition and surface runoff, and they were partitioned between different media (Fausser et al., 2009). The partitioning biphasic include water-SPM, SPM-surface sediment, sediment-pore water, surface sediment-overlying water and overlying water-pore water (He et al., 2016a). The water-SPM partitioning of PAEs exerts an important impact on their migration and transformation in the lake ecosystem, and it is valuable for the risk assessment of PAEs in the particulate phase (Means, 1995; Dueri et al., 2008). However, current studies have mainly focused on the occurrence and risk assessment of PAEs (e.g., Zhu et al., 2018; Zhang et al., 2016a; Zheng et al., 2014; He et al., 2013), and only a few studies have measured the partitioning of PAEs (He et al., 2016b; Zeng et al., 2009).

Generally, organic matter and the octanol-water partitioning coefficient (K_{ow}) of PAEs both play a key role in the partition equilibrium constant (Zeng et al., 2009). Usually, the organic carbon normalized partitioning coefficient (K_{oc}) is computed to describe the partitioning of organic contaminants. However, the calculated K_{oc} values often exhibit a wide range of variation and differ from the K_{ow} values (Deng et al., 2006; He et al., 2016b), and the discussion regarding these phenomena has been deficient.

Lake Chaohu ($117^{\circ}17' - 117^{\circ}51' E$, $31^{\circ}25' - 31^{\circ}43' N$), the fifth largest shallow freshwater lake in China, is located in the middle of Anhui Province. It has vital ecosystem service functions such as flood storage, climate regulation and biodiversity maintenance (Wu et al., 2018). It is the most important water source for industry, agriculture and daily life in the cities and towns of its catchment, especially in Hefei City and Chaohu City (Yin et al., 2018). In addition, Lake Chaohu provides a great amount of ecological and economic values for its catchment (Zhang et al., 2016b). There are nine main inflowing rivers to Lake Chaohu and only one outflowing river connecting to the Yangtze River (Fig. 1). These rivers flow through the urban areas of Hefei City and Chaohu City, as well as the ambient farmland. With the rapid

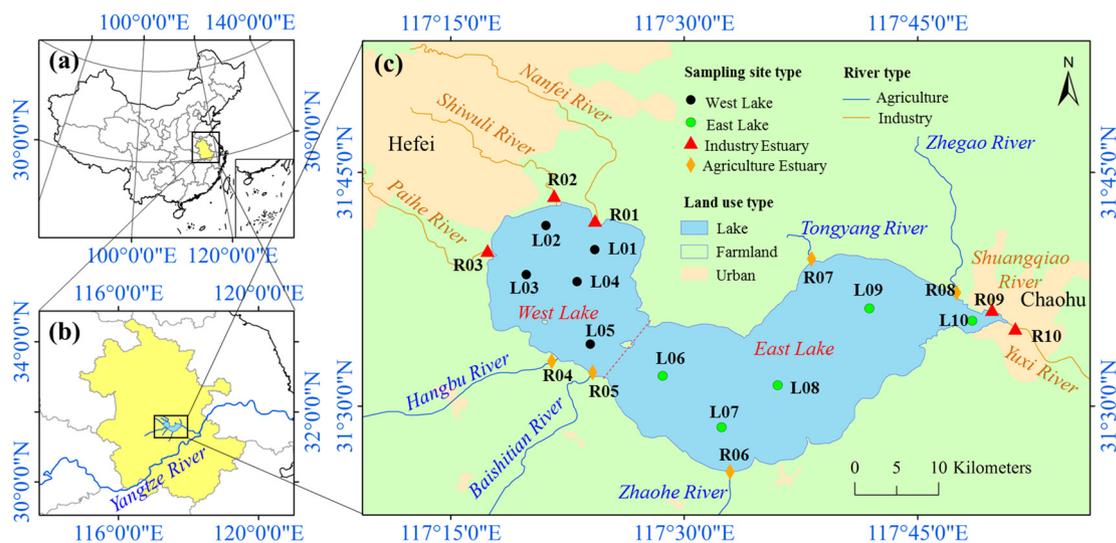


Fig. 1. Locations of (a) Anhui Province, (b) Lake Chaohu and (c) the sampling sites in the water-suspended particulate matter (SPM) system of Lake Chaohu.

socioeconomic development around Lake Chaohu, the gross level of PAEs in the input rivers from agricultural and industrial products has been increasing, resulting in serious PAE contamination in Lake Chaohu (Kang et al., 2016). The sustainable development of fisheries was affected and the safety of drinking water was threatened (He et al., 2016a). However, current studies mainly concerned with the occurrence and risk assessment of PAEs in Lake Chaohu (He et al., 2013, 2014, 2016b; Kang et al., 2016; Yang et al., 2009). To our knowledge, no studies have focused on the water-SPM partitioning of PAEs in Lake Chaohu. Hence, the objectives of this study are: (1) to investigate the seasonal occurrence and composition of PAEs in the water-SPM system of Lake Chaohu, (2) to ascertain the spatiotemporal variations of PAE partitioning in the water-SPM system, and (3) to analyze the impact factors for the spatiotemporal occurrence and partitioning of PAEs. This study is expected to reveal if the spatiotemporal occurrence, composition and partitioning of PAEs in the water-SPM system of natural large lake are different from those of urban lakes (Zeng et al., 2008, 2009; Zheng et al., 2014).

2. Materials and methods

2.1. Reagents and materials

High-performance liquid chromatography (HPLC) grade methanol, n-hexane (HEX), dichloromethane (DCM), and pesticide grade acetone (ACE) were all purchased from Thermo Fisher Scientific, Waltham, Massachusetts, USA. Anhydrous sodium sulfate, silica and alumina were all purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Anhydrous sodium sulfate was baked at 650 °C for 10 h before use. Silica and alumina were baked at 450 °C for 6 h, activated at 130 °C for 12 h and deactivated 3% by ultrapure water before use. Glass fiber filters (GFFs) wrapped with aluminum foil were baked at 450 °C for 6 h and were weighed before use. All glassware was cleaned in an ultrasonic cleaner (KQ-500B, Kunshan Ultrasonic Instrument, Jiangsu, China) and then dried at 450 °C for 6 h. C18 solid phase extraction (SPE) columns (ENVI-18, 6 mL, 500 mg) were purchased from Supelco Co., Bellefonte, Pennsylvania, USA.

Each compound in the PAE stock standard mixture, including five USEPA priority pollutants (DMP, DEP, DBP, BBP and DEHP) and one nonpriority pollutant (diisobutyl phthalate (DIBP)), had a 1000 $\mu\text{g}\cdot\text{mL}^{-1}$ concentration in hexane. 3,4,5,6-deuterated DEP and 3,4,5,6-deuterated DnOP were selected as internal standards (IS), and 3,4,5,6-deuterated DBP was selected as surrogate standard (SS). The PAE stock standard mixture, IS and SS were all purchased from AccuStandard Inc., New Haven, Connecticut, USA, and diluted to a working standard solution by HEX and ACE.

2.2. Sampling and pretreatment

Water and SPM samples were collected from 20 sampling sites per three months from August 2011 to Feb 2012. Samples in August 2011, November 2011 and February 2012 represented summer, autumn and winter samples, respectively. Among the 20 sampling sites, 10 sites (L01 to L10) were located inside the lake, and the other 10 sites (R01 to R10) were located in the estuaries (Fig. 1). The detailed information of the sampling sites was included in Table S1.

Water samples were collected by mixing water from different depths. The water depth for each sampling site during sampling periods was different. During August and November 2011, the water depth of all the sample sites was >1 m. During February 2012, the water depth of L01 to L10, R01, R03, R08 and R10 was >1 m, while the water depth of other sites was shallower than 1 m. For sampling sites with a depth >1 m, approximately 3.3 to 3.4 L of the surface water (0 to 0.15 m depth), intermediate water (0.5 to 0.65 m depth) and bottom water (0 to 0.15 m above sediment) were gathered, respectively. For sampling sites with a depth shallower than 1 m, 5 L of surface and bottom water

were gathered. Then, water samples from the different depths were mixed and stored in 10 L brown glass bottles. The bottles were sequentially cleaned by tap water, ultrapure water and sampling site water.

After intense shaking, a two-liter aliquot of each gathered water sample was filtered through a GFF using a filtration device equipped with a peristaltic pump (80EL005, Millipore Co., Massachusetts, USA) and a 142-mm diameter filter plate. The SPM was intercepted on the GFF. The GFFs were dried at room temperature in the field. After taking back to laboratory, they were stored in a desiccator for at least seven days before weighing. The dry weight of the SPM was obtained by the difference between the two weights. In the laboratory, 200 ng of SS was added to the GFF before Soxhlet extraction. Particulate PAEs were extracted with DCM for 48 h in the Soxhlet extractor. The extracts were concentrated into approximately 1 mL at 30 °C by a rotary evaporator (R-201, Shanghai Shen Sheng Technology Co., Ltd., Shanghai, China). 10 mL of HEX was added for solvent exchange. The solution was again concentrated into approximately 1 mL and then transferred to an anhydrous sodium sulfate-silica-alumina (1 cm, 12 cm and 6 cm from top to bottom respectively) chromatography column for clean-up. The initial eluates of 20 mL of HEX and 70 mL of a HEX:DCM (7:3) mixture were discarded. PAEs were eluted by 40 mL of a HEX:ACE (8:2) mixture. The eluate was concentrated into approximately 1 mL by rotary evaporation. 5 mL of HEX was added for solvent exchange, and the solution was again concentrated into approximately 1 mL. 200 ng of IS was added before transferring the solution to a 2 mL GC vial.

One liter of filtered water was collected in a precleaned brown glass bottle for dissolved PAE analysis. 200 ng of SS was added into the water before passing through the SPE column. The SPE column was activated by 12 mL of the HEX:DCM (1:1) mixture, 6 mL of methanol and 6 mL of ultrapure water. Then, the filtered water sample with SS was passed through a SPE column by negative pressure. After extraction, the SPE column was dried by vacuum pump, wrapped with aluminum foil, and stored in a desiccator before analysis. In the laboratory, 18 mL of the HEX:DCM (1:1) mixture (3 repetitions) was used to elute the target compounds. The eluate was dehydrated by passing through a 5 g anhydrous sodium sulfate column and then concentrated into approximately 1 mL by rotary evaporation. The processes of solvent exchange, concentration and bottling were all the same with those for SPM.

2.3. Sample analysis

The extracted PAEs were analyzed using an Agilent 6890 gas chromatograph (GC) coupled with a 5973 mass spectrometer detector (MSD) (Agilent Technologies Inc., California, USA). A DB-5MS capillary column (30 m \times 0.25 mm i.d. \times 0.25 μm , J&W Scientific, USA) was used. The analysis method was the same with our previous study (He et al., 2013). The instrument was operated in electron impact (EI) and selective ion monitoring (SIM) modes. The samples were injected by an Agilent 7683B automatic sampler. The inlet temperature was 280 °C, and the inlet volume was 1 μL in splitless mode with a venting time of 0.75 min. Helium (purity $\geq 99.999\%$) was applied as the carrier gas with a flow rate of 1.0 $\text{mL}\cdot\text{min}^{-1}$. The initial oven temperature was 60 °C for 2 min, which was ramped to 300 °C at a rate of 8 $^{\circ}\text{C}\cdot\text{min}^{-1}$, where it was maintained for 15 min. The temperature of the transfer line, ion source and quadrupole were 300 °C, 246 °C and 150 °C, respectively. The internal calibration method was employed for quantitation.

Particulate organic carbon (POC) was determined using the TOC-5000A equipped with an SSM-5000A solid sampler (Shimadzu, Japan). Water-filtered baked small GFFs were soaked in hydrochloric acid at a concentration of 0.01 $\text{mol}\cdot\text{L}^{-1}$ for 12 h to remove inorganic carbons. Then, the GFFs were washed to neutral and were freeze-dried. POC was obtained by firing at 900 °C in an SSM-5000A solid sampler.

2.4. Quality control and quality assurance (QC/QA)

For water and SPM samples, two to three parallel samples with procedural blanks were processed for each quarterly sampling site. The R-squared values of the linear calibration curves of each compound were all larger than 0.99. The SS was added to the samples to monitor the pre-treatment and analysis processes. The method recoveries for water and the SPM of the studied PAEs ranged from 74.3% to 102.1% and from 70.6% to 105.6%, respectively. The instrument detection limits (IDLs) ranged from 0.1 part per billion (ppb) to 0.5 ppb. Please see Table S2 for details regarding each compound.

2.5. Koc calculation

Usually, organic carbon normalized partitioning coefficients (Koc) are employed to describe the partitioning behavior of hydrophobic organic contaminants (HOCs) (Liu et al., 2013; Qin et al., 2014). The following equations were used to calculate the Koc values to describe the partitioning of PAEs in the water-SPM system of Lake Chaohu:

$$K_d = \frac{C_{SPM}}{C_{water}} \quad (1)$$

$$K_{oc} = \frac{K_d}{f_{POC}} \quad (2)$$

where C_{SPM} and C_{water} were the PAE contents in the SPM and in the water represented by $\mu\text{g}\cdot\text{g}^{-1}$ and $\mu\text{g}\cdot\text{L}^{-1}$, respectively. K_d was the distribution ratio calculated by the observed data in the unit of $\text{L}\cdot\text{g}^{-1}$. f_{POC} was the percentage of POC.

2.6. Statistical analysis

The skewness and kurtosis were used to describe the data distribution, and Shapiro-Wilk test were employed to test if the occurrence of PAEs is normally distributed. The significance level was set at $p = 0.05$ with the null hypothesis of normal distribution. The results of the skewness, kurtosis and the Shapiro-Wilk test are shown in Tables S3 to S5. According to Tables S3 to S5, approximately 33% to 50% of data were neither normally distributed nor lognormally distributed. Therefore, the occurrence of PAEs in the water-SPM system of Lake Chaohu were described by median and range, and a nonparametric method, Wilcoxon

test, was used to compare the spatiotemporal differences of PAEs. LogKoc values were presented as range, mean value and standard deviation (SD). The relationship between logKow and logKoc was fitted using loess method. All statistical analyses were performed using R software.

3. Results and discussion

3.1. The occurrence and temporal distribution of dissolved and particulate PAEs

The occurrence of the six PAEs in water and SPM from Lake Chaohu in summer, autumn and winter were shown in Table 1. According to Table 1, PAEs were detected in most of the samples analyzed. This indicated that PAEs were ubiquitous contaminants in Lake Chaohu. The concentrations of the Σ_6 PAEs in the dissolved and particulate phases ranged from 0.370 to 13.2 $\mu\text{g}\cdot\text{L}^{-1}$ and 14.4 to 7129 $\mu\text{g}\cdot\text{g}^{-1}$ with median values of 1.79 $\mu\text{g}\cdot\text{L}^{-1}$ and 147 $\mu\text{g}\cdot\text{g}^{-1}$, respectively. Temporally, the concentrations of Σ_6 PAEs in dissolved and particulate phases ranged from 1.54 to 13.2 $\mu\text{g}\cdot\text{L}^{-1}$, 1.28 to 5.39 $\mu\text{g}\cdot\text{L}^{-1}$, and 0.370 to 1.48 $\mu\text{g}\cdot\text{L}^{-1}$ and from 14.4 to 400 $\mu\text{g}\cdot\text{g}^{-1}$, 17.0 to 7129 $\mu\text{g}\cdot\text{g}^{-1}$, and 58.3 to 1500 $\mu\text{g}\cdot\text{g}^{-1}$, with median values of 2.52 $\mu\text{g}\cdot\text{L}^{-1}$, 2.12 $\mu\text{g}\cdot\text{L}^{-1}$, and 1.06 $\mu\text{g}\cdot\text{L}^{-1}$, and 103 $\mu\text{g}\cdot\text{g}^{-1}$, 101 $\mu\text{g}\cdot\text{g}^{-1}$, and 356 $\mu\text{g}\cdot\text{g}^{-1}$ in summer, autumn and winter, respectively.

The Σ_6 PAEs in water and SPM phases exhibited different seasonal trends. In SPM phase, all PAEs showed the same temporal distribution. The highest concentration of PAEs was observed in winter, and no temporal difference was found between summer and autumn. This result differed from the reports of urban lakes in Guangzhou (Zeng et al., 2009). Particulate PAEs in urban lakes were at the lowest concentration in winter, but their winter concentration in Lake Chaohu was the highest. In winter, due to the less precipitation, the water level of Lake Chaohu is low. Monsoons can greatly enhance the sediment resuspension process (Whipple et al., 2018; Bianucci et al., 2018). Therefore, the PAEs may be released to a greater extent from the sediment (He et al., 2016b; Kang et al., 2016) to the SPM, likely resulting in the high concentrations in the SPM.

In regard to the individual concentrations of the dissolved PAEs, DIBP and DBP exhibited the highest values in the summer, autumn and winter, which were followed by DMP and DEP. BBP and DEHP demonstrated the lowest occurrence level. Comparing with other studies, concentrations of dissolved DMP, BBP and DEHP in Lake Chaohu were

Table 1
The occurrence of dissolved and particulate PAEs in Lake Chaohu.

Media	Season	Statistics	PAEs					
			DMP	DEP	DIBP	DBP	BBP	DEHP
Water ($\mu\text{g}\cdot\text{L}^{-1}$)	Summer	Range	0.021–0.193	0.078–0.174	0.918–11.1	0.463–11.2	0.001–0.003	N.D. ^a –0.067
		Median ^b	0.044	0.122	1.35	0.680	0.002	0.016
		FOD ^c	100%	100%	100%	100%	100%	65%
	Autumn	Range	N.D.–0.111	0.024–0.160	0.832–2.64	0.426–3.65	0.001–0.011	N.D.–0.086
		Median	0.015	0.062	1.34	0.640	0.002	0.010
		FOD	70%	100%	100%	100%	100%	70%
	Winter	Range	0.006–0.099	0.010–0.102	0.210–1.08	0.098–0.465	0.001–0.004	0.002–0.217
		Median	0.027	0.025	0.643	0.276	0.002	0.032
		FOD	100%	100%	100%	100%	100%	100%
SPM ($\mu\text{g}\cdot\text{g}^{-1}$)	Summer	Range	0.627–13.4	0.599–12.08	7.94–225	3.26–108	N.D.–0.688	1.99–48.6
		Median	3.28	5.07	63.3	20.2	0.022	13.7
		FOD	100%	100%	100%	100%	85%	100%
	Autumn	Range	0.430–226	0.475–149	9.58–4383	4.86–1307	N.D.–4.69	1.69–1059
		Median	4.683	3.21	56.4	19.1	0.043	13.1
		FOD	100%	100%	100%	100%	75%	100%
	Winter	Range	12.8–434	3.22–55.9	25.5–548	10.6–285	N.D.–28.4	6.08–372
		Median	95.3	13.3	137	74.7	0.439	46.8
		FOD	100%	100%	100%	100%	79%	100%

^a N.D.: not detected.

^b Reported medians were calculated by removing N.D.

^c FOD: frequency of detection.

lower than those in lakes in Beijing on average, while other PAE congeners were opposite (Zheng et al., 2014); except for DBP and DEHP, the concentrations of other PAE congeners were higher than the results in the urban lakes of Guangzhou (Zeng et al., 2008, 2009). Temporally, PAEs with different hydrophobicity levels exhibited different temporal distributions in the dissolved phase (Fig. 2). PAEs with low hydrophobicity (LHB), DMP and DEP, were at the highest levels in summer with median values of 0.044 and $0.122 \mu\text{g}\cdot\text{L}^{-1}$, respectively. The concentration of DMP in autumn was significantly lower than that in winter, while DEP showed an opposite temporal distribution to DMP. For moderately hydrophobic (MHB) PAEs such as DIBP, DBP and BBP, and the highly hydrophobic (HHB) PAE, DEHP, there were no significant differences between the concentrations in summer and autumn. However, the concentrations of DIBP, DBP and BBP were lowest in winter, while the concentration of DEHP was highest in winter. Except for DEHP, temporal patterns of other PAE congeners were also observed in the urban lakes in Guangzhou (Zeng et al., 2009). The spatial variation of dissolved PAEs should be related to their input by runoff (He et al., 2013) and atmospheric deposition (Zeng et al., 2010), SPM adsorption (Chi and Kang, 2006), degradation (Jiang et al., 2018; Azarova et al., 2003), biotic uptake (Brown and Thompson, 1982a, 1982b) and variations of dissolved organic matter (DOM) (Ji et al., 2018; Mendoza and Zika, 2014; Goodman et al., 2011; Jaffe et al., 2008).

3.2. The spatial distribution of dissolved and particulate PAEs

The spatial distribution of individual PAEs was displayed in Fig. 3. For dissolved PAEs, the concentrations of DMP, BBP and DEHP in estuary were significantly higher than those in lake area ($p < 0.05$). However, the concentrations of DEP, DIBP and BBP did not significantly differ between estuary and lake area. For particulate PAEs, only BBP was not observed to have a significant spatial difference, the other five PAEs all posed a spatial distribution with a higher concentration in estuary ($p < 0.05$). This indicated that river inputs likely represent an important source of PAEs in Lake Chaohu.

The spatial distribution of PAEs in the water-SPM system of Lake Chaohu between the west and the east lake zones and between agricultural and industrial estuaries were tested. The only significant spatial difference observed was that the concentration of dissolved DMP in

the west lake was higher than that in the east lake ($p < 0.05$). There were no specific differences in PAEs between lake zones or river types of Lake Chaohu. This finding was probably due to the extensive usage range of PAEs. This result also illustrated that agriculture and industry may contribute similar PAE content.

3.3. The composition of dissolved and particulate PAEs

Of the six PAEs, DMP, DEP, DIBP and DBP, were detected in all of the dissolved and particulate phases during summer, autumn and winter (Table 1). BBP was detected in all of the dissolved water and was detected in up to 75% of the particulate phase in each season. DEHP was detected in up to 65% of the dissolved water and was detected in all of the particulate phases during each season.

The composition of the six PAE congeners in dissolved and particulate phases during summer, autumn and winter were presented in Fig. 4. It was obvious that DIBP and DBP were the most abundant species in dissolved phase, contributing a total fraction ranging from 80.6% to 98.0% ($92.8\% \pm 4.1\%$, mean \pm S.D.). DIBP was the most dominant PAE in dissolved phase during summer, autumn and winter with a fraction ranging from 13.1% to 91.6% ($58.7\% \pm 21.8\%$), 29.7% to 69.3% ($61.6\% \pm 8.7\%$) and 49.1% to 76.8% ($62.3\% \pm 5.4\%$), respectively. The next dominant PAE in dissolved phase was DBP. The DBP fraction ranged from 5.6% to 84.9% ($33.8\% \pm 9.0\%$), 26.8% to 67.7% ($34.9\% \pm 22.1\%$) and 19.8% to 31.5% ($27.0\% \pm 2.5\%$), respectively.

In particulate phase, the fractions of DEP and BBP were similar to those in dissolved phase with average values of approximately 4% and 0.1%, respectively. The fraction of DMP in particulate phase was significantly larger than that in dissolved phase, especially in winter ($22.4\% \pm 6.7\%$, mean \pm S.D.). DIBP remained the dominant PAE with fractions ranging from 52.2% to 65.4% ($58.2\% \pm 5.4\%$), 41.8% to 67.8% ($57.3\% \pm 3.6\%$) and 26.8% to 48.6% ($38.5\% \pm 5.6\%$) during summer, autumn and winter, respectively. DBP was also the second dominant PAE in particulate phase, with fractions ranging from 17.0% to 28.9% ($21.2\% \pm 4.1\%$), 14.4% to 29.6% ($21.1\% \pm 2.6\%$) and 13.2% to 25.0% ($18.4\% \pm 2.9\%$). In a completely different finding from dissolved DEHP, particulate DEHP was the third abundant PAE. In particulate phase, the fractions of DEHP ranged from 7.0% to 19.0% ($13.1\% \pm 6.5\%$), 5.1% to 36.9% ($13.2\% \pm 3.4\%$) and 7.0% to 38.4% ($16.3\% \pm 7.7\%$). An increased fraction of

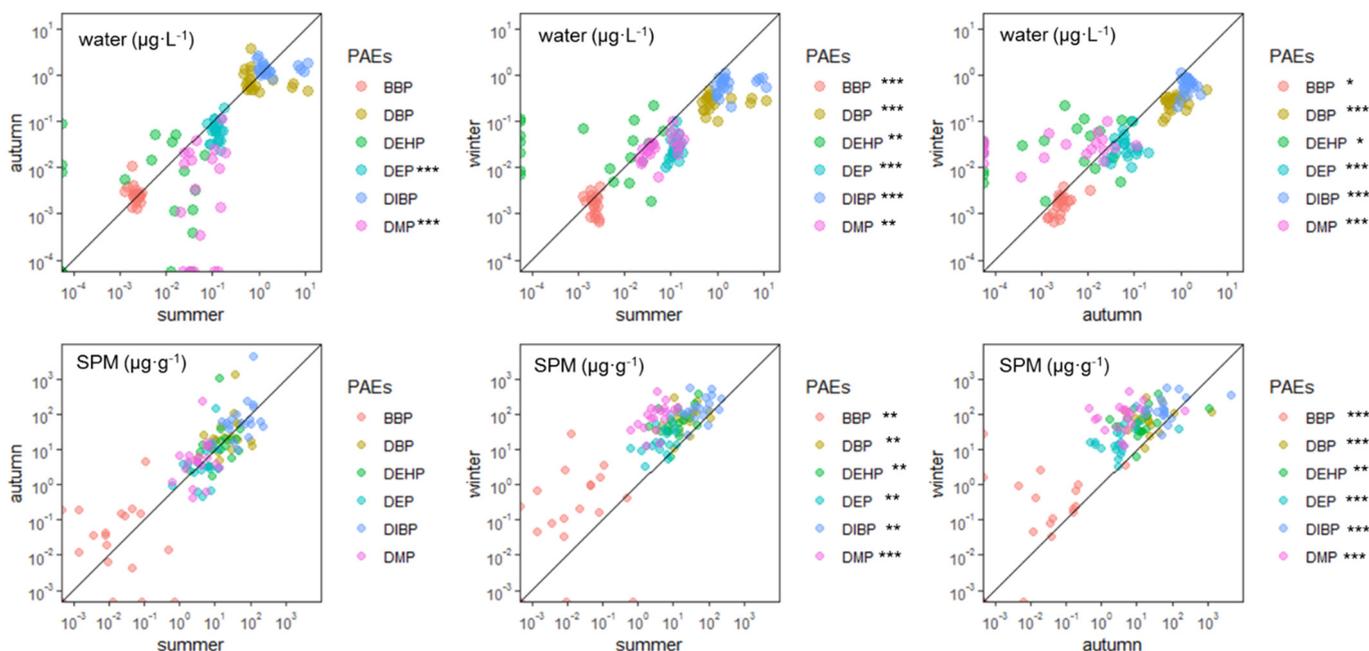


Fig. 2. Comparison of the PAE occurrences across different seasons. * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$; method: paired Wilcoxon test (two-tailed), the PAE occurrences on the same sampling site in binary seasons were paired for comparison.

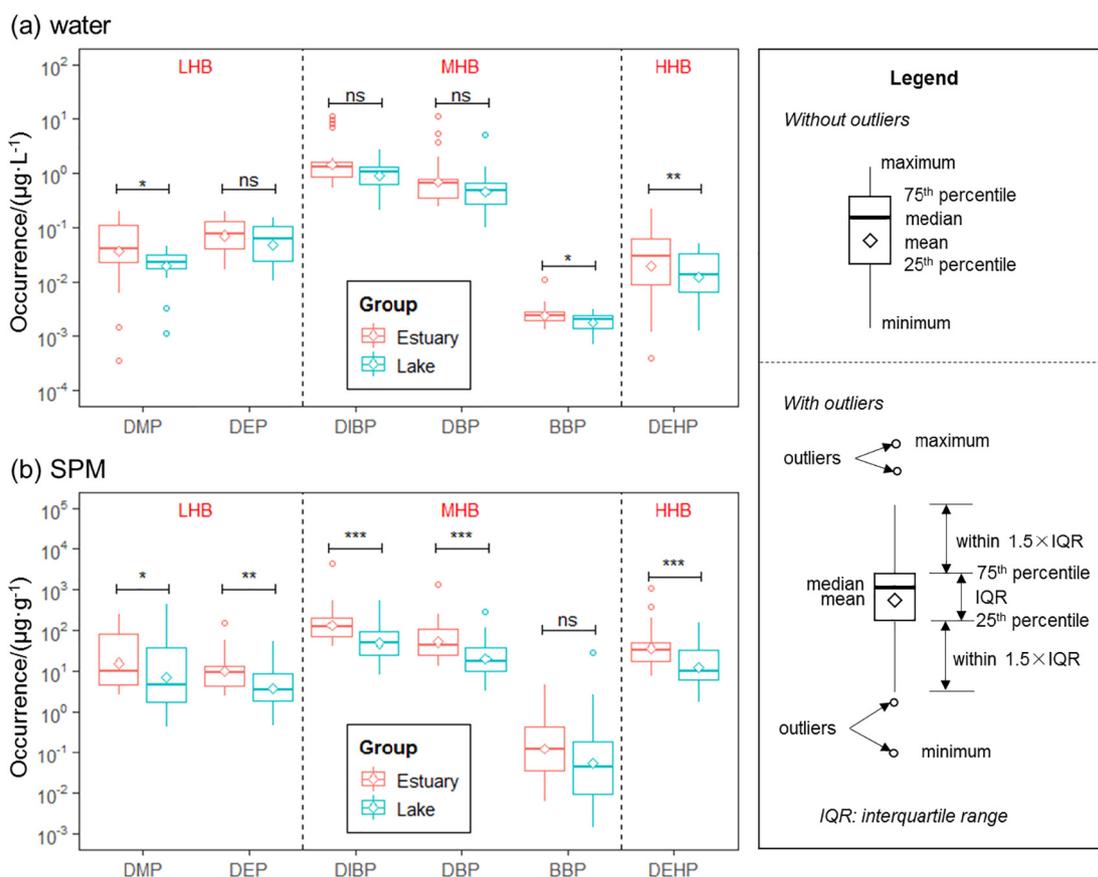


Fig. 3. The spatial distribution of PAEs in the water-suspended particulate matter (SPM) system of Lake Chaohu. * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, ns: no significance, method: Wilcoxon test (two-tailed), the occurrences of PAE congeners in estuary and lake area were compared. LHB: low hydrophobic, MHB: moderate hydrophobic, HHB: high hydrophobic.

DEHP in winter was observed for both dissolved and particulate phases as a consequence of sediment resuspension due to its high hydrophobicity (Gao and Wen, 2016) and high residual levels in the sediment (Kang et al., 2016) combined with favorable hydrological conditions (low water level and strong northwest monsoon).

Although DEHP and DBP were the most consumed PAEs in China (CPCIA, 2009), our results and previous studies (He et al., 2013; Kang et al., 2016) showed that DEHP was not the most abundant of PAE congeners in Lake Chaohu. The fraction of DEHP in Lake Chaohu was lower than that in Lake Luoma (Xu et al., 2017a) and the urban lakes in Guangzhou (Zeng et al., 2009) and Beijing (Zheng et al., 2014). The low environmental occurrence of DEHP is likely related to its limited transport capacity due to its high octanol/water distribution coefficient (Kow) (Gao and Wen, 2016). Obviously, DIBP and DBP were reported as the most abundant PAEs in Lake Chaohu. DBP has been listed among the priority pollutants, and its use has been limited worldwide in locations such as the USA (Keith and Telliard, 1979), Europe (EU, 2005) and Canada (Statutes of Canada, 2010), but DIBP has not been limited strictly by laws or received much attention in literatures. Notably, DIBP was detected in high levels in environmental residues not only in Lake Chaohu but also in other aquatic systems (Zeng et al., 2009; Paluselli et al., 2018; Zhang et al., 2018), and DIBP was also demonstrated to exert hormonal effects similar to DBP (Borch et al., 2007). Therefore, DIBP represents a potentially hazardous material in the environment. Recently, the United States Consumer Product Safety Commission (CPSC) issued a revised rule to limit the content of DIBP in infant products (CPSC, 2017). In China, only three PAEs, DMP, DBP and DnOP, were listed on the “black list of China’s priority pollutants in water” (Zhou et al., 1991). Presently, there is no national standard limiting PAEs. Considering the high residual levels and potent toxicity of PAEs, there exists an urgent need to establish a national standard for

the environmental limitation on PAE values, especially for the high-residue PAE congeners.

3.4. The partitioning of PAEs in the water-SPM system of Lake Chaohu

The concentrations of dissolved and particulate PAEs during summer, autumn and winter were used to calculate the Koc values in the water-SPM system. The statistical characteristics of logKoc values were presented in Table 2, and their relationships with the logKow values were shown in Fig. 5.

The logKoc values for DMP, DEP, DIBP, DBP, BBP and DEHP ranged from 1.29 to 5.75 $L \cdot g^{-1}$ ($3.32 \pm 0.84 L \cdot g^{-1}$, mean \pm S.D.), 0.85 to 4.55 $L \cdot g^{-1}$ ($2.79 \pm 0.61 L \cdot g^{-1}$), 1.15 to 4.65 $L \cdot g^{-1}$ ($2.63 \pm 0.52 L \cdot g^{-1}$), 1.19 to 4.52 $L \cdot g^{-1}$ ($2.53 \pm 0.59 L \cdot g^{-1}$), 0.78 to 4.73 $L \cdot g^{-1}$ ($2.38 \pm 0.86 L \cdot g^{-1}$) and 3.08 to 5.39 $L \cdot g^{-1}$ ($3.98 \pm 0.66 L \cdot g^{-1}$), respectively, and there existed approximately 2 to 3 unit variations in logKoc for individual PAEs. Temporally, logKoc for LHB and MHB PAEs in winter were observed at the highest values, while logKoc for DEHP demonstrated the opposite. LogKoc values for individual PAEs were similar in summer and autumn (Table 2). The spatiotemporal variations of logKoc values for PAEs were probably related to the kinetic process and the partitioning mechanism of PAEs.

Generally, the partitioning of HOCs in the environment was not considered to be at equilibrium (Qin et al., 2014; Liu et al., 2013). However, Chi and Kang (2006) demonstrated that the adsorption of DBP and DEHP attained the partitioning equilibrium in just 2 h under precise control and experienced continuous shaking. In aquatic environments such as Lake Chaohu, the adsorption process was influenced by various factors, such as the degradation, biological uptake, allogenic input, and internal release of PAEs, as well as hydrodynamic variations. It was

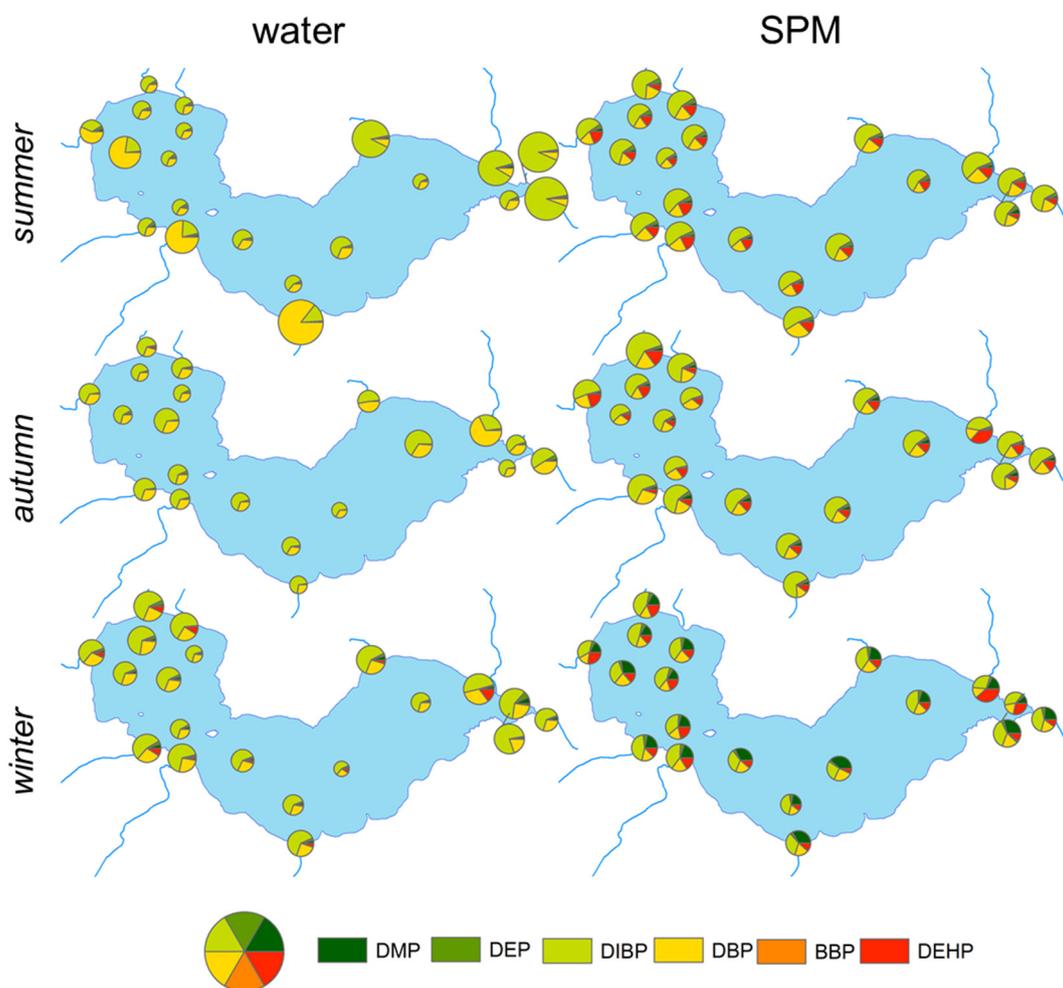


Fig. 4. Spatiotemporal composition of PAEs in the water-SPM system of Lake Chaohu. Pie size refers to the occurrence of Σ_6 PAEs for water and the occurrence of $\log_{10} \Sigma_6$ PAEs for SPM.

difficult to ensure whether the partitioning of PAEs was in, near or distant from equilibrium.

For the Koc model, it was assumed that the partitioning was only related to the particulate organic matter (POM). In actuality, the partitioning equilibrium coefficient is governed by the affinity to the effective fraction of organic matter (Tao et al., 1999). However, it was difficult to quantify the content of the fraction by the adsorptive effect alone due to the extremely complex structure and constitution of organic materials and the various character of HOCs. Therefore, employing the content of POC to substitute for the effective fraction resulted in a bias in the calculated values. In addition, the partitioning equilibrium coefficient is also related to the natural colloids such as dissolved organic matter (DOM) and black carbon (Zeng et al., 2009; Liu et al., 2013), which is not considered by the Koc model.

As shown in Fig. 5, no linear relationship was observed between $\log K_{oc}$ and $\log K_{ow}$ for PAEs. The HHB congener, DEHP, had the highest $\log K_{oc}$ values, followed by LHB congeners and MHB congeners with the lowest $\log K_{oc}$ values. Our results were far from other results regarding PAE levels in the urban lakes of Guangzhou (Zeng et al., 2009) and the seawater of False Creek Harbor (Mackintosh et al., 2006), and they were inconsistent with other hydrophobic organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl esters (PBDEs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) (Qin et al., 2014; Mackintosh et al., 2006; Streets et al., 2006; Liu et al., 2008b). However, the linear relationship was also not observed for organochlorine pesticides (OCPs) in Lake Chaohu (Liu et al., 2013). It seemed that the hydrophobicity of PAEs and OCPs may have little impact on their partitioning

Table 2

The organic carbon normalized water-SPM partitioning coefficients ($\log K_{oc}$) of PAEs in Lake Chaohu (unit: $L \cdot g^{-1}$).

Season	Statistics	DMP	DEP	DIBP	DBP	BBP	DEHP
Summer	Range	2.33–3.30	1.90–3.16	1.81–3.04	1.39–3.17	0.91–3.54	3.20–5.24
	Mean \pm S.D. ^a	2.80 \pm 0.30	2.60 \pm 0.28	2.50 \pm 0.36	2.35 \pm 0.42	2.09 \pm 0.67	4.00 \pm 0.53
	N ^b	20	20	20	20	17	13
Autumn	Range	1.29–5.75	0.85–4.55	1.15–4.65	1.19–4.52	0.78–4.33	3.08–5.39
	Mean \pm S.D.	3.35 \pm 1.22	2.58 \pm 0.83	2.56 \pm 0.75	2.38 \pm 0.78	2.19 \pm 0.87	4.28 \pm 0.86
	N	12	18	18	18	13	13
Winter	Range	2.89–4.80	2.44–3.85	2.49–3.21	2.47–3.48	1.56–4.73	3.18–4.98
	Mean \pm S.D.	3.91 \pm 0.45	3.23 \pm 0.35	2.86 \pm 0.24	2.90 \pm 0.31	2.91 \pm 0.82	3.75 \pm 0.44
	N	17	17	17	17	14	17

^a S.D.: standard deviation, Mean \pm S.D. reflected the discrete degree of samples.

^b N: the number of samples.

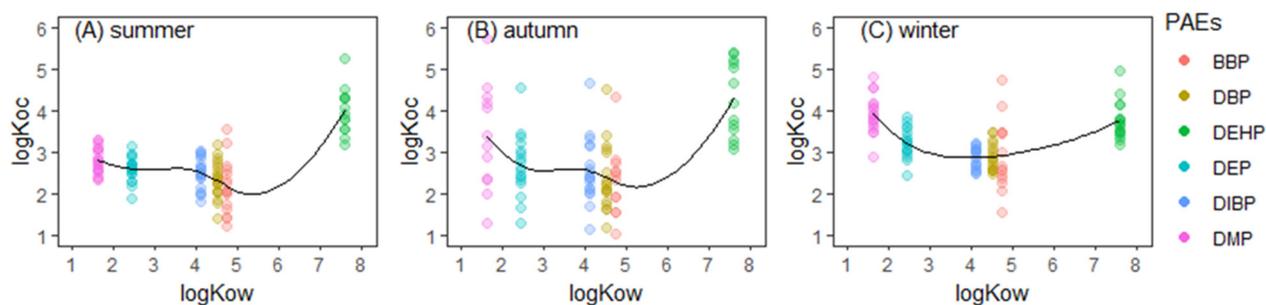


Fig. 5. Relationship between logKow and logKoc for PAEs in the water-SPM system of Lake Chaohu in (A) summer, (B) autumn and (C) winter. Black line: trend line of logKow and logKoc, smooth method: loess.

in the complex environmental system. According to the definition of K_{ow} , only the relative solubility of chemicals in water and octanol is considered to affect equilibrium. However, octanol is quite simple as a substitute for the solid phase in realistic environments. Moreover, PAHs, PCBs, PBDEs and PCDD/Fs share similar molecular structure characteristics that differ from those of PAEs and OCPs. The molecular structures of PAEs are more flexible than those of PAH-like compounds due to the carbon-carbon sigma bonds of the alkane chain. The existence of ester groups makes the phthalate fraction more hydrophilic, especially for the PAEs containing a short alkane chain (Gao and Wen, 2016). Therefore, PAEs possibly experience different partitioning behaviors than PAH-like compounds, and it is not surprising that no linear relationship was found between logKoc and logKow for PAEs. The Koc model used the POC content to normalize the K_d value and obtain the Koc value. Therefore, since Lake Chaohu is a typical eutrophic lake in China, the difference in results between Lake Chaohu and other studied areas was probably due to variations between the structure and constitution of POM (Xu et al., 2017b). However, current studies lacked the analysis of POM. To better explain the observed differences, the structure and constitution of POM should be further studied in the future.

4. Conclusion

PAEs were ubiquitous contaminants in Lake Chaohu. The Σ_6 PAEs in the water and SPM phases exhibited different seasonal trends. PAEs with different hydrophobicity levels displayed different temporal distributions in dissolved phase. In particulate phase, all PAEs exhibited the same temporal distribution. Significant spatial differences in PAEs are seen in the lake and estuary, but there were no specific differences between lake zones and river types for PAEs in Lake Chaohu. River input likely represents an important source of PAEs in Lake Chaohu. DIBP and DBP were the most abundant PAEs in Lake Chaohu, and DIBP should generate increased attention in the future. The logKoc markedly varied for individual PAEs, and approximately 2 to 3 unit variations of logKoc existed for individual PAEs. It was difficult to ensure whether the partitioning of PAEs was in, near or distant from equilibrium. No linear relationship was found between logKoc and logKow for PAEs. Koc might not be suitable for describing the partitioning of PAEs in the water-SPM system. The hydrophobicity of PAEs may have little impact on their partitioning in the complex environmental system, and the Kow model may be inappropriate to predict the partitioning of PAEs in natural large lakes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.01.161>.

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