Occurrence and spatio-seasonal distribution of organophosphate tri- and di-esters in surface water from Dongting Lake and their potential biological risk☆

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ABSTRACT

In this study, 24 surface water samples were collected from Dongting Lake, China, in the wet and dry seasons, then the concentrations, composition profiles and spatio-seasonal variations of nine organophosphate triesters (OPEs) and five organophosphate diesters (Di-OPs) were determined. Significantly higher total OPE concentrations ($\sum$OPEs) were observed in the wet season (49.5−148 ng L^{-1}) than in the dry season (5.00−45.7 ng L^{-1}) suggesting higher input via tributaries discharge as well as wet deposition in the studied region. Whereas lower levels of TnBP and (triphenyl phosphate (TPHP) in wet season reflected their possible degradation under solar irradiation. Comparable levels of total Di-OPs ($\sum$Di-OPs) were found in the wet season (3.41−13.9 ng L^{-1}) and dry season (1.01−12.3 ng L^{-1}). Tri(2-chloroethyl) phosphate and tris(2-chloroisopropyl) phosphate were the main OPE components, while diphenyl phosphate, di-n-butyl phosphate and bis(1,3-dichloro-2-propyl) phosphate were the main Di-OP components. High levels of OPEs and Di-OPs were found in Datong Lake suggesting possible local emissions potentially related to fishery activity in the land-locked lake. Samples at river mouths to the lake also have higher levels of target OPEs and Di-OPs, the results disclosed obvious discharges from tributaries in Hunan Province. Negligible non-carcinogenic and carcinogenic risks were determined based on the measured concentrations in source waters. A limited ecological risk aquatic organisms in the Dongting Lake was identified, with most risk from TPHP.

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1. Introduction

Organophosphate triesters (OPEs) are widely used as flame retardants and plasticizers in many products, such as electronic devices, textiles, plastic materials, and emulsion paint, due to their excellent flame retardancy and flexibility (van der Veen and de Boer 2012; Wang et al., 2020), or as industrial additives in hydraulic oil and lubricants (Hou et al., 2016). Organophosphate triesters have also been used as substitutes for polybrominated diphenyl ethers (PBDEs) after the use of PBDEs was restricted or banned, which has resulted in a substantial increase in OPE production and consumption. For example, the global consumption of OPEs was about 102,000 tons in 1992 and 680,000 tons in 2015 (Wei et al., 2015). Organophosphate triesters are typically mixed into various materials during production, and consequently they are likely to be released to the surrounding environment via volatilization, diffusion, and abrasion over their life cycle, including the manufacturing, usage, and recycling stages (Wei et al., 2015; Xu et al., 2019). It has been reported that OPEs are ubiquitous in the

environment, including both the indoor and outdoor environments (Hu et al., 2020; Wang et al., 2020; Zhang et al., 2020), surface water (Shi et al., 2020; Zhong et al., 2020), drinking water (Ding et al., 2015; Choo and Oh 2020), and the marine environment (Zeng et al., 2020; Zhong et al., 2020). Discharges from domestic sewage and industrial wastewater have played an important role in the entry of OPEs into the aquatic environment (Xu et al., 2019; Wang et al., 2020).

In contrast to the many studies of OPEs in the environment and biota samples, there has been a limited focus on organophosphate diesters (Di-OPs), with most studies considering their presence in biological samples and human urine (Hou et al., 2016; Wang et al., 2020). Organophosphate diesters are commonly considered to be metabolites of OPEs in the human body (Hou et al., 2016). In recent years, several studies have reported the co-occurrence of OPEs and Di-OPs in indoor and outdoor environments (Tan et al., 2019; Hu et al., 2020; Wang et al., 2020), and sludge samples (Gao et al., 2016; Fu et al., 2017), suggesting their possible ubiquity in the environment. However, little information is available about Di-OPs in aquatic systems.

Dongting Lake, located in the middle reaches of the Yangtze River, is the second largest freshwater lake in China receiving large inflows from tributaries in Hunan Province, including the Yuanjiang, Zishui, Xiangjiang, and Lishui rivers, as well as a portion of the surface water from the Yangtze River (Zhang et al., 2020). Domestic and industrial wastewater is also discharged indirectly/directly into Dongting Lake via these tributaries (Lin et al., 2018). Dongting Lake also acts as source water for the inhabitants of the densely populated cities surrounding the lake, such as Yueyang City, Changde City, and Yiyang City, and consequently, there is great concern about water pollution in the lake. In our previous study, the

occurrence of antibiotics and potential ecosystem risks were identified (Zhang et al., 2020). To the best of our knowledge, little is known about the possible presence of OPEs and Di-OPs in Dongting Lake.

In this study, nine OPEs and five Di-OPs were selected as target compounds. The main objectives of this study were to: 1) investigate the occurrence and spatio-seasonal distribution of OPEs and Di-OPs in Dongting Lake; 2) trace their possible sources; and 3) evaluate the potential ecological and human risks presented by OPE exposure via drinking water ingestion.

2. Materials and methods

2.1. Chemicals and materials

Nine OPEs and five Di-OPs were selected as target analytes. Detailed information about these chemicals as well as their respective manufacturers are presented in Table S1 (Supporting Information). Detailed information about surrogates (d_{15}-TEP, d_{27}-TBP, d_{15}-TPHP, d_{12}-TCEP, d_{12}-BCIPP, and d_{10}-DPhP), internal standard (hexamethylbenzene, HMB), and solvents were provided in Supporting Information.

2.2. Sample collection and pretreatment

Nine surface water samples were collected at the inlets of the main tributaries and Dongting Lake Hydrological Observation Stations in November 2017 (dry season), while 15 surface water samples were obtained in July 2018 with 6 additional sampling location in wet season. The sampling sites are shown in Fig. 1. A description of the sampling protocol has been published in our
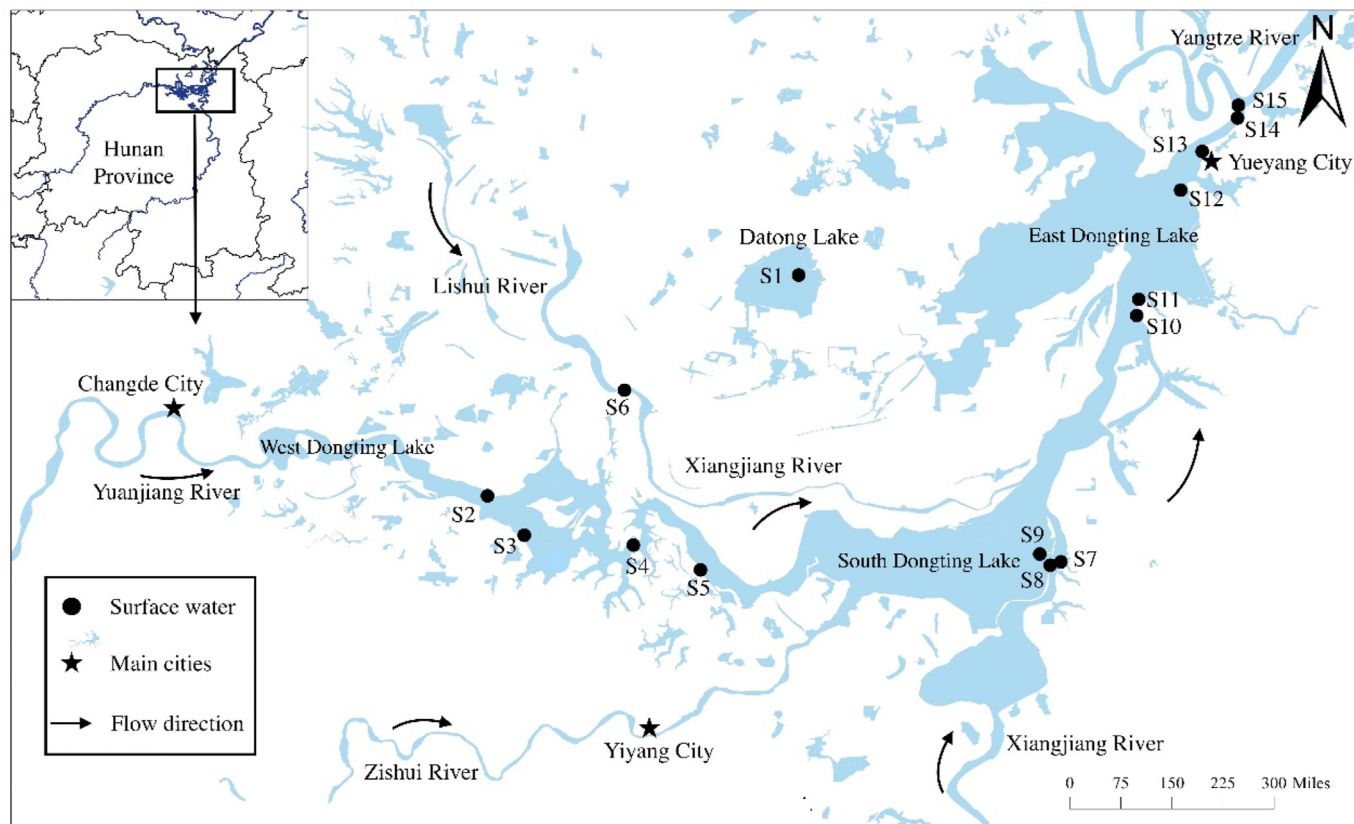

Fig. 1. Maps of the sampling sites in Dongting Lake, China.

previous work (Zhang et al., 2020), and provided in Supporting Information in the present study. Details about sampling location could be found in Table S2. At each sampling site 1 L of surface water was collected in pre-cleaned amber bottles and then transported immediately to the laboratory in an ice bath. All water samples were filtered through glass fiber filters (GF/Fs). The resultant aqueous samples were stored at 4 °C and treated within 48 h for the extraction and enrichment of target OPEs and Di-OPs by solid phase extraction (SPE). A detailed description is provided in the Supporting Information.

2.3. Instrumental analysis

Identification and determination of OPEs was conducted with GC-MS (QP 2010; Shimadzu Corp., Kyoto, Japan) in electron ionization (EI) mode equipped with a TG-5ms column (30 m × 0.25 mm inner diameter × 0.25 μm film; Thermo Fisher Scientific, Inc., Waltham, MA, USA). Helium was used as the carrier gas at a flow rate of 1 mL min^{-1}. The identification and determination of Di-OPs was conducted using LC-MS/MS (Agilent Technologies, Santa Clara, CA, USA) equipped with an Eclipse Plus C-18 column (250 mm × 4.6 mm × 5 μm, Agilent Technologies) in negative mode. Water (containing 0.1% formic acid) and methanol were used as mobile phases at a flow rate of 400 μL min^{-1}. The detailed instrumental parameters have been published previously (Hu et al., 2020) and are also provided in the Supporting Information. The limits of detection (LODs) for target OPEs, calculated as the standard deviation of seven repeat injections with a low concentration differentiated from the background, were in the range of 0.894–2.32 ng L^{-1}, while the LODs of Di-OPs were in the range of 0.0348–0.214 ng L^{-1}, with a signal/noise ratio of 3. In the present study, those compounds were defined as < LOD which were found at lower levels than LOD or not detected during instrumental analysis.

2.4. Quality control and quality assurance

Strict quality control and quality assurance protocols were adopted during the analytical procedure for all target compounds. Specifically, procedural blanks ($n = 3$), spiked blanks ($n = 3$, analytes spiked into solvents), and spiked matrix ($n = 3$, analytes spiked into real water samples) were analyzed as real water samples in every batch of samples. Four OPEs (TCEP, TCIPP, TBOEP, and TPHP) were detected at trace amounts (<LOD) in the blank samples, while no Di-OPs was found in any of the blank samples. Surrogates (four deuterated OPEs and two deuterated Di-OPs) were added in all samples. The recovery of d$_{15}$-TEP (28.0 ± 43.4%) was very low due to its high volatility (Please refer TEP in Table S1), consequently TEP concentrations were not reported in the present study. Acceptable recovery rates were achieved from all samples for d$_{27}$-TBP, d$_{12}$-TCEP, d$_{15}$-TPHP, d$_{12}$-BCIPP, and d$_{10}$-DPhP at 78.2 ± 10.7%, 81.6 ± 10.4%, 81.1 ± 6.58%, 62.3 ± 5.34% and 90.7 ± 6.52%, respectively. Recoveries of target compounds and surrogates from spiked blanks and spiked matrix were provided in Table S3 in Supporting Information. In the present study, all the reported values were background-subtracted for those chemicals present in the blanks, but were not corrected with recoveries.

2.5. Statistical analysis

Statistical analyses were carried out using SPSS 20 software packages, only for those target compounds showing detected frequency (DFs) higher than 50%, the results < LOD during instrumental analysis were treated as zero, while the calculated values below LODs were replaced by 1/2 LODs (Marchiandi et al., 2021).

Pearson's correlation analysis was carried out to examine the relationship between Di-OP and their respective parent OPE, and a one-way analysis was performed to determine the statistically significant differences of target chemicals between dry season and wet season. A statistical significance was reported when p < 0.05.

2.6. Ecological risk assessment and health risk assessment

We conducted a potential ecological risk assessment according to a published reference, and classified risk quotients (RQs) into three groups: limited risk with RQ < 0.1, medium risk with 0.1< RQ < 1, and high risk with RQ > 1 (Niu et al., 2019).

In the present study, only S13 was adjacent to the source water in the lake. We roughly assessed the potential human health risk (Ding et al., 2015) using measured OPE concentrations at this location. Due to a lack of toxicity data, no assessment was possible for Di-OPs. The daily intake (DI) of OPEs via drinking water was calculated using the following equation (1):

$$DI = (C \times IR \times AP) / BW \tag{1}$$

where C is the concentration of each OPE in water (ng L^{-1}); IR is the ingestion rate of water (L day^{-1}), which was 0.78 and 2 L for children and adults, respectively; BW is body weight, which was assumed to be 24 and 70 kg for children and adults, respectively; and AP is the percentage absorption, which was assumed to be 100%. The non-carcinogenic risk (Ding et al., 2015) and carcinogenic risk (Li et al., 2018) were characterized respectively. The non-carcinogenic risk was calculated as follows:

$$HQ = DI / RfD \tag{2}$$

where RfD is the reference dose recommended by Li et al. (2018). The non-carcinogenic risk was considered to be limited when HQ < 1, while there was a potential risk when HQ > 1.

The carcinogenic risk (CR) was assessed using equation (3):

$$CR = DI \times SFO \tag{3}$$

where SFO is the oral carcinogenic slope factor (ng kg^{-1}bw day^{-1}) for each OPE (Li et al., 2018). It was considered to be negligible when the CR was lower than 10^{-6}, while there was a potential carcinogenic risk when CR > 10^{-6} and a high carcinogenic risk when CR > 10^{-4}.

3. Results and discussion

3.1. Concentrations and composition profiles of OPEs in surface water

In this study, TPrP was not detected in any of the water samples, while TEP was detected in seven samples in dry season but only in S10 in the wet season. It was generally not reported due to its high volatility (Table S1), as indicated by the poor recoveries of d$_{15}$-TEP. The concentrations of the other seven OPEs are summarized in Table 1, with detailed information given in Table S4. The total concentration of all seven OPEs ($\sum$OPEs) from all 24 surface water samples were in the range of 5.00–148 ng L^{-1}, with an average value of 59.4 ng L^{-1}. Generally, TCEP and TCIPP were found in all samples in the range of 2.26–44.5 ng L^{-1} (average value of 22.7 ng L^{-1}) and 1.64–106 ng L^{-1} (average value of 29.0 ng L^{-1}), and were identified as the main components. Low TPHP concentrations were found in most samples, with the exception of S1 (27.8 ng L^{-1}) in the dry season. It was noted that TBOEP and TMPP were seldom detected in these samples, with values close to or lower than the

Table 1
Summarized concentrations and distribution of OPEs in dry and wet season (ng L^{-1}).

Compounds	Dry season				Wet season			
	Min	Max	Average	DFs (%)	Min	Max	Average	DFs (%)
TnBP	1.04	2.56	1.87	100	<LOD	23.4	12.5	26.7
TBOEP	<LOD	<LOD	/	0	<LOD	<LOD	/	0
TCEP	2.26	12.6	7.89	100	16.7	44.5	31.6	100
TCIPP	1.64	6.05	6.00	100	27.3	106	43.8	100
TDCIPP	<LOD	0.871	0.590	22.2	<LOD	6.59	3.46	86.7
TPHP	<LOD	27.8	11.0	88.9	0.830	4.01	1.52	100
TMPP	<LOD	<LOD	/	0	<LOD	0.759	0.475	26.7

LOD: limit of detection; /: not calculated; DFs: detected frequency.
Min: minimum concentration; Max: maximum concentration.

LOD, which might be due to these compounds having fewer applications and a higher hydrophobicity (van der Veen and de Boer 2012). TnBP was found in nine samples in the dry season and four out of 15 samples in the wet season.

The composition profiles of OPEs in the dry and wet seasons are shown in Fig. 2. TBOEP and TMPP were excluded from the figure due to their low DFs and occasional presence at trace levels in these samples. It was notable that TPHP was the main component only in S1 in the dry season, accounting for about 60.9% of total OPEs. Its possible emission sources are discussed in Section 3.2. Fig. 2 clearly shows that TCEP and TCIPP were the main components accounting for 58.5–98.8% of the total OPEs in both sampling campaigns, with the exception of S1. A similar composition profile has been found in other surface waters in China, such as the Pearl River (Shi et al., 2020), Haihe River (Niu et al., 2019), tributaries draining to the Bohai Sea (Wang et al., 2015), and urban streams in Beijing (Gao et al., 2015), as well as in the Ruhr River in Germany (Andresen and Bester 2006), River Aire in the UK (Cristale et al., 2013), and Sydney in Australia (Teo et al., 2015). The TCEP (2.26–44.5 ng L^{-1}) and TCIPP (1.64–106 ng L^{-1}) concentrations in this study were similar to most of the published data mentioned above; however, they were lower than the concentrations reported in areas that have been heavily affected by anthropogenic activities. For example, high TCEP (694 ng L^{-1}) and TCIPP (840 ng L^{-1}) concentrations were found in urban streams in Beijing (Gao et al., 2015), and the River Aire (TCEP at 119–316 ng L^{-1} and TCIPP at 113–26050 ng L^{-1}) (Cristale et al., 2013). TCEP and TCIPP are important additive flame retardants used in versatile products such as PVC, polyurethane foam (PUF), textile, etc., and likely being leased from those OPE-containing products resulting in their ubiquity in the environment (van der Veen and de Boer. 2012; Wei et al., 2015). The results demonstrated that anthropogenic activities posed obvious effect to global environment.

3.2. Spatio-seasonal variation of OPEs in Dongting Lake and their possible emission sources

There was an obvious seasonal variation of the $\sum$OPE concentration in surface water in Dongting Lake, as indicated in Figure S1. In the cities surrounding Dongting Lake, there is much more precipitation in the wet season (115.7–159.3 mm) than in the dry season (52.9–67 mm), which might result in the dilution of organic pollutants in the lake (Zhang et al., 2020). However, the opposite results were obtained in our study. The $\sum$OPE concentration in the wet season (49.5–148 ng L^{-1}, average value of 83.4 ng L^{-1}) was about one order of magnitude higher than in the dry season (5.00–45.7 ng L^{-1}, average value of 19.4 ng L^{-1}). It was also found that the significant variation between the dry and wet seasons could be mainly ascribed to the very different contributions from TCEP and TCIPP. TCEP concentrations (16.7–44.5 ng L^{-1}, average 31.6 ng L^{-1}) in the wet season were considerably higher (p < 0.001) than those in the dry season (2.26–12.6 ng L^{-1}, average of 7.89 ng L^{-1}). Similarly, considerably higher levels of TCIPP were detected (27.3–106 ng L^{-1}, average of 43.8 ng L^{-1}) in the wet season than in the dry season (1.64–6.00 ng L^{-1}, average of 4.26 ng L^{-1}) (p < 0.001), while there was no obvious seasonal variation in the concentrations of the other OPEs.

In nine locations (S1–5, S11–13, and S15) in both sampling campaigns, the $\sum$OPE concentration in the wet season (49.5–108 ng L^{-1}, average 71.1 ng L^{-1}) was about one order of magnitude higher than in the corresponding samples in the dry season (5.65–49.5 ng L^{-1}, average 20.8 ng L^{-1}). In the wet season, six additional sampling sites were added at river mouths and an unidentified drain-outlet, including S6–9 in South Dongting Lake, and S10 and S14 in East Dongting Lake. Much higher $\sum$OPE concentrations (71.1–148 ng L^{-1}) were found in these sampling sites. These results indicated that large amounts of OPEs were transported into Dongting Lake via tributaries in Hunan Province. It has been reported that OPEs were ubiquitous airborne pollutants across China (Liu et al., 2016), and also detected in municipal landfill leachates (Qi et al., 2019) and municipal sludge (Fu et al., 2017) in Hunan Province, these results suggested their widely presence in various environment media, such as surface water and sediment, soil and atmosphere in Hunan Province. Higher amount of precipitation (115.7–159.3 mm) was recorded in region surrounding the Dongting Lake in wet season in 2018 than in dry season (52.9–67 mm) in 2017 (Zhang et al., 2020). Consequently, we could speculate safely that higher concentrations of OPEs might be occurred in surface water in wet season from different sources, such as higher wet precipitation with airborne OPEs, increasing runoff from soil and roads, and re-suspension of sediment in rivers. Finally, the enhanced OPEs were transported to the Dongting Lake via tributaries to the Lake, resulting in elevated OPEs in surface water in Dongting Lake. In our previous study, we also found that
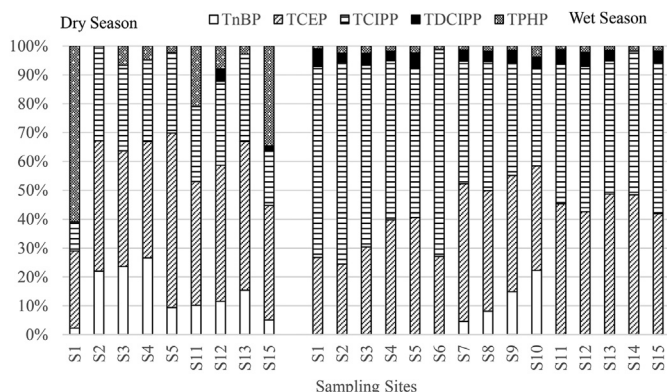

Fig. 2. Composition profiles of OPEs in dry season and wet season.

high concentrations of antibiotics were transported into Dongting Lake via tributaries (Zhang et al., 2020).

In the present study, the spatial distribution of OPEs in the wet season could be evaluated because water samples were collected from 15 sampling sites distributed in different parts of the Lake. Unlike the previously reported situation for antibiotics which exhibited obvious spatial variation due to local emission source related to pig breeding and aquaculture (Zhang et al., 2020), there was no obvious spatial variation of the OPE distribution, the results suggested that OPEs in the Dongting Lake might mainly be originated from dry/wet deposition and input from tributaries attached to the lake while with limited local emission (with exception of Datong Lake). Generally, slightly higher OPE concentrations were found in South Dongting Lake (average value of 109 ng L^{-1}) and Datong Lake (108 ng L^{-1}), followed by East Dongting Lake (average value of 78.9 ng L^{-1}) and West Dongting Lake (average value of 42.1 ng L^{-1}).

Datong Lake, a small closed lake with a well-developed aquaculture industry, receives no obvious discharges from industrial wastewater or domestic sewage, but TCIPP and TPHP concentrations of 71.7 ng L^{-1} and 27.8 ng L^{-1}, respectively, were found at S1. This suggested local emissions from the materials used in the fisheries, such as PUF, PVC, plastic, and resins (van der Veen and de Boer 2012). Meanwhile, atmospheric deposition (Liu et al., 2016) might play an important role to the presence of chlorinated OPEs in the land-locked lake, especially in summer, the wet season, higher concentrations of chlorinated OPEs were measured than winter. Further study should be carried out for water-air exchange in the region tracing OPEs emission sources, environmental geochemical processes and ultra-fate. The highest TnBP concentration was detected in S10, suggesting its potential discharge from an unidentified outlet, which might be ascribed to TnBP being used as an additive in hydraulic fluids, lacquers, and plastics (van der Veen and de Boer 2012). Further studies should be conducted to determine the possible emission sources and implement effective pollution control in the lake. The highest TCIPP concentration was detected in S6 in Wanzihu, an important aquaculture area in South Dongting Lake. This suggests local emissions from OPE-containing materials used in fishery aquaculture activities (van der Veen and de Boer 2012). In our previous study, high levels of lomefloxacin and chlortetracycline were detected in this sampling location suggesting their emission from fishery aquaculture activities (Zhang et al., 2020).

3.3. Concentrations and composition profiles of Di-OPs in surface water

The target Di-OPs were detected in surface water samples showing different DFs. Their concentrations and DFs are summarized in Table 2, detailed values are provided in Table S5. It can be seen that the total Di-OPs concentration ($\sum$Di-OPs) was in the range of 1.01–13.9 ng L^{-1} (average of 7.00 ng L^{-1}), which was about

Fig. 3. Composition profiles of Di-OPs in dry season and wet season.

one order of magnitude lower than the OPE concentrations in these samples.

The composition profiles of Di-OPs are presented in Fig. 3. DBP, BDCIPP, and DPhP were detected in 23 samples (with the exception of S11 in the dry season) in the range of 0.360–6.32 ng L^{-1} (average of 2.40 ng L^{-1}), 1.02–8.49 ng L^{-1} (average of 2.12 ng L^{-1}), and 0.430–6.65 ng L^{-1} (average of 1.56 ng L^{-1}), accounting for 3.45–51.7%, 14.1–73.1%, and 12.1–54.7% of total Di-OPs, respectively. DEP (<LOD–1.07 ng L^{-1}, average of 0.618 ng L^{-1}) was found in most samples, while BCIPP (<LOD–1.37 ng L^{-1}, average of 0.755 ng L^{-1}) was found in 23 samples with the exception of S12 in the dry season.

In wet season, the average DPhP concentration (1.84 ng L^{-1}) was higher than those of DBP (1.68 ng L^{-1}) and BDCIPP (1.34 ng L^{-1}), while in dry season the average DBP (2.79 ng L^{-1}) and BDCIPP (2.54 ng L^{-1}) concentrations were slightly higher than that of DPhP (1.41 ng L^{-1}). Totally, DPhP, DBP and BDCIPP were considered as main Di-OPs. This composition profile was dissimilar to those reported in indoor dust (Tan et al., 2019; Hu et al., 2020) and sludge (Gao et al., 2016; Fu et al., 2017), in which DPhP was the predominant compound. This might be ascribed to their different physico-chemical properties and possible degradation in the environment. DBP is more likely to be partitioned into the aqueous phase than DPhP due to its higher water solubility (430 mg L^{-1}) than DPhP (82.4 mg L^{-1}), while DPhP is prone to be adsorbed into the solid phase (e.g., dust and sludge) because of its higher logKow and log Koa (Table S1). In addition, DPhP in water can be degraded under UV irradiation, while DBP survives under the same levels of UV irradiation (Hu, 2020).

3.4. Spatio-seasonal variation of Di-OPs in Dongting Lake and their possible emission sources

As indicated in Table S5 and Figure S2, similar Di-OPs

Table 2
Summarized concentrations and distribution of Di-OPs in dry and wet season (ng L^{-1}).

Compounds	Dry season				Wet season			
	Min	Max	Average	DFs (%)	Min	Max	Average	DFs (%)
DEP	<LOD	1.05	0.705	66.7	<LOD	0.720	0.570	73.3
DBP	<LOD	2.83	1.68	88.9	0.400	6.32	2.79	100
BCIPP	<LOD	1.07	0.805	88.9	0.430	1.37	0.728	100
BDCIPP	<LOD	1.73	1.34	88.9	1.24	8.49	2.54	100
DPhP	<LOD	6.65	1.84	88.9	0.560	2.65	1.41	100

LOD: limit of detection; DFs: detected frequency; Min: minimum concentration.
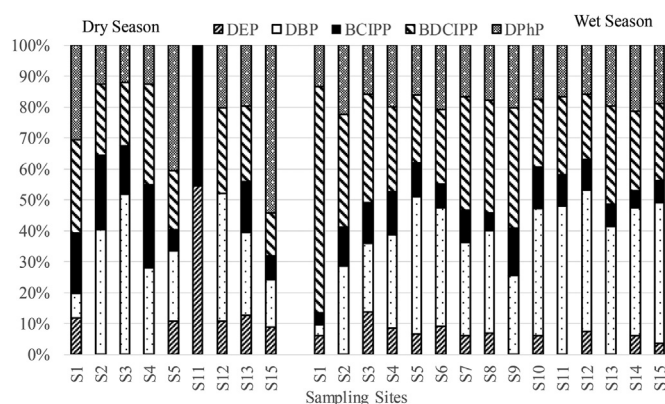Max: maximum concentration.

concentrations were measured in surface water in the dry season (1.01−12.3 ng L^{-1}, average value of 5.51 ng L^{-1}) and wet season (3.41−13.9 ng L^{-1}, average value of 7.89 ng L^{-1}). Unlike for the OPEs, there was no seasonal variation of Di-OPs in Dongting Lake.

The spatial distribution of Di-OPs was investigated in the wet season, with the highest concentration found in Datong Lake (11.6 ng L^{-1}), followed by East Dongting Lake (6.55−13.9 ng L^{-1}), and South Dongting Lake (5.55−8.35 ng L^{-1}). The lowest levels were found in West Dongting Lake (3.41−8.83 ng L^{-1}). The spatial distribution of Di-OPs was different from that of OPEs, which might be related to their different emission sources, physicochemical properties, and the resultant different environmental geochemistry processes.

TEP has been used as additive in PUF, PVC, polyesters, and resins (van der Veen and de Boer 2012), consequently it could be speculated that TEP might be released into receiving waters from a range of materials used in fishery activities and then degraded to its respective DEP. It has also been reported that organophosphorus pesticides, such as chlorfenvinphos, can be metabolized to DEP (Reemtsma et al., 2011). We considered that DEP might have originated from the degradation of TEP and organophosphorus pesticides, which might be used in agricultural activities surrounding the Lake.

In the present, no obvious correlation was established between TPHP vs DPHP in both sampling seasons ($p > 0.1$), and TnBP vs DBP in dry season, the results suggested different emission sources of paired TPHP-DPhP and TnBP-DBP. For example, the highest DBP concentration was found at S15 in the wet season without TnBP being detected, while the highest DPhP concentration was found at S15 in the dry season with TPHP at 11.0 ng L^{-1} showing DPhP/TPHP ratio of 0.6. The results suggested possibly direct emission of DBP and DPhP adjacent to the sampling location. It has been reported that DBP and DPhP are not only degradation products of their respective parent compound (TnBP and TPHP) in the human body and the environment (Hu, 2020; Hou et al., 2016) or released during industrial process of OPEs-containing materials (Xu et al., 2019), but are also directly as chemicals. DBP is used as a plasticizer and industrial additive (Quintana et al., 2006), DPhP is used as a catalyst in polymerization, an additive in paints and coatings (Björnsdotter et al., 2018), or is present as an impurity in OPE formulas (Du et al., 2020). Consequently, we speculated that DBP and DPhP might have originated from the large range of emission sources mentioned above.

It was notable that a significantly higher TPHP concentration (27.8 ng L^{-1}) was detected in S1 in the dry season than in the wet season (1.07 ng L^{-1}), while similar DPhP concentrations were detected in the dry season (1.36 ng L^{-1}) and wet season (1.55 ng L^{-1}) in this location. It has been speculated that there occurred a significant emission source of TPHP in dry season potentially related to aquaculture in the land-locked lake. In addition, TPHP is degraded to a greater extent under the longer sunshine hours (198−255 h) in the wet season (Zhang et al., 2020) with DPhP as main degradation product. Simultaneously, DPhP might be further degraded (Hu, 2020) resulting in a similar residual DPhP concentration in the water of Dongting Lake.

Chlorinated OPEs are resistant to biotic/abiotic degradation in the environment, but BCIPP and BDCIPP were detected widely in Dongting Lake, especially significant correlation ($p < 0.01$) was found between TDCIPP and BDCIPP in wet season. It is possible that they could have originated from similar sources, such as human metabolism (Hou et al., 2016), or as degradation products during the manufacturing of OPE containing materials (Xu et al., 2019), and were then discharged into Dongting Lake via tributaries.

3.5. Potential ecological and human health risks

The ecological risks presented by TCEP, TCIPP, TDCIPP, and TPHP were assessed due to their higher DFs and presence in samples at levels higher than the LOD. In addition, the different ecological risks were assessed for algae, crustaceans, and fish using the different predicted no-effect concentration (PNEC) values of specific OPEs (Niu et al., 2019). The results are presented in Table S6. In the dry season, the RQs of TCEP and TCIPP for algae, crustaceans, and fish were much lower than 0.1, indicating limited ecological risks to these organisms in Dongting Lake, while the RQs of TPHP were 0−0.056, 0−0.0278, and 0−0.0397 for algae, crustaceans, and fish, respectively, suggesting a limited but higher ecological risk than that presented by TCEP and TCIPP. In the wet season, TCIPP was detected at 106 ng L^{-1} at S12, with an RQ of 0.0116 for crustaceans. The remaining RQ values of the target OPEs for aquatic organisms were much lower than 0.1.

In this study, S13 was adjacent to an alternative water source in Dongting Lake. Due to limited removal efficiencies during drinking water treatment (Choo and Oh 2020), the measured OPE concentrations were used for risk assessment. The calculated DIs for those chemicals with a high DFs at concentrations > LOD are listed in Table S7. In the dry season the DIs for TnBP, TCEP, TCIPP, and TPHP were 0.0868, 0.2889, 0.1703, and 0.0157 ng for children, and 0.0763, 0.2540, 0.1497, and 0.0138 ng for adults, respectively. While in the wet season the DIs for TCEP, TCIPP, TDCIPP, and TPHP were 1.0563, 1.001, 0.0819, and 0.0298 ng for children, and 0.9286, 0.8800, 0.0720, and 0.0262 ng for adults, respectively. The risk assessment results indicated that all the HQs were much lower than 1 (2.24×10^{-6}−1.25×10^{-3}), suggesting a negligible non-carcinogenic risk via drinking water for local people. Due to the lack of SFO value (Li et al., 2019), only the CRs of TnBP and TCEP were calculated. In the dry season, CR values of TnBP and TCEP were 7.81×10^{-10} and 5.78×10^{-10} for children, and 6.87×10^{-10} and 5.08×10^{-10} for adults, respectively, while in the wet season, the CR values of TCEP were 9.51×10^{-9} and 8.36×10^{-9} for children and adults, respectively. All the calculated CRs were much lower than 10^{-6} suggesting a negligible carcinogenic risk via drinking water for local people.

4. Conclusion

Twenty-four water samples were collected in Dongting Lake in the dry and wet seasons, and the concentrations, composition profiles, and spatial and temporal distributions of OPEs and Di-OPs were investigated. The $\sum$OPEs concentrations varied in the range of 5.00−148 ng L^{-1}, exhibiting an obvious temporal variation with TCEP and TCIPP as the main OPE components. The $\sum$Di-OPs concentration varied in the range of 1.01−13.9 ng L^{-1}, with no obvious spatio-seasonal variation. The $\sum$OPEs concentrations in Dongting Lake were low compared to the published data, and they presented a limited risk to aquatic organisms in Dongting Lake as well as the local inhabitants surrounding the lake. For a comprehensive risk assessment in the region, further studies should be conducted to determine the occurrence and distribution of OPEs and Di-OPs in sediment in Dongting Lake, especially for hydrophobic compounds such as TPHP.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117031.

Credit author statement

Liang Xu have collected samples, carried out the analytical procedure of the samples, drafted the first version of the Ms, and revised the Ms according to reviewers' comments. Biao Z**hang** and **Qiongpu Hu** have collected samples, and carried out the analytical procedure of the samples with Liang Xu. **Yi Liu** and **Ting Shang** have participated in samples analyses. **Xiangying Zeng** have made substantial contribution to conceptualization, review & editing, as well as approved the revision according to reviewers' comments. **Zhiqiang Yu** have contributed to editing during Ms preparation, and approved the final Version.

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