



Trophic transfer of organophosphorus flame retardants in a lake food web[☆]

Haoqi Zhao^a, Fanrong Zhao^a, Jixuan Liu^a, Shiyi Zhang^a, Di Mu^a, Lihui An^b, Yi Wan^a, Jianying Hu^{a,*}

^a Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing, 100871, China

^b State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, 100012, China

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ABSTRACT

Despite increasing use of organophosphorus flame retardants (OPFRs), their food web transfer behavior is not well known. In this study, concentrations of fourteen OPFRs were measured in 17 species from Taihu Lake, China, and their trophodynamics were assessed. Of the 14 OPFRs, nine were detected in at least 70% of the food web samples, including tris(ethyl) phosphate (TEP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(isobutyl) phosphate (TIBP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tris(n-butyl) phosphate (TNBP), tris(phenyl) phosphate (TPHP), tris(methylphenyl) phosphate (TMPP), and 2-ethylhexyl diphenyl phosphate (EHDPP). The total OPFR concentrations were 100 ± 23 ng/g ww in plankton, 17 ± 11 ng/g ww in invertebrates, and 9.8 ± 6.2 ng/g ww in fish. TIBP (93 ± 16 ng/g ww) was the dominant OPFR in plankton, whereas TCEP (2.4 ± 3.9 ng/g ww) and TPHP (3.3 ± 16 ng/g ww) were dominant in fish. While negative relationships between concentration and aquatic species trophic level were observed for all nine OPFRs, only those for TCIPP ($p = 0.022$), TDCIPP ($p = 0.029$), and TMPP ($p = 0.021$) were statistically significant, with trophic magnification factors (TMFs) of 0.55, 0.39, and 0.42, respectively. This study provides fundamental information for assessing ecological risks of OPFRs.

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1. Introduction

The use of organophosphorus flame retardants (OPFRs) has increased significantly with the production phase-out of polybrominated diphenyl ethers (PBDEs) (Van der Veen and de Boer, 2012). The global production of OPFRs reached 200,000 tons in 2014 (Li et al., 2014), and some OPFRs such as tris(n-butyl) phosphate (TNBP), tris(methylphenyl) phosphate (TMPP), and tris(2-ethylhexyl) phosphate (TEHP) are listed as high-production volume (HPV) chemicals (U.S. EPA, 2014). In China, the consumption of OPFRs was 11,000 tons in 1995, which has been constantly increasing to 70,000 tons in 2007 and 179,000 tons in 2012 (Li et al., 2017). Due to their widespread use, OPFRs are ubiquitous in various environmental media, including sediment (Cristale et al., 2013a; Gorga et al., 2014; Cao et al., 2012), surface water (Cristale et al., 2013; Bollmann et al., 2012; Wang et al., 2011), the atmosphere

(Jimenez et al., 2014; Moller et al., 2011; Aragon et al., 2012), wild fish and bird tissues (Kim et al., 2011; Brandsma et al., 2015; Greaves and Letcher, 2014), and even in human tissues (Ding et al., 2016; Kim et al., 2014; Zhao et al., 2017). Adverse effects of OPFRs have been observed in both aquatic organisms and humans, such as fecundity decrease, thyroid endocrine disruption, and developmental toxicity in zebrafish (Zhu et al., 2015; Wang et al., 2013; Han et al., 2014), neurotoxicity in Chinese minnow (Yuan et al., 2016), and hormone and sphingolipid homeostasis disruption in humans (Meeker and Stapleton, 2009; Zhao et al., 2016). Thus, the environmental risks of OPFRs have received increasing attention.

Bioaccumulation and biomagnification potentials are vital criteria for assessing the ecological risks of OPFRs. The predicted bioconcentration factors (BCFs) for OPFRs ranged from 0.4 for tris(2-chloroethyl) phosphate (TCEP) to 1×10^6 for TEHP, with both TMPP (BCF: 8564) and TEHP considered as very bioaccumulative compounds (BCF ≥ 5000) under the REACH criterion (European Union, 2006; Hou et al., 2016). Bioaccumulation is also evident from the widespread occurrence of OPFRs in aquatic species at lower trophic levels (e.g., invertebrates and fish) (Ma et al., 2013;

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* Corresponding author.

E-mail address: hujy@urban.pku.edu.cn (J. Hu).

Brandsma et al., 2015; Álvarez-Muñoz et al., 2015), and in species occupying higher trophic levels, such as seabirds (Greaves and Letcher, 2014; Chen et al., 2012). BCFs of tributyl phosphate (TBP, the mixture of TNBP and tris(isobutyl) phosphate (TIBP); 6–35), TCEP (0.7–2.2), tris(1,3-dichloroisopropyl) phosphate (TDCIPP; 3–113), and tris(phenyl) phosphate (TPHP; 32–500) have been evaluated in killifish, goldfish, and zebrafish in laboratory (Sasaki et al., 1981; Wang et al., 2016), and the bioaccumulation factors (BAFs) of eight OPFRs (from 27.8 for TDCIPP to 1983 for TEHP) were measured in crucian carp and loach from Beijing, China (Hou et al., 2017). The measured BCF and BAF were generally higher than the predicted BCF for OPFRs with $\log K_{ow} < 5$, and *vice versa* for OPFRs with $\log K_{ow} > 5$ (Table S1). While the bioaccumulation of OPFRs is relatively well-known, only two previous studies have addressed their trophic transfer. Potential biomagnification was proposed for TPHP in demersal fish species from Manila Bay, Philippines, where concentrations of TPHP were positively correlated with the stable nitrogen isotope ratios ($\delta^{15}N$) of the fish tissue (Kim et al., 2011). However, TPHP, TEHP, tris(2-chloroisopropyl) phosphate (TCIPP), TDCIPP, TMPP, and 2-ethylhexyl diphenyl phosphate (EHDPP) showed trophic dilution in a marine food web from the Western Scheldt estuary, Netherlands, while TIBP and tris(2-butoxyethyl) phosphate (TBOEP) showed trophic magnification, although the results relied on a small sample size ($n = 34$) with low OPFR detection frequencies (6%–50%) (Brandsma et al., 2015). Thus, the trophodynamics of OPFRs are still controversial up to now, and additional study is required for a better evaluation.

In this study, concentrations of fourteen OPFRs were measured in plankton, five invertebrate species, and eleven fish species (99 samples in total) from Taihu Lake, China, and their trophic transfer behaviors were investigated. A comprehensive food web and a sensitive analytical method enabled OPFR detection at different trophic levels with high detection frequencies, supporting a reliable assessment of OPFR trophodynamics. This study provides fundamental information for future ecological risk assessments.

2. Materials and methods

2.1. Chemicals and reagents

Sources for most chemicals and reagents used in this study can be found in our previous work (Zhao et al., 2017), with the exception of TIBP (Adamas Reagent Ltd.; Shanghai, China).

2.2. Site description and sample collection

Taihu Lake is a shallow, large freshwater lake (maximum depth: 2.6 m, area: 2400 km²) located in the southern part of the Yangtze River Delta, one of the most developed regions in China. Northern Taihu Lake, including Meiliang Bay and Zhushan Bay, has suffered from severe eutrophication from domestic and agricultural discharges (Yi et al., 2017). Beyond eutrophication, Taihu Lake is also contaminated with organic chemicals, such as OPFRs, which are consistently detected in surface water and sediment at levels up to several $\mu\text{g/L}$ and $\mu\text{g/g dw}$, respectively (Liu et al., 2018; Cao et al., 2012; Chen et al., 2018). The largest OPFR manufacturer in China, Jiangsu Yoke Technology Co. Ltd., is located ~15 km away from Taihu Lake (Ou, 2011), and industrial discharges have been proposed as the principal source of OPFR contamination in the tributaries of northern Taihu Lake (Liu et al., 2018). The food web species in this study were collected from the Meiliang Bay in August 2014, including plankton ($n = 6$, dominated by blue-green algae (*Cyanobacteria*)), five invertebrate species (clam ($n = 6$), snail ($n = 6$, pooled), freshwater mussel ($n = 6$, pooled), white shrimp ($n = 6$) and freshwater shrimp ($n = 6$)), and eleven fish species (whitebait

($n = 6$, pooled), ricefield eel ($n = 6$), crucian ($n = 6$), pipefish ($n = 6$), silver fish ($n = 6$), carp ($n = 3$), whitefish ($n = 6$), redfin culter ($n = 6$), catfish ($n = 6$), wolffish ($n = 6$) and yellow-head catfish ($n = 6$)) (Table 1; Fig. S1). Plankton were collected from six sites in Meiliang Bay with a 77 μm mesh net. Invertebrate and fish samples were collected using bottom trawlers. Samples were transferred to the laboratory on dry ice and frozen at -20°C until analysis. Biota trophic levels were determined from nitrogen isotope ratios, as described in the Supporting Information.

2.3. Sample extraction and cleanup

Invertebrate soft tissue and fish muscle tissue were freeze-dried, ground, and passed through 180 μm mesh prior to analysis. Ground tissue (0.1 g) was spiked with 50 μL of 4.0 $\mu\text{g/L}$ internal standards and equilibrated overnight. Tissue was extracted with 4 mL ethyl acetate in ultrasonic environment for 1 h, then shaken at 325 rpm for 10 min on an orbital shaker. After centrifugation (4000 rpm, 10 min), the supernatant was transferred to a pre-weighed glass bottle, and the tissue was re-extracted by the same procedure. The combined extracts were concentrated to dryness under nitrogen gas, and the glass bottle re-weighed to determine lipid weight of the tissue. Residue in the glass bottle was re-dissolved in 3 mL *n*-hexane and loaded onto a NH₂ SPE cartridge preconditioned with 15 mL dichloromethane and 3 mL *n*-hexane. After rinsing the cartridge with 3 mL 4:1 hexane/dichloromethane (v/v), the target OPFRs were eluted with 4 mL dichloromethane. The eluent was concentrated nearly to dryness and then diluted in 100 μL methanol for UPLC-MS/MS analysis.

2.4. UPLC-MS/MS analysis

Quantification of the fourteen OPFRs used an Acquity Ultra Performance Liquid Chromatography interfaced to a Premier XE quadrupole mass spectrometer (Waters, Milford, MA, USA). The instrument method generally followed that in our previous study (Zhao et al., 2016), with modification of the UPLC elution gradient to allow simultaneous analysis of OPFRs. Additional details are provided in the Supporting Information.

2.5. Quality assurance and quality control

The analytical method was validated based on precision, recovery, blank contamination, linearity, limits of detection (LODs), and limits of quantification (LOQs). To prove method reliability for different biological matrices, OPFR spike-recovery experiments were performed in four species: plankton, one invertebrate (snail) and two fishes (whitebait and yellow-head catfish) at 0.5, 1, and 5 ng/g wet weight (ww) ($n \geq 3$ for each species at each concentration). Spiked samples were processed by the analytical method outlined above, and recovered concentrations were background-corrected by subtracting the average background concentrations in non-spiked samples. For the three spike levels (0.5, 1, and 5 ng OPFR/g ww), OPFR recoveries ranged from $46 \pm 9\%$ (EHDPP in snail) to $103 \pm 5\%$ (TBOEP in plankton), $48 \pm 4\%$ (TPHP in snail) to $112 \pm 1\%$ (TBOEP in plankton), and $66 \pm 13\%$ (TPHP in snail) to $120 \pm 14\%$ (TDCIPP in plankton), respectively (Table S3). Internal standard recovery ranged from $45 \pm 18\%$ (TCEP-d₁₂) to $98 \pm 28\%$ (TMPP-d₂₁) in biota, and generally matched the recovery of the corresponding OPFRs.

Calibration curves for all fourteen OPFRs showed reliable linearity ($r^2 > 0.995$) from 0.050 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$. The signal-to-noise ratios of the chromatographic peaks for 0.050 $\mu\text{g/L}$ OPFRs were 13–50. OPFR peaks in sample extracts were identified by matching retention time ($\pm 2\%$) and relative abundance of ion transitions

Table 1

Name, feeding habit, body size, water content, lipid content, and stable isotope ratios of species in the food web from Taihu Lake.

Species name		Habitat ^a	Feeding habit ^a	Body length (cm)	Body weight (g)	n	Water content (%)	Lipid content ^c (%)	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
Plankton	plankton	pelagic	autotrophy	–	–	6	94.6 ± 1.1	5.9 ± 2.0	–21.6 ± 3.4	13.5 ± 1.0
Invertebrate	clam (<i>Lamellibranchia</i>)	benthic	omnivorous	–	–	6 ^b	87.1 ± 1.8	14.3 ± 2.8	–28.8 ± 0.1	10.0 ± 0.1
	snail (<i>Bellamya purificata</i>)	benthic	omnivorous	–	–	6 ^b	75.5 ± 1.1	6.4 ± 2.4	–21.5 ± 0.4	17.6 ± 0.4
	freshwater mussel (<i>Lamellibranchia</i>)	benthic	omnivorous	–	–	6 ^b	83.2 ± 0.8	7.6 ± 2.0	–25.4 ± 0.2	18.1 ± 0.1
	white shrimp (<i>Exopalaemon modestus</i>)	pelagic	omnivorous	4.5	0.42 ± 0.12	6 ^b	80.8 ± 0.5	8.6 ± 2.3	–19.5 ± 0.4	19.9 ± 0.1
	freshwater shrimp (<i>Macrobranchium nipponense</i>)	pelagic	omnivorous	7.0	1.1 ± 0.3	6	76.4 ± 0.8	10.3 ± 2.1	–20.4 ± 0.4	20.2 ± 0.4
Fishes	whitebait (<i>Hemisanx prognathous</i>)	pelagic	carnivorous (small fish, shrimp)	5.1 ± 0.5	0.25 ± 0.05	6 ^b	84.0 ± 0.3	5.0 ± 1.2	–27.0 ± 0.4	14.6 ± 0.2
	ricefield eel (<i>Monopterus albus</i>)	benthic	omnivorous (insects, small fish)	50 ± 3	146 ± 58	6	78.3 ± 0.9	9.2 ± 1.8	–21.9 ± 1.0	16.5 ± 1.1
	crucian (<i>Carassius auratus</i>)	benthic	omnivorous (plankton, small fish)	16 ± 2	51 ± 17	6	79.8 ± 1.0	10.4 ± 1.6	–22.5 ± 2.9	18.8 ± 2.0
	pipefish (<i>Tylosurus crocodilus</i>)	pelagic	carnivorous (small fish)	13 ± 1	3.5 ± 0.7	6	76.2 ± 2.2	17.3 ± 7.7	–21.8 ± 0.3	19.1 ± 0.7
	silver fish (<i>Protosalanx hyalocranius</i>)	pelagic	carnivorous (small fish, shrimp)	12 ± 1	4.7 ± 0.8	6	81.4 ± 0.8	10.6 ± 0.8	–23.3 ± 0.2	19.2 ± 0.8
	carp (<i>Carassius cuvieri</i>)	benthic	omnivorous (plankton, debris)	17 ± 2	111 ± 69	3	73.3 ± 5.8	8.8 ± 1.6	–20.6 ± 0.4	19.3 ± 1.0
	whitefish (<i>Alburnus</i>)	pelagic	carnivorous (small fish)	27 ± 3	192 ± 17	6	79.0 ± 0.9	16.1 ± 5.1	–22.0 ± 0.2	20.7 ± 0.4
	redfin culter (<i>Cultrichthys erythropterus</i>)	benthic	carnivorous (invertebrate, small fish)	20 ± 2	70 ± 9	6	76.2 ± 1.6	9.9 ± 3.3	–22.0 ± 0.3	20.7 ± 1.1
	catfish (<i>Silurus asotus</i>)	benthic	carnivorous (plankton, shrimp, small fish)	29 ± 3	201 ± 51	6	78.2 ± 1.7	15.5 ± 2.3	–22.1 ± 0.8	20.8 ± 0.6
	wolffish (<i>Anarrhichthys Ocellaus</i>)	benthic	carnivorous (invertebrate, small fish)	12 ± 1	4.8 ± 1.2	6	82.4 ± 0.8	11.5 ± 2.6	–21.1 ± 0.6	21.6 ± 0.5
	yellow-head catfish (<i>Pelteobagrus fulvidraco</i>)	benthic	carnivorous (invertebrate, small fish)	17 ± 2	74 ± 27	6	80.4 ± 1.5	17.5 ± 3.0	–21.3 ± 0.4	22.4 ± 0.3

^a Ni and Zhu, 2005.^b Pooled sample (≥2 individuals).^c Lipid content is the ratio of lipid mass to dry weight mass.

(±20%) to the analytical standards.

Due to the ubiquity of OPFRs in the environment and commercial materials, several measures were taken to minimize lab contamination. All glassware was baked at 450 °C for 10 h before use; cap rubber linings were covered with aluminum foil to avoid contact with the extraction solvent; and SPE cartridges were rinsed with 15 mL dichloromethane before loading samples. Ten procedure blanks (one blank per 10 tissue samples; 4 mL ethyl acetate in empty centrifuge tubes) were processed alongside environment samples. All OPFRs, except tripropyl phosphate (TPPrP), triisopropyl phosphate (TiPP) and tris(2,3-dibromopropyl) phosphate (TDBPP), were detected in the procedure blanks (0.004–0.28 ng/g ww). All reported OPFR concentrations were blank-subtracted.

For OPFRs detected in procedure blanks, the LOD and LOQ were defined, respectively, as 3- and 10-fold the standard deviation in the blanks. For OPFRs without detectable blank contamination, the concentrations of matrix-spiked standards for which the chromatographic peaks showed signal-to-noise ratios of 3 and 10 were defined as the LOD and LOQ, respectively. LODs ranged from 0.001 ng/g ww to 0.14 ng/g ww for the biota (Table S3).

2.6. Trophic magnification factor

Trophic magnification factors (TMFs) were calculated as reported previously (details provided in the Supporting Information). TMFs were calculated only for OPFRs detected in >70% of the biota samples. Concentrations below the LOD were assigned as half the LOD, as reported previously (Peng et al., 2014). Regressions with *p*-values < 0.05 were considered significant (SPSS 20 software; SPSS Inc., Chicago, USA).

3. Results and discussion

3.1. Occurrence of OPFRs in biota

Of the 14 OPFRs, all except for TDBPP were detected in biota samples, with detection frequencies ranging from 29% for TBOEP to 100% for TDCIPP (Table 2). The total OPFR concentration (Σ OPFRs) in biota generally decreased with increasing trophic level: 100 ± 23 ng/g ww in plankton, 17.1 ± 11.0 ng/g ww in invertebrates, and 9.8 ± 6.2 ng/g ww in fish. The decrease in Σ OPFRs with increasing trophic level was consistent with the result in a pelagic food web from the Western Scheldt estuary in the Netherlands, where the highest Σ OPFRs was also observed in plankton (Brandtsma et al., 2015). The highest concentration of TIBP (93 ± 16 ng/g ww) was observed in plankton; those of TCIPP (9.9 ± 3.1 ng/g ww), TDCIPP (6.4 ± 1.6 ng/g ww), TBOEP (6.7 ± 3.9 ng/g ww), TMPP (0.22 ± 0.15 ng/g ww), EHDPP (1.1 ± 0.6 ng/g ww), and TEHP (5.9 ± 2.2 ng/g ww) were observed in freshwater mussel; those of tris(ethyl) phosphate (TEP, 2.8 ± 2.4 ng/g ww), TCEP (11 ± 12 ng/g ww), TPPrP (0.33 ± 0.28 ng/g ww), TiPP (0.33 ± 0.26 ng/g ww), and TNBP (1.8 ± 1.6 ng/g ww) in carp; and that of TPHP (5.1 ± 2.1 ng/g ww) in silver fish. As OPFRs were measured in fish muscle tissue in this study, the results were only compared with studies that also reported OPFR concentrations in fish muscle tissues, given the tissue-specific bioaccumulation of OPFRs (Hou et al., 2017). The lipid weight-based Σ OPFRs ranged from 92 to 999 ng/g lw in fish species from Taihu Lake, comparable to those (110–1900 ng/g lw) observed in 20 fish species from Manila Bay, the Philippines (Kim et al., 2011). Likewise, the average Σ OPFRs in crucian carp from Taihu Lake (419 ± 252 ng/g lw) was similar with that from Beijing, China (451 ng/g lw) (Hou et al.,

Table 2
OPFR detection frequencies and concentrations (ng/g ww) in aquatic organisms from Taihu Lake, China.^{a,b} The detection frequencies and average OPFR concentrations are shown in bold, while the OPFR concentration ranges are shown in parentheses.

Species	TEP	TCEP	TPrP	TiPP	TCIPP	TIBP	TDCIPP	TBOEP	TNBP	TDBPP	TPHP	TMPP	EHDPP	TEHP
Detection Frequency	90%	84%	58%	67%	100%	96%	93%	29%	91%	0%	75%	73%	85%	54%
PL	0.51 (0.22–0.90)	0.53 (ND–1.6)	0.003 (ND–0.009)	0.023 (0.015–0.028)	1.7 (0.94–3.6)	93 (80–109)	0.75 (0.34–1.1)	0.11 (0.033–0.26)	0.54 (0.28–1.1)	ND	0.63 (0.060–2.8)	0.079 (0.019–0.17)	0.057 (0.020–2.3)	2.2 (0.38–4.7)
LBC	0.32 (0.30–0.34)	1.4 (0.80–2.6)	0.014 (0.006–0.035)	0.063 (0.032–0.10)	2.0 (1.9–2.3)	0.98 (0.86–1.1)	1.2 (1.0–1.7)	0.12 (ND–0.25)	0.37 (0.28–0.40)	ND	0.57 (ND–0.77)	0.18 (0.11–0.29)	0.14 (0.052–0.34)	2.5 (1.8–3.4)
BP	0.17 (0.14–0.18)	0.66 (0.22–1.4)	0.001 (ND–0.004)	0.013 (ND–0.034)	2.8 (2.2–3.5)	3.4 (2.4–4.6)	1.1 (0.64–1.6)	0.49 (ND–2.1)	0.48 (0.39–0.56)	ND	0.45 (ND–1.0)	0.014 (ND–0.038)	0.073 (ND–0.20)	4.1 (1.6–7.2)
LBF	ND	1.4 (ND–3.9)	0.014 (ND–0.047)	ND	9.9 (4.8–13)	1.3 (0.84–1.7)	6.4 (4.1–8.2)	6.7 (ND–12)	1.4 (0.83–2.1)	ND	1.7 (ND–3.6)	0.22 (ND–0.42)	1.1 (ND–2.2)	5.9 (3.4–9.6)
EM	0.18 (0.12–0.25)	0.61 (0.31–0.92)	ND	0.004 (ND–0.010)	1.0 (0.64–1.3)	6.3 (3.6–9.1)	0.53 (0.20–0.88)	0.18 (ND–0.31)	0.39 (0.22–0.57)	ND	ND	0.032 (ND–0.062)	0.046 (ND–0.090)	0.071 (0.032–0.12)
MN	0.18 (ND–0.33)	0.67 (ND–1.5)	0.001 (ND–0.004)	0.005 (ND–0.011)	6.2 (3.7–10)	0.96 (ND–1.6)	5.4 (2.8–7.9)	ND	0.55 (0.27–1.1)	ND	2.0 (ND–3.7)	0.014 (ND–0.027)	0.11 (ND–0.13)	0.037 (ND–0.099)
HP	0.12 (0.11–0.13)	0.47 (0.28–0.63)	0.009 (ND–0.049)	0.021 (ND–0.11)	0.44 (0.37–0.52)	0.20 (ND–0.42)	0.12 (ND–0.21)	ND	0.27 (0.15–0.57)	ND	0.59 (ND–1.2)	0.016 (ND–0.037)	0.13 (ND–0.61)	0.041 (0.023–0.053)
MA	0.74 (0.35–1.4)	2.9 (0.82–7.8)	0.11 (0.054–0.18)	0.13 (0.078–0.31)	1.6 (0.87–2.2)	0.56 (0.41–0.84)	0.32 (0.15–0.53)	0.29 (ND–1.0)	0.71 (0.39–1.0)	ND	0.48 (0.25–0.63)	0.069 (ND–0.15)	0.30 (0.050–0.86)	0.039 (ND–0.076)
CA	1.3 (0.42–2.4)	1.9 (0.42–3.2)	0.17 (0.10–0.26)	0.11 (0.051–0.19)	1.1 (0.61–1.8)	0.47 (0.23–0.67)	0.23 (0.11–0.56)	0.21 (ND–0.40)	0.66 (0.31–1.0)	ND	0.41 (0.16–0.69)	0.049 (ND–0.097)	0.74 (0.10–1.5)	0.052 (ND–0.13)
TC	0.33 (ND–0.59)	2.5 (ND–9.0)	0.11 (0.066–0.15)	0.095 (0.054–0.16)	1.7 (1.5–2.1)	0.32 (0.20–0.63)	0.87 (0.25–3.4)	ND	0.30 (ND–0.78)	ND	1.3 (0.22–5.2)	0.038 (ND–0.084)	0.69 (0.19–2.0)	0.34 (0.11–1.4)
PHA	0.60 (0.27–0.99)	0.78 (ND–2.7)	0.049 (ND–0.094)	0.063 (0.021–0.12)	2.7 (2.1–3.5)	9.0 (5.0–15)	0.15 (0.061–0.24)	0.16 (ND–0.34)	0.46 (0.23–0.71)	ND	5.1 (2.0–7.6)	0.13 (0.059–0.22)	0.25 (0.20–5.0)	ND
CC	2.8 (0.11–4.5)	11 (ND–25)	0.33 (0.012–0.53)	0.33 (0.022–0.48)	2.4 (0.25–4.5)	1.5 (0.11–2.4)	0.49 (ND–1.0)	0.54 (ND–1.3)	1.8 (ND–3.2)	ND	0.72 (ND–1.5)	0.11 (ND–0.21)	0.15 (ND–0.31)	ND
AB	1.4 (0.35–2.6)	3.4 (ND–13)	0.13 (ND–0.34)	0.19 (0.023–0.41)	0.83 (0.30–1.9)	0.61 (0.24–1.4)	0.084 (ND–0.15)	0.36 (ND–1.0)	0.60 (ND–1.5)	ND	0.44 (ND–1.6)	0.027 (ND–0.041)	0.11 (ND–1.8)	ND
CE	2.0 (1.5–3.0)	4.9 (2.3–14)	0.23 (0.15–0.36)	0.19 (0.13–0.27)	1.1 (0.64–1.8)	0.92 (0.63–1.5)	0.30 (0.13–0.54)	0.25 (ND–0.58)	0.85 (0.51–1.3)	ND	0.70 (0.33–1.2)	0.022 (ND–0.051)	0.51 (0.17–0.99)	ND
SA	0.29 (0.16–0.52)	1.3 (0.40–2.5)	ND	0.008 (ND–0.032)	1.1 (0.67–1.6)	3.9 (3.1–4.8)	0.16 (ND–0.47)	0.31 (ND–0.88)	0.76 (0.36–1.4)	ND	2.9 (1.0–4.1)	0.047 (ND–0.10)	0.16 (0.085–0.27)	0.015 (ND–0.024)
AO	0.38 (0.18–0.59)	0.92 (ND–2.7)	0.13 (0.085–0.18)	0.14 (0.084–0.17)	0.80 (0.44–1.0)	0.33 (0.13–0.66)	0.13 (0.060–0.20)	0.14 (ND–0.26)	0.19 (ND–0.29)	ND	0.28 (0.09–0.67)	0.024 (ND–0.032)	0.086 (0.047–0.103)	0.25 (0.19–0.34)
PF	0.22 (ND–0.16)	0.34 (0.20–0.50)	ND	0.005 (ND–0.011)	0.62 (0.36–0.78)	0.46 (ND–0.81)	0.12 (ND–0.21)	0.18 (ND–0.30)	0.45 (0.32–0.62)	ND	1.2 (ND–3.8)	0.033 (0.020–0.045)	0.11 (0.066–0.20)	0.015 (ND–0.029)

^a PL = plankton; LBC = Clam (*Lamellibranchia*); BP = snail (*Bellamya purificata*); LBF = freshwater mussel (*Lamellibranchia*); EM = white shrimp (*Exopalaemon modestus*); MN = freshwater shrimp (*Macrobrachium nipponense*); HP = whitebait (*Hemilalanx prognathous*); MA = ricefield eel (*Monopterus albus*); CA = crucian (*Carassius auratus*); TC = pipefish (*Tylosurus crocodilus*); PHA = silver fish (*Protosalanx hyalocranius Abbott*); CC = carp (*Carassius cuvieri*); AB = whitefish (*Alburnus*); CE = redfin culter (*Cultrichthys erythropterus*); SA = catfish (*Silurus asotus*); AO = wolffish (*Anarrhichthys Ocellaus*); PF = yellow-head catfish (*Pelteobagrus fulvidraco*); ND, not detected. All values were indicated by arithmetic mean (range).

^b ND = not detected.

2017). In eel from Taihu Lake, ΣOPFRs ranged from 232 to 649 ng/g lw, one order of magnitude higher than ΣOPFRs (7.0–330 ng/g lw) in the same species from Belgium (Malarvannan et al., 2015).

As shown in Fig. 1, the OPFR profiles differed in plankton, invertebrates, and fishes from Taihu Lake. TIBP was the dominant OPFR in plankton, accounting for 94% of ΣOPFRs, but only accounted for 22 ± 23% in invertebrates and 11 ± 11% in fish. In contrast, contributions of TCIPP, TDCIPP and TEHP to ΣOPFRs were, respectively, 23 ± 9%, 15 ± 10%, and 14 ± 12% in invertebrates, relative to 1.4%, 0.7%, and 1.7% in plankton. TCEP and TPHP dominated the ΣOPFRs in fish, with contributions of 22 ± 14% and 21 ± 22%, respectively. Chlorinated (TCEP, TCIPP, TDCIPP) and aryl-OPFRs (TPHP) generally dominated ΣOPFRs in invertebrates and fishes, which may be attributed either to their occurrence as the dominant OPFRs in water and sediment of Taihu Lake (Liu et al., 2018) or to their relatively high bioaccumulation potentials (particularly for TPHP whose BCF was measured as the second largest among the OPFRs) (Hou et al., 2017). This result echoed that of a study in Sweden, where TDCIPP and TPHP were identified as the dominant OPFRs in mussels and fish (Sundkvist et al., 2010). However, the contribution of TBOEP to ΣOPFRs was low in fish from Taihu Lake (2.6 ± 1.4%), relative to that (>50%) in fish from the Pearl River Delta, China and in invertebrates and fish from Western Scheldt, Netherlands (Ma et al., 2013; Brandsma et al., 2015). This difference was consistent with the relative TBOEP concentrations in these aquatic environments, as TBOEP was the dominant OPFR in sediment (7.0 ng/g dw) and suspended particulate matters (33 ng/g dw) from Western Scheldt, Netherlands (Brandsma et al., 2015), but was only a minor OPFR (0.11 ng/L) in water of Taihu Lake and was not detected in sediment (Liu et al., 2018).

3.2. Trophic transfer of OPFRs

The stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope ratios

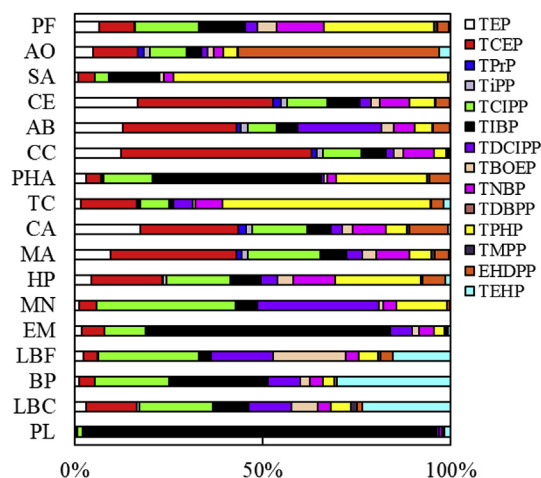


Fig. 1. Profiles of OPFRs in organisms in the food web from Taihu Lake. From bottom to top of the figure were plankton, invertebrates, and fish species. Species within each group were arranged according to their trophic levels. Plankton: PL; Invertebrate species: LBC = Clam (*Lamellibranchia*), BP = snail (*Bellamya purificata*), LBF = freshwater mussel (*Lamellibranchia*), EM = white shrimp (*Exopalaemon modestus*), MN = freshwater shrimp (*Macrobrachium nipponense*); Fish species: HP = whitebait (*Hemisalax prognathous*), MA = ricefield eel (*Monopterus albus*), CA = crucian (*Carassius auratus*), TC = pipefish (*Tylosurus crocodilus*), PHA = silver fish (*Protosalax hyalocranius Abbott*), CC = carp (*Carassius cuvieri*), AB = whitefish (*Alburnus*), CE = redfin culter (*Cultrichthys erythropterus*), SA = catfish (*Silurus asotus*), AO = wolf-fish (*Anarrhichtys Ocellaus*), PF = yellow-head catfish (*Pelteobagrus fulvidraco*). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

correlated significantly ($p = 0.002$) for species in the food web of Taihu Lake (Fig. 2). The $\delta^{15}\text{N}$ value was $13.5 \pm 1.0\text{‰}$ in plankton, ranged from $10.0 \pm 0.1\text{‰}$ (clam) to $20.2 \pm 0.4\text{‰}$ (freshwater shrimp) in invertebrates, and ranged from $14.6 \pm 0.4\text{‰}$ (whitebait) to $22.4 \pm 0.4\text{‰}$ (yellow-head catfish) in fishes. Trophic level of plankton was assigned as 2.0, and was 1.1–3.8 for invertebrates and 2.3–4.4 for fishes, similar to the results of another trophodynamics study in Taihu Lake, where the trophic levels of invertebrates and fish were measured as 2.78–4.22 and 2.48–4.24, respectively (Fang et al., 2014).

Nine OPFRs (TEP, TCEP, TCIPP, TIBP, TDCIPP, TNBP, TPHP, TMPP, and EHDPP) were detected in >70% of the 99 food web samples. No significant correlations were observed between log-transformed wet weight concentrations of OPFRs and trophic level. On a lipid weight basis, the log-transformed concentrations of all 9 OPFRs decreased with increasing trophic level (Fig. S2). The correlations were statistically significant for TCIPP, TDCIPP, and TMPP, and TMFs were estimated to be 0.55, 0.39, and 0.42, respectively (Table 3, Fig. 3). In a food web containing plankton, three invertebrate species, six fish species, and bird eggs from Western Scheldt estuary in the Netherlands, negative correlations were reported between concentrations of TCIPP, TDCIPP, TPHP, TMPP, EHDPP and trophic levels (consistent with the current study), but positive correlations were observed for TIBP and TBOEP (Brandsma et al., 2015). However, TIBP was only detected in 29% of the 34 samples from the

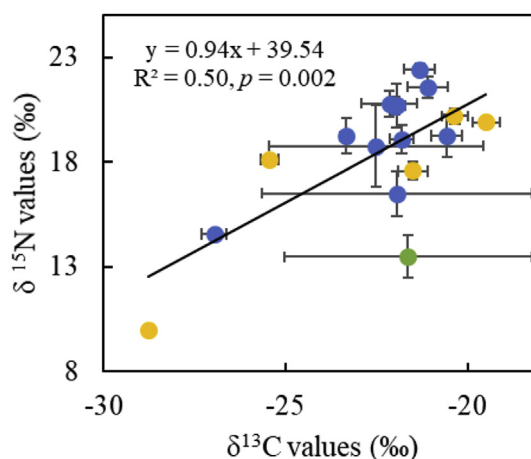


Fig. 2. Positive correlation between $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of organisms from Taihu Lake. Plankton, invertebrate, and fish species were shown in green, yellow, and blue dots, respectively. Error bar indicated \pm standard deviation. Regression was based on the arithmetic means of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of each species. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Trophic magnification factors (TMFs) of OPFRs and related parameters of the regression analyses between logarithm of lipid-weight based OPFRs concentrations and trophic levels.

Compound	TMFs	p	r ²
TEP	– ^a	0.283	0.08
TCEP	– ^a	0.120	0.15
TCIPP	0.55	0.022	0.30
TIBP	– ^a	0.143	0.14
TDCIPP	0.39	0.029	0.28
TNBP	– ^a	0.067	0.21
TPHP	– ^a	0.356	0.06
TMPP	0.42	0.001	0.52
EHDPP	– ^a	0.184	0.11

^a p-value above 0.05.

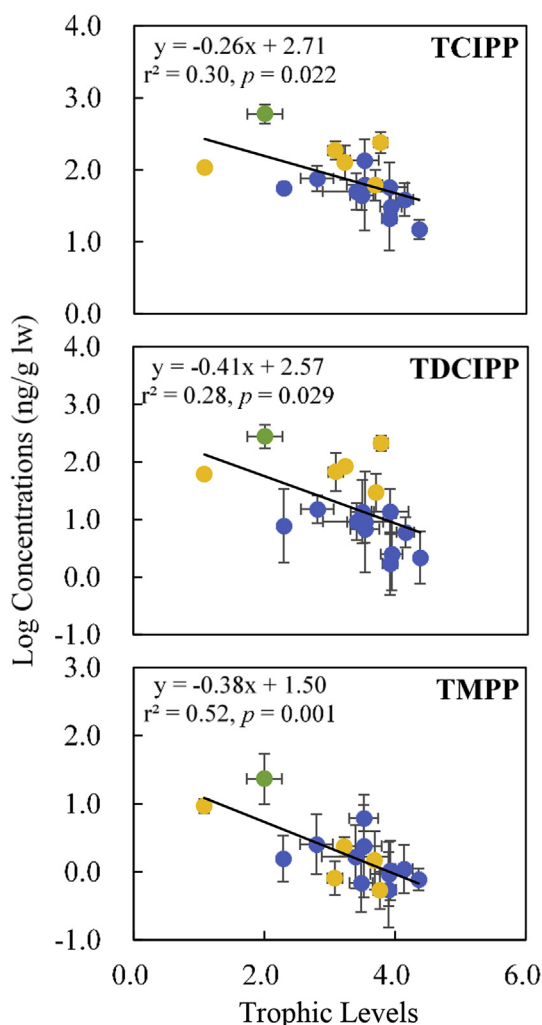


Fig. 3. Negative correlations between log-transformed concentrations of TCIPP, TDCIPP, and TMPP (ng/g lw) and trophic levels of species in the food web. Plankton, invertebrate, and fish species were shown in green, yellow, and blue dots, respectively. Error bar indicates \pm standard deviation. Regression was based on the geometric mean concentrations in each species. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Netherlands (Brandsma et al., 2015), lending large uncertainty to their conclusion. Trophic transfer behavior of TBOEP was not discussed in the present study, as its detection frequency was only 29%. Among the 9 OPFRs investigated in demersal fishes from Manila Bay, Philippines, only TPHP showed significant trophic transfer behavior. A significantly positive relationship was observed between TPHP concentration and $\delta^{15}\text{N}$ in fish, suggesting biomagnification (Kim et al., 2011). The negative correlation observed for TPHP in the present study may be caused by different structures of the food webs: the trophic transfer evaluation in the Philippines was based only on fish species, while the present study evaluated a comprehensive food web with species at a wide range of trophic levels.

According to the UNEP criteria ($\log K_{ow} > 5$), TMPP ($\log K_{ow}$: 5.11), EHDPP ($\log K_{ow}$: 5.73), and TEHP ($\log K_{ow}$: 9.49) have high biomagnification potentials in aquatic food webs (Table S1) (UNEP, 2001; Arnot and Gobas, 2006). However, the present study demonstrated trophic dilution behavior for TMPP and EHDPP among other OPFRs. Recent studies have suggested that chemicals with high biotransformation rates are less likely to biomagnify in aquatic food webs (Walters et al., 2016; Zheng et al., 2016). Further,

TNBP and TBOEP can be rapidly metabolized *in vitro* in fish liver microsomes, with 27% and 25% of the administered compounds depleted in 200 min (Hou et al., 2018). High metabolism rates of TBP, TDCIPP, and TPHP were observed *in vivo* in killifish, with half-lives of 58 h, 31 h and 5 h, respectively (Sasaki et al., 1981). Significant biotransformation of TPHP, TPrP, TNBP, TBOEP, TCEP, TDCPP, and TMPP was also observed in zebrafish, with all metabolites excreted within three days of depuration (Wang et al., 2016; Wang et al., 2017). Therefore, the observed trophic dilution behavior of OPFRs was likely caused by their rapid metabolism in fish. This paper provides strong evidence that OPFRs with $\log K_{ow}$ and BCF values that meet the criteria of bioaccumulation may still exhibit trophic dilution in freshwater lake food webs.

4. Conclusion

In the present study, thirteen OPFRs were detected in plankton, five invertebrate, and eleven fish species from Taihu Lake, China. TIBP was the dominant OPFR in plankton, while TCEP, TCIPP, TDCIPP, and TPHP were the dominant OPFRs in invertebrates and fish. Concentrations of all OPFRs with detection frequencies $>70\%$ showed negative correlations with trophic levels, and the correlations for TCIPP, TDCIPP, and TMPP were statistically significant with estimated TMFs of 0.55, 0.39, and 0.42, respectively. This study provides the first reliable indication that OPFRs exhibit trophic dilution in freshwater lake food webs, and the results will support ecological risk assessments for OPFRs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2018.07.077>.

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