



Original Research

Water temperature governs organophosphate ester dynamics in the aquatic food chain of Poyang Lake

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ARTICLE INFO

Article history:

Received 14 July 2023

Received in revised form

8 February 2024

Accepted 10 February 2024

Keywords:

Organophosphate esters

Driving factor

Bioaccumulation and biomagnification

Ecological risk

ABSTRACT

Organophosphate esters (OPEs) are increasingly recognized as pervasive environmental contaminants, primarily from their extensive application in flame retardants and plasticizers. Despite their widespread presence, the intricacies of OPE bioaccumulation within aquatic ecosystems remain poorly understood, particularly the environmental determinants influencing their distribution and the bioaccumulation dynamics across aquatic food chains. Here we show that water temperature plays a crucial role in modulating the dispersion of OPE in the aquatic environment of Poyang Lake. We quantified OPE concentrations across various matrices, uncovering levels ranging from 0.198 to 912.622 ng L⁻¹ in water, 0.013–493.36 ng per g dry weight (dw) in sediment, 0.026–41.92 ng per g wet weight (ww) in plankton, 0.13–2100.72 ng per g dw in benthic invertebrates, and 0.31–3956.49 ng per g dw in wild fish, highlighting a pronounced bioaccumulation gradient. Notably, the intestines emerged as the principal site for OPE absorption, displaying the highest concentrations among the seven tissues examined. Among the various OPEs, tris(chloroethyl) phosphate was distinguished by its significant bioaccumulation potential within the aquatic food web, suggesting a need for heightened scrutiny. The propensity for OPE accumulation was markedly higher in benthic invertebrates than wild fish, indicating a differential vulnerability within aquatic biota. This study lays a foundational basis for the risk assessment of OPEs as emerging contaminants and underscores the imperative to prioritize the examination of bioaccumulation effects, particularly in benthic invertebrates, to inform future environmental safeguarding strategies.

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1. Introduction

Environmental chemicals, widely distributed in environmental media worldwide, are concerning because of their unknown hazards and risks to the ecosystem [1–3]. Organophosphate esters (OPEs), a type of environmental chemical, are widely used as flame retardants and plasticizers when added to products by physical bonding [4,5]. OPEs have been produced and applied for approximately 150 years, and their production and use are increasing

annually, turning them into high-yield chemicals [6–8]. Given this, it is worth noting that OPEs are highly mobile and are detected in the environment around the globe, including in water, sediment, dust, air, soil, and biota [9]. OPEs have been reported to cause endocrine disruption, with effects on the thyroid hormone, sex hormone, and reproduction and development, and have demonstrated neurotoxicity, hepatotoxicity, and cardiotoxicity [5].

Owning their great variety of substituent groups, OPEs differ considerably in their physicochemical properties (Table S1), demonstrating wide solubility (1.46×10^{-5} – 1.11×10^4 mg L⁻¹ at 25 °C), strong hydrophobicity (log K_{OW} of –0.65 to 9.49), and potential bioaccumulation (0.43–855.3). In addition, OPEs also exhibit photodegradation and autoxidation, which are both affected by

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Abbreviations

| | | | |
|----------|-------------------------------------|--------|---------------------------------------|
| BAF | Bioaccumulation factor | TCEP | Tris(chloroethyl) phosphate |
| BPA-BDPP | Bisphenol A bis(diphenyl phosphate) | TCIPP | Tris(2-chloroisopropyl) phosphate |
| BSAF | Biota-sediment accumulation factor | TCP | Tricresyl phosphate |
| CDP | Cresyl diphenyl phosphate | TDCIPP | Tris(1,3-dichloroisopropyl) phosphate |
| DO | Dissolved oxygen | TDS | Total dissolved solids |
| EHDPP | 2-ethylhexyl diphenyl phosphate | TEHP | Tris(2-ethylhexyl) phosphate |
| LOD | Limit of detection | TEP | Tris(ethyl) phosphate |
| LOQ | Limit of quantification | TIBP | Tris(isobutyl) phosphate |
| LRAT | Long-range atmospheric transport | TIPP | Tris(isopropyl) phosphate |
| NTU | Turbidity | TIPPP | Tris(4-isopropylphenyl) phosphate |
| OPEs | Organophosphate esters | TL | Trophic level |
| PCA | Principal component analysis | TMF | Trophic magnification factor |
| PCB | Polychlorinated biphenyl | TMP | Tris(methyl) phosphate |
| RDA | Redundancy analysis | TNBP | Tris(butyl) phosphate |
| RDP | Resorcinol bis(diphenyl phosphate) | TOC | Total organic carbon |
| RQ | Risk quotient | TPHP | Tris(phenyl) phosphate |
| TBOEP | Tris(2-butoxyethyl) phosphate | TPP | Tris(propyl) phosphate |
| | | WT | Water temperature |

sunlight, temperature, NO concentration, and oxygen content [10,11]. Research showed that the photodegradation rates of aryl-OPEs were greater than those of alkyl- and chloroalkyl-OPEs, indicating that the latter two are more resistant to photolysis [11]. The metabolic transformation of OPEs also differs significantly among aquatic organisms, with tris(phenyl) phosphate (TPHP) and cresyl diphenyl phosphate (CDP) showing higher metabolization rates [12,13]. This is an important factor affecting the bio-concentration potential and bioavailability of OPEs to aquatic organisms [12]. Long-range atmospheric transport (LRAT) and trophic transfer (biomagnification) are properties of OPEs that should be given more attention [14], as they were confirmed in polar regions with vulnerable and fragile ecosystems, inland lakes with industrial development, and coastal regions with dense populations [14–17]. However, understanding the mechanisms driving the physico-chemical properties and bioaccumulation or biomagnification potential of OPEs remains a challenge to understanding their environmental fate.

Biodiversity is an important component regulating ecosystem function [18–20]. Extreme high temperatures and drought can seriously reduce biodiversity and restrict ecosystems [21–23]. The Yangtze River basin experienced extremely high temperatures and drought in August 2022, the most severe in China since the 1960s. Such events can seriously harm the biotic population and significantly change the hydrology and water quality in this basin [22,24]. In addition, climate change can also influence the behavior and distribution of organic pollutants [3]. Previous research has shown that global warming may enhance the LRAT potential of polychlorinated biphenyl (PCB) by reducing environmental levels and enhancing mobility potential [3]. Sediment is considered an important sink of OPEs in aquatic ecosystems, and a major exposure route for benthos [25], and more attention has been given to sediment. Understanding the occurrence of OPEs in sediment is significant to evaluate their bioavailability to the benthos and changes caused to benthic populations [16,26]. However, knowledge regarding the potential mechanisms involved in the occurrence of OPEs in aquatic ecosystems and the effects of climate change on their bioaccumulation/biomagnification is rather scant, especially about the relationship between trophic transfer and biodiversity.

This study focuses on Poyang Lake, selected for its exposure to extreme climatic conditions, specifically the extremely high

temperatures and drought in August 2022. The objectives of this study were to (1) investigate the spatial distribution characteristics of OPEs in surface water and sediment under climate change, (2) estimate the differences in the bioaccumulation and biomagnification potential of OPEs in aquatic food webs in inland lakes, and (3) assess the ecological risk of OPEs to aquatic organisms based on multiple risk assessments.

2. Materials and methods

2.1. Chemicals and reagents

The standards of tris(methyl) phosphate (TMP), tris(ethyl) phosphate (TEP), tris(propyl) phosphate (TPP), tris(isopropyl) phosphate (TIPP), tris(butyl) phosphate (TNBP), tris(isobutyl) phosphate (TIBP), tris(2-ethylhexyl) phosphate (TEHP), tris(2-butoxyethyl) phosphate (TBOEP), 2-ethylhexyl diphenyl phosphate (EHDPP), TPHP, tricresyl phosphate (TCP), CDP, tris(4-isopropylphenyl) phosphate (TIPPP), resorcinol bis(diphenyl phosphate) (RDP), bisphenol A bis(diphenyl phosphate) (BPA-BDPP), tris(chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) were purchased from Dr. Ehrenstorfer GmbH (Germany), and their physicochemical properties were shown in Table S1. The internal standards of TPP-d₂₁, TNBP-d₂₇, TPHP-d₁₅, and TCIPP-d₁₈ were obtained from Chiron AS (Norway) and Toronto Research Chemicals Inc. (Canada). The acetonitrile, methanol, dichloromethane, and *n*-hexane in this study were high performance liquid chromatography (HPLC) grade and purchased from Thermo Fisher Scientific (Waltham, MA, USA). The formic acid was liquid chromatography–mass spectrometry (LC-MS) grade and purchased from Sigma-Aldrich (Darmstadt, Germany).

2.2. Sampling sites and sample collection

Poyang Lake is a swallow and seasonal lake in the Yangtze River basin and the largest freshwater lake in China. In consideration of the extremely high temperatures and drought experienced in the Yangtze River basin in August 2022, 27 water samples, 23 sediment samples, nine sampling sites of benthos (including 13 species of benthos), 14 sampling sites of plankton, five fish species (*Hemiculter leucisculus*, *Pelteobagrus fulvidraco*, *Cyprinus carpio*, *Parabramis*

pekinensis, and *Carassius auratus*), and feathers from two bird species (*Bubulcus ibis* and *Cygnus columbianus*) were collected for analysis. All sampling and aquatic organism information were shown in Fig. S1 and Tables S2–S3 in the Supporting Information.

Surface water (0.5–1 m deep) was collected with a clean hydrophore and stored in 1 L brown glass bottles. Sediment samples were collected with a clean stainless steel grab bucket and stored in glass bottles. Benthos was collected with a Surber sampler and rinsed with methanol and Milli-Q water prior to wrapping in aluminum foil and sealing in a clean aluminum foil bag. Plankton was sampled with a No. 25 plankton net, stored in clean glass bottles, then filtered through and collected in glass microfiber filters (GF/A 1.6 mm, Whatman, Kent, UK) before wrapping in aluminum foil. All collected fish samples were cleaned with Milli-Q water, the body lengths and weights were recorded, and the fish were sealed inside a clean aluminum foil bag. Different fish tissues were carefully dissected, including the brain, heart, gill, liver, intestines, pulmonary alveoli, and skinless dorsal muscle. Feathers of *Bubulcus ibis* and *Cygnus columbianus* were sealed in clean aluminum foil bags. Except for the water samples, which were kept at 4 °C, all sediment and biota samples were kept at –20 and –80 °C, respectively, until the analysis time. The use of plastic products was avoided during sampling. Hydrological data, including water temperature (WT, °C), dissolved oxygen (DO, mg L⁻¹), pH, total dissolved solids (TDS, g L⁻¹), turbidity (NTU), and conductivity (mS cm⁻¹), were measured by a water quality analyzer (YSI ProPlus, USA), and the total organic carbon (TOC) of sediment samples was measured by a TOC analyzer with a solid sample module (Multi N/C 3100-HT1300, Analytik Jena, Germany) as described in Supporting Information SIII and detailed in Table S2.

2.3. Sampling extraction and instrumental analysis of OPEs

Surface water, sediment, and biota samples were extracted and purified based on previous studies, with minor modifications [16,27–30]. The detailed pretreatment procedures were available in Supporting Information SI. In addition, 18 OPEs in this study were detected using an ultra-performance liquid chromatography-tandem mass spectrometer (Waters Co., Milford, MA, USA). The corresponding instrument information and detailed analysis methods are shown in Supporting Information SII and Table S4.

A strict quality control and assurance protocol was conducted during sampling, storage, transport, extraction, and detection. All equipment and utensils were rinsed with methanol and Milli-Q water before use and between samples. The internal standard method was performed to quantify the target OPEs, for which the correlation coefficients (R^2) of calibration curves (13 concentration levels) were >0.99. Field, solvent, and procedure blanks were performed to exclude contamination and interferences during the whole procedure. The recovery rates of OPEs from surface water, sediment, and biota samples ranged from 58.88 to 139.4%, 78.18–138.94%, and 59.73–115.09%, respectively. In this study, the limit of detection (LOD) and the limit of quantification (LOQ), which were defined as signal-to-noise (S/N) ratios of 3 and 10, respectively, ranged from 0.001 to 14.905 and 0.002–48.525 µg L⁻¹. Moreover, concentrations of OPEs below the LOD were replaced by 0, while those between the LOD and LOQ were assigned the value of LOQ/2 [27,31].

2.4. Bioaccumulation and trophic level analysis

The bioaccumulation and biomagnification of OPEs in all aquatic organisms were evaluated by previous research with minor modifications [16,32]. The stable carbon and nitrogen isotope values were calculated to estimate the trophic levels (TLs) and carbon

sources of aquatic organisms (Table S3). The bioaccumulation factor (BAF) and biota-sediment accumulation factor (BSAF) used the OPEs concentrations in water, sediment, and aquatic organisms to describe the bioaccumulation potential of OPEs in aquatic systems. Additionally, the trophic magnification factor (TMF) was adopted to quantify the biomagnification potential of OPEs in aquatic food webs. The detailed calculation process was shown in Supporting Information SIV and SV.

2.5. Risk quotient method: a screening-level risk assessment

The ecological risks of 14 OPEs in surface water were assessed by the risk quotient (RQ) method [33]. According to the calculated RQ values, the ecological risks of OPEs in surface water were classified into levels, i.e., no risk (RQ < 0.01), low risk (0.01 < RQ < 0.1), medium risk (0.1 < RQ < 1), and high risk (RQ > 1) [33,34]. Expected risk prioritization was used to assess the ecological risk of 14 OPEs at 27 sampling sites in Poyang Lake. The detailed procedures were provided in Supporting Information SVI.

2.6. Statistical analysis

All statistical analyses in this study were carried out using IBM SPSS Statistics 26.0 (IBM Corporation, Armonk, NY, USA) and Origin 2023 (OriginLab Corporation, Northampton, MA, USA). First, the normality of OPEs parameters was checked using the nonparametric one-sample Kolmogorov-Smirnoff test. Multivariate correlation analysis was performed to evaluate the correlation between the physical habitat and the distribution of OPEs. If these concentrations were abnormally distributed, the Spearman correlation coefficient was selected; if they were normally distributed, the Pearson correlation coefficient was selected. The redundancy analysis (RDA) was conducted to evaluate the driving factors of the distribution of OPEs in the different physical habitats of Poyang Lake. The principal component analysis (PCA) was performed to determine the variations in OPEs concentrations in aquatic organisms. The significance level (p -value) was set as $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***)

3. Results and discussions

3.1. Distribution and composition differences of OPEs in surface water and sediment

A total of 17 target OPEs were detected in Poyang Lake (Table S5), with the mean concentrations of individual OPEs ranging from 0.198 to 912.622 ng L⁻¹ (Fig. 1a). The total concentration of OPEs detected in Pak Sha Chau (5086.012 ng L⁻¹) was the greatest than other sites, followed by Clam Lake and Duchang village (Fig. S4a). The coefficient of variance of OPEs abundance in Poyang Lake ranged from 28.11% to 336.24%. The coefficients of variance of TMP, TNBP, TPHP, and TCIPP were greater than 100% (Fig. 1b). The detection frequency of OPEs ranged from 11.11% to 100%, with the most frequently detected OPEs being TEP, TIPP, TNBP, TIBP, EHDPP, TPHP, CDP, TCEP, and TDCIPP (100%) (Fig. S2a). TEP (log K_{OW} = 0.80) and TDCIPP (log K_{OW} = 3.65) were the dominant compounds in Poyang Lake, accounting for 12.06–69.18% and 22.62–83.06% of the total OPEs, respectively (Fig. S3a). Furthermore, the correlation analysis results showed that the concentrations of OPEs in surface water were negatively correlated with their hydrophobicity (log K_{OW}) (Fig. S6a), which was also observed in previous research [33]. The distribution characteristics of OPEs in surface water conformed to the hydrophobic characteristics. The results of homology analysis between individual OPEs showed that TIPPP and TIBP, TCIPP and TMP/TIBP/TBOEP/TPHP,

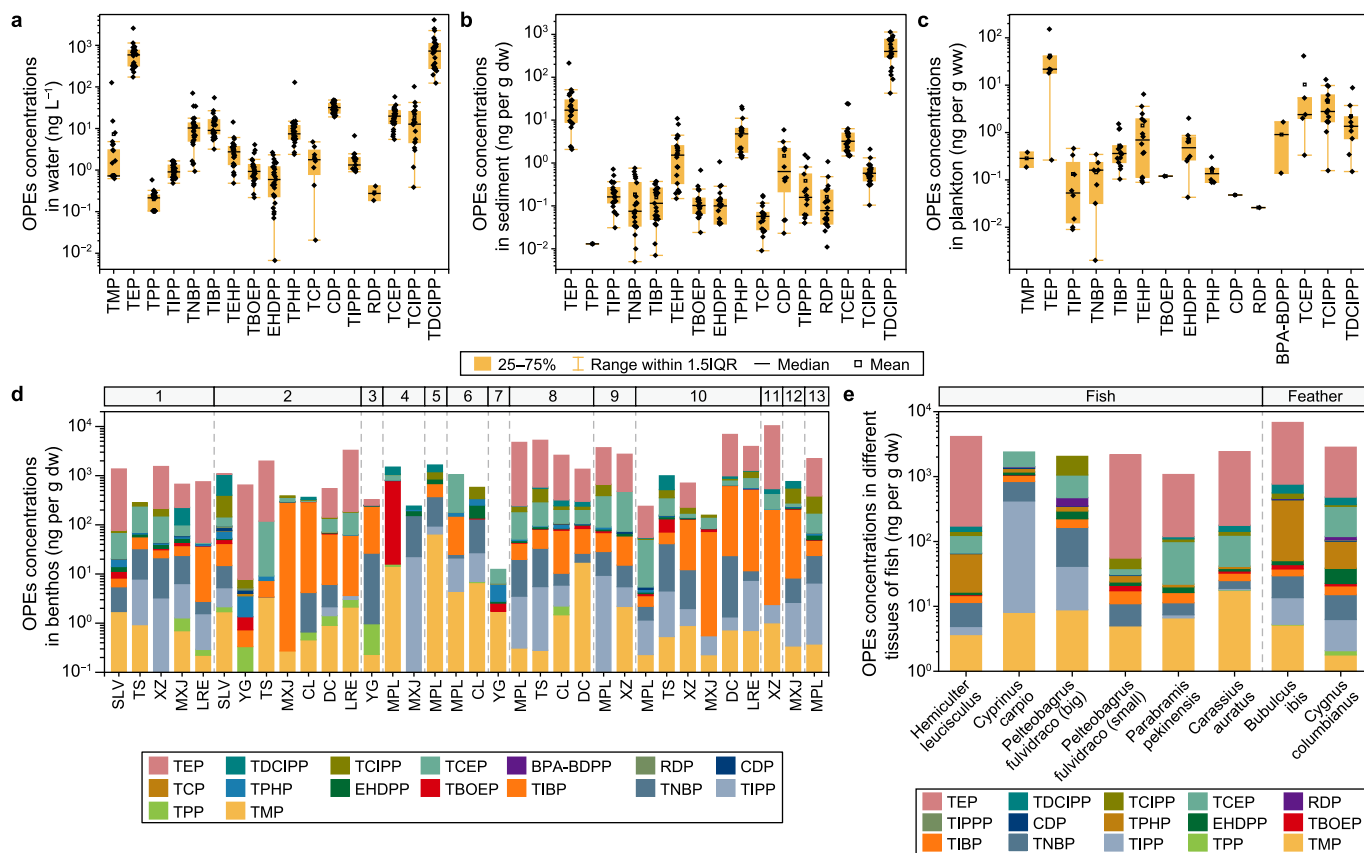


Fig. 1. Distribution characteristics of OPEs in the aquatic environment of Poyang Lake, including surface water (a), sediment (b), plankton (c), benthos (d), and fish and feathers (e). 1, *Parafossarulus sinensis*; 2, *Sinotia quadrata*; 3, *R. Auricularia*; 4, *Limnoperna lacustris*; 5, *Sphaerium lacustre*; 6, *Corbicula fluminea*; 7, *Lamprotula bazini*; 8, *Anodonta*; 9, *Hyriopsis cumingii*; 10, *Unionidae*; 11, *Cuneopsis capitata*; 12, *Macrobrachium nipponense*; 13, *Hemisanax prognathus regan*.

TDCIPP and TEHP/TPHP/TCIPP, and TCEP and TIPP/EHDPP exhibited significant correlations in Poyang Lake, particularly TDCIPP and TPHP, suggesting possible common pollution sources and similar environmental behavior (Fig. S5a). This was also similar to the results of systematic cluster analysis of OPEs (Fig. S5c). In addition, it was found that WT, DO, NTU, and conductivity ($p < 0.05$) may play important roles in driving the occurrence and distribution of OPEs in surface water, particularly WT and NTU ($p < 0.01$), and TEP, CDP, and TIPP ($p < 0.01$) may be the most susceptible OPEs (Figs. 2a and S7a). High water temperature has been reported to increase water evaporation rates, leading to the loss of organic pollutants, especially highly hydrophobic ones, while concentrations of hydrophilic or low hydrophobic pollutants may increase because the rate of water reduction was higher than that of solute reduction [35].

For sediment, 16 target OPEs were detected in Poyang Lake, with mean concentrations ranging from 0.013 to 493.36 ng per g dry weight (dw) (Table S6 and Fig. 1b) and \sum OPEs concentrations ranging from 75.239 to 1151.989 ng per g dw (Fig. S4b). TDCIPP was the dominant compound, accounting for 56.53–98.58% of the total OPEs in sediment from Poyang Lake (Fig. S3b). The coefficient of variance of OPEs abundance ranged from 4.41% to 149.53%, with the coefficient of variance of TPP being 0% and that of TEP, TNBP, TEHP, CDP, TIPP, RDP, and TCEP being greater than 100% (Fig. S2b). The detection frequency of OPEs ranged from 13.04% to 100%, and TIPP, TNBP, TIBP, TEHP, TBOEP, TCEP, TCIPP, and TDCIPP (100%) were the most frequently detected OPEs in sediment from Poyang Lake (Fig. S2b). The results of the correlations analysis showed significant correlations between TNBP and TIPP ($p < 0.001$), TIBP and TNBP ($p < 0.01$), EHDPP and TIBP, TPHP, and EHDPP ($p < 0.01$), TCP and

TIPP, TIPP and TIBP, TCEP and TEP ($p < 0.01$)/TIPP/TIPPP, and TDCIPP and CDP ($p < 0.05$), suggesting similar pollution sources and similar environmental behavior in Poyang Lake (Fig. S5b and d). It is worth noting that although the concentrations of OPEs in sediments were negatively correlated with log TOC, there was a U-shaped correlation with log K_{OW} (Fig. S6b and c). The redundancy analysis of physical habitats showed that WT, DO, and TDS may be important driving factors in the distribution of TEHP ($p < 0.01$), EHDPP ($p < 0.05$), and TCP ($p < 0.05$), respectively (Figs. 2b and S7b). Under high temperatures, the faster disappearance of contaminants in sediment was reported to be due to an increase in microbial metabolic activity, especially for contaminants with high hydrophobicity (i.e., TEHP: log $K_{OW} = 9.49$, lufenuron: log $K_{OW} = 5.12$) [35,36]. The concentration range of OPEs in this study tended to be of a similar order of magnitude to a previous study in Poyang Lake [29]. Many previous research studies have reported a wide range of OPE concentrations in surface water and sediment worldwide, depending on local human activities and climate change [33]. For instance, concentrations of most OPEs in surface water and sediment of Poyang Lake were comparable to those in Laizhou Bay in the Bohai Sea (2017–2018), while concentrations of TEP and TDCIPP detected in this study were far higher than those in Laizhou Bay [37]. However, concentrations of OPEs detected in this study were greater than those in Jiaozhou Bay, Qi'ao Island Mangrove Nature Reserve, and Qin Zhou Bay [38–40]. Moreover, it was consistently reported that chlorinated OPEs (i.e., TDCIPP) were the most frequent and abundant compounds reported in previous research [33], similar to this study. This further demonstrated that it is related to the wide use of TDCIPP as a commercial chemical [29,33].

detected compounds (Fig. S2d and Table S7). It may be attributed to the stronger human activity in Poyang Lake, which diffused widely commercially used OPEs into the aquatic environment [29,33,44]. Interestingly, the occurrences and distributions of TMP ($R_{\text{Spearman}} = 0.80, p < 0.05$) and RDP ($R_{\text{Spearman}} = 0.71, p < 0.05$) in benthos were significantly increased with increasing pH and NTU, respectively, while the concentration of TPP exhibited a significantly negative correlation with pH ($R_{\text{Spearman}} = -0.75, p < 0.05$) (Figs. 2d and S6d). However, the mode of action of these driving factors is still unknown.

The OPEs profiles in fish were different from those in plankton and benthos. As shown in Table S8 and Fig. 1e, there were 16 target OPEs detected in different fish from Poyang Lake (ranging from 0.31 ng per g dw TPP in *Carassius auratus* to 3956.49 ng per g dw TEP in *Hemiculter leucisculus*). The contribution of TEP to the total OPEs in wild fish muscle was generally the greatest, while it was not detected in *Carassius auratus* and *Pelteobagrus fulvidraco* (big) (Fig. S3e). The total concentrations of 16 OPEs in wild fish muscle ranged from 1073.88 ng per g dw (*Parabramis pekinensis*) to 4129.48 ng per g dw (*Hemiculter leucisculus*) (Fig. 1e). These results were generally higher than those in fish species collected from Taihu Lake in 2014, 2016, and 2019 [16,45,46]. TMP, TNBP, TIBP, EHDPP, and TPHP were the most frequent and abundant OPEs in fish muscle in Poyang Lake, followed by TIPP, TCEP, and TCIPP (Table S8). These results indicate that the prevalent contamination of aquatic organisms with OPEs may be caused by the wide distribution of OPEs and OPE-related manufacturing industries [25,29,33]. In addition, total concentrations of alkyl-OPEs, aryl-OPEs, and chlorinated-OPEs in fish muscle samples in Poyang Lake ranged from 224.47 to 3971.69, 5.60 to 349.97, and 24.74–1569.69 ng per g dw (Table S8 and Fig. S8b). Concentrations of these three groups in wild fish muscle samples from Poyang Lake followed the order alkyl- > chlorinated- > aryl-OPEs (except in *Pelteobagrus fulvidraco* (big)) (Fig. S8b). These results may be attributed to the differences in physicochemical properties (i.e., log K_{OW} and bioconcentration factor) among the three functional groups of OPEs [33,45]. Notably, most OPEs concentrations detected in aquatic environments were probably residual levels or unmetabolized OPEs due to the rapid metabolism of OPEs in the body [12,47].

Interestingly, 15 OPEs were frequently detected in feathers of *Bubulcus ibis* and *Cygnus columbianus* collected from Poyang Lake, with concentrations ranging from 0.14 (TPP) to 6039.70 (TEP) ng per g dw and from 0.29 (TPP) to 2342.13 (TEP) ng per g dw, respectively (Table S8, Figs. S7a and 1e). TIPP and TCEP were detected only in *Cygnus columbianus*, at 2.89 and 228.72 ng per g dw, respectively. Alkyl-OPEs were the frequent and abundant compounds in these feathers, followed by chlorinated- and aryl-OPEs (Fig. S8b). Additionally, it was found that concentrations of OPEs in *Bubulcus ibis* were much greater than those in *Cygnus columbianus* (Fig. 1e). An important explanation for the differences observed in this study may be the differences in the food chains these birds participate in Poyang Lake. *Bubulcus ibis*, as a wading bird, feeds mainly on aquatic insects, while *Cygnus columbianus* feeds mainly on aquatic plants.

3.2.2. Tissue-specific distribution of OPEs in wild fish

Distributions of OPEs in other tissue compartments, including brain, heart, gill, liver, intestine, and alveoli from five wild fish species, were further investigated (Table S8, Figs. 3 and S7a). Overall, the concentrations and distributions of individual OPEs in different tissues ranged from 0.12 ng per g dw (TPP) to 7755.88 ng per g dw (TEP), with the most abundant compound being TEP, followed by TCEP, TCIPP, TPHP, TMP, and TDCIPP, suggesting that the concentrations followed order chlorinated > alkyl- > aryl-OPEs

(Fig. 3 and Table S8). The mean concentrations of \sum OPEs were the highest in the intestine (ranging from 2224.46 to 6612.82 ng per g dw), followed by the gill (ranging from 1472.81 to 8192.34 ng per g dw) > the liver (ranging from 760.51 to 7613.53 ng per g dw) \geq the brain (ranging from 622.63 to 5826.26 ng per g dw) > the alveoli (ranging from 190.93 to 5538.12 ng per g dw) > the heart (ranging from 823.32 to 1249.73 ng per g dw) (Fig. S8a and Table S8). The distribution characteristics of OPEs in different tissues from five wild fish species in Poyang Lake were similar to those in six fish species from Zhushan Bay of Taihu Lake [45]. These results were driven by selective deposition of OPEs to a given tissue, enzyme-mediated metabolism, or chemical degradation in the organisms [47]. The liver showed a stronger accumulation potential of OPEs than the other tissues (i.e., brain, alveoli, and heart), which is related to the detoxifying activities of the liver, including the high affinity of the metabolic enzyme cytochrome P450 for OPEs and the high binding of OPEs to blood protein [48–50]. Due to their rapid metabolism in the liver before transport, lower concentrations of OPEs were detected in other tissues [13,51]. Another factor to be considered was the lipid contents of tissues and the partition coefficients between tissues and blood, especially for the distribution of hydrophobic OPEs [48,52]. However, the concentrations of \sum OPEs in the intestine of five fish species were generally higher than those in the gill (Figs. 3a and S8a), suggesting that dietary uptake was the primary route to accumulate OPEs in fish [45].

Among the 16 selected OPEs, TMP was the most frequent compound in each tissue (detection frequency: 91.67%), followed by TIBP (88.89%), TCIPP (88.89%), and TBOEP (80.56%) (Fig. S2e and Table S8). Theoretically, the differential distribution of OPEs in different tissues was driven by their differential metabolism rates that may impede their bioaccumulation [12,13,51,53]. However, higher concentrations of some OPEs in these tissues may also be attributed to their absorption from water and sediment and ingestion of other organisms [33,45]. In addition, the distribution pattern of OPEs in different tissues was further analyzed via PCA (Fig. 3b), suggesting a differential contribution of OPEs. The PCA results showed that the muscle and liver variations were the most considerable, followed by the heart, gill, brain, alveoli, and intestine. Furthermore, the intestine was the tissue with the most accumulated OPEs (i.e., RDP, TPHP, CDP, TBOEP, TNBP, and TIBP), followed by the heart, which accumulated TMP, TEP, and EHDPP; EHDPP tended to accumulate in brain, muscle, and heart; TEP accumulated in alveoli; and TDCIPP easily accumulated in the liver.

3.3. Bioaccumulation and biomagnification characteristics of OPEs in the aquatic food web

3.3.1. Biota-sediment accumulation characteristics of OPEs in aquatic organisms

BSAFs of most OPEs in aquatic organisms were more than 1, indicating bioaccumulation from sediment in aquatic organisms, except for TDCIPP (BSAF < 1) (Table S10). The reason may be attributed to the low hydrophobicity, high soil adsorption, wide commercial applications of TDCIPP, and higher sediment concentrations (Fig. 1b) [29,33]. BSAFs values of OPEs in aquatic organisms from Poyang Lake were much higher than those in mangrove organisms from Qi'ao Island, as BSAFs values of nine OPEs in the latter were greater than 1, occurring bioaccumulation potential [39]. The results showed that log BSAFs of OPEs in Poyang Lake were higher than those observed in Taihu Lake, European river basins, and Pearl River Delta [16,54,55]. In addition, the BSAF values of OPEs in wild fish were greater than those in benthos, suggesting that wild fish with high trophic levels were likely to accumulate OPEs from sediment (Table S10). It was also found that BSAF values of OPEs in fish (0.3–0.7) were higher than those in invertebrates (0.1–0.5)

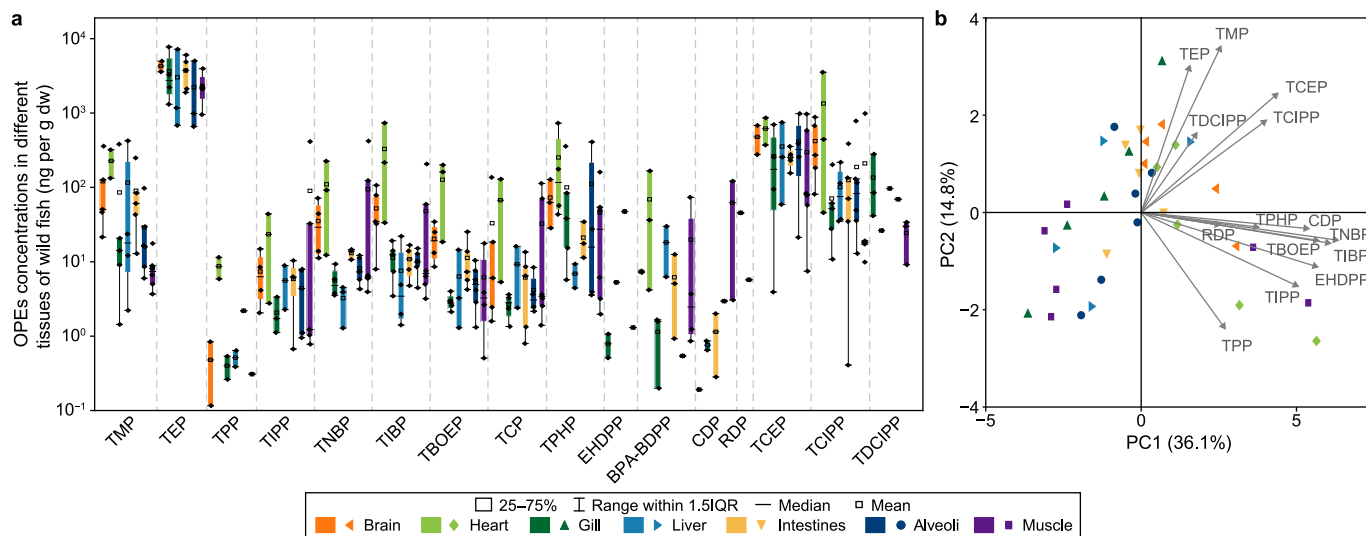


Fig. 3. a. Concentrations of OPEs in the brain, heart, gill, liver, intestines, alveoli, and muscle of wild fish collected from Poyang Lake. b. Principal component analysis (PCA) regarding the distribution characteristics of OPEs in different fish tissues.

from Laizhou Bay, North China, which were more than one order of magnitude lower than those in this study [37]. It was suggested that BSAFs of OPEs showed a species specificity in aquatic organisms (Fig. 4a and S10). It was worth noting that there was an inverted U-shaped correlation between $\log K_{OW}$ and \log BSAF of OPEs in wild fish and benthos (Fig. 4b). This phenomenon was also observed in benthic invertebrates from Taihu Lake and marine species from Laizhou Bay [16,37]. Previous research has shown that the desorption of organic contaminants from sediment and their absorption from pore water can lead to their accumulation in sediment and that absorption of these compounds from ingested sediment may also be an important reason for their accumulation in biota [26,56]. Thus, the differences in BSAF of OPEs may be attributed to the higher $\log K_{OW}$ of OPEs that are prone to be strongly adsorbed in organic matter in sediment, reducing their bioavailability to aquatic organisms. Additionally, the metabolism and elimination of OPEs in wild fish may also play an important role in their bioaccumulation [49].

3.3.2. Trophic level and carbon source analysis in the aquatic food web

The $\delta^{13}C$ and $\delta^{15}N$ values of aquatic organisms showed little variation, ranging from -33.71‰ (*Unionidae*) to -24.17‰ (*Sinotaia quadrata*) and from 9.44‰ (*Lamprotula bazini*) to 15.40‰ (*Carassius auratus*) (Table S3), which was consistent with the range in Taihu Lake [16]. Although the mean $\delta^{13}C$ (-28.61‰) and $\delta^{15}N$ (13.34‰) values of wild fish in Poyang Lake were higher than those of benthos ($\delta^{13}C = -29.48\text{‰}$, and $\delta^{15}N = 11.42\text{‰}$), the difference between these species groups was small. Additionally, the $\delta^{13}C$ values were significantly negatively linearly correlated with $\delta^{15}N$ values (Pearson's $r = -0.75$, $R^2 = 0.56$) in Poyang Lake (Fig. S11). Thus, an analysis of these aquatic organisms showed that they belong to the same aquatic food web in Poyang Lake [32,57].

The TLs of aquatic organisms calculated by the $\delta^{13}C$ and $\delta^{15}N$ values ranged from 1.98 to 3.55 in Poyang Lake, among which the TLs of benthos were 1.98 (*Lamprotula bazini*)–3.21 (*Hyriopsis cumingii*), and those of wild fish ranged from 2.46 (*Cyprinus carpio*) to 3.55 (*Carassius auratus*) (Table S3 and Fig. 5a). The observed variance in TLs among these species is attributed to factors such as habitat restrictions and dietary diversity. These findings differ from those reported in other studies [16,32,57]. In addition, the TL values

of aquatic organisms were positively correlated with the carbon source (ranging from 0 to 2.65, mean of 1.63) in Poyang Lake (Pearson's $r = 0.75$, $R^2 = 0.56$) (Fig. 5a). The carbon source values of other aquatic organisms were greater than 1, except for *Parafossarulus sinensis* (0.40) and *Sinotaia quadrata* (0) (Table S3). The results showed that these organisms were more dependent on pelagic sources, suggesting that the collected organisms belong to the same aquatic food web [32,58]. However, large benthic invertebrates in this study showed a poor probability of being preyed upon by the collected wild fish, which might instead prey on some small bivalves and mussels [16].

3.3.3. Biomagnification characteristics of OPEs in aquatic food webs

Based on these formulas in Supporting Information SIV and V, BAFs and TMFs of all detected OPEs for all aquatic organisms were estimated and presented in Tables S10–S11 and Fig. S12. Log BAF of >3.3 shows bioaccumulation potential, while a value >3.7 shows stronger bioaccumulation [59,60]. The TMFs and mean log BAFs of OPEs in all aquatic organisms, including benthos and wild fish, ranged from 0.45 (TDCIPP) to 9.17 (RDP) and 1.99 ± 0.52 (CDP) to 3.76 ± 0.62 (TCEP) (Fig. S12). TEP, TBOEP, EHDPP, RDP, TCEP, and TCIPP with TMF >1 and \log BAF >3.3 showed potential bioaccumulation and biomagnification in aquatic food web of Poyang Lake (Fig. 5b). While TMP, TPHP, and CDP only showed a bioaccumulation potential, and TPP, TIPP, and TIBP only showed a bioaccumulation potential, except for TNBP and TDCIPP (TMF <1 and BAF <3.3). A negative correlation was found between \log BAFs and concentrations of OPEs in surface water (Fig. S13c), reflecting the propensity to hydrophobicity [33]. Previous in vivo studies have reported that lower exposure concentrations of OPEs might enhance their bioavailability in organisms, whereas higher exposure concentrations might improve their metabolism and reduce bioaccumulation, suggesting that metabolic transformation of OPEs was also a key factor [12,61,62]. The trophic magnification of OPEs was also found in the fish food web in Taihu Lake, where the mean TMFs were noted to be higher than those reported in this study [16]. The results regarding the marine food web of Laizhou Bay showed that TMF values of 17 OPEs were greater than 1, suggesting potential biomagnification, but their values were slightly lower than those in this study [37]. The potential biomagnifications of TEHP, EHDPP, TPHP, TCP, and TCIPP which were slightly lower TMF

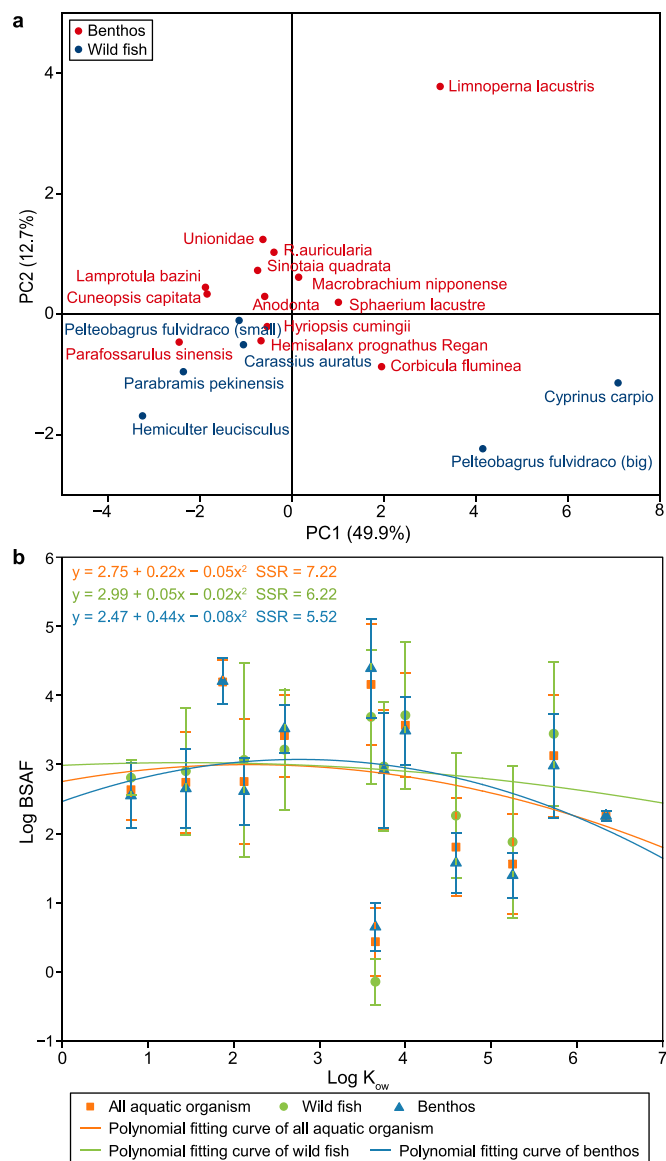


Fig. 4. Correlation analysis regarding the BSAFs of OPEs. **a**, PCA of the differential characteristics of BSAFs in different benthos and wild fish. **b**, Correlation analysis between log K_{ow} and log BSAF of OPEs.

values than those in Poyang Lake except for TPHP ($TMF_{Pearl\ River} = 5.92 > TMF_{Poyang\ Lake} = 1.18$), were reported in the estuarine food web of the Pearl River [60]. In contrast, most OPEs were not biomagnified in mangrove animals from Qi'ao Island in the Pearl River Estuary [39]. It is worth noting that TMF values of 11 OPEs in the tropical marine food web of the South China Sea were less than 1, undergoing trophic dilution rather than biomagnification [63]. The results showed that the biomagnification of OPEs tended to occur in the benthic aquatic food web rather than the marine or pelagic food web [33,64,65].

Interestingly, further study found that the bioaccumulation and biomagnification of OPEs in benthic invertebrates were much stronger than those in wild fish, especially for TIPP, TIBP, TCEP, and TCIPP, with stronger bioaccumulation ($\log BAF > 3.7$), followed by TEP, TPP, TBOEP, and EHDPP, with potential bioaccumulation ($\log BAF > 3.3$) (Fig. 5c and d). The results of PCA regarding BAFs in aquatic organisms have found that most OPEs, especially TNBP, TIBP, TPP, TIPP, TCIPP, and TDCIPP, tended to accumulate in benthos,

while RDP, EHDPP, and TCEP were prone to accumulate in wild fish (i.e., *Cyprinus carpio* and *Pelteobagrus fulvidraco* (big)) (Fig. S13a–b). The results showed that benthos exhibited a higher bioaccumulation of OPEs than wild fish, which was in line with the conclusion drawn in a previous study [32,63]. The reason may be that the metabolization of pollutants in benthos was weaker than that in collected wild fish, resulting in difficulty in their excretion [26]. It may also be attributed to their dominant composition and mutual coupling in aquatic food webs [37]. Moreover, habitat type, lipid storage, physiology, and metabolism differences are also important factors, suggesting species dependence [12,16,33,39,63,66]. Previous research suggested that differences in ecosystem characteristics, including food chain or food web, habitat, and biotransformation of OPEs, might play an important role in the differences among these studies, affecting the trophic transfer of OPEs and their degree of biomagnification [32,37,56,60,67,68]. It was reported that the metabolism rates of aryl-OPEs were larger than those of alkyl- and chlorinated-OPEs, and the *in vitro* ones in humans were the fastest, followed by rats, fish, and birds [12,13,69]. Ingestion of OPEs-contaminated sediment seemed to be the main exposure source and route for OPEs to be bioavailable to benthic organisms [33]. Additionally, there was no significant linear correlation between log BAFs and log K_{ow} of OPEs (Fig. S13d), contrary to the findings of previous research, which may be explained by the species-specific biochemical composition weakening the effect of log K_{ow} on the bioaccumulation potential [60].

3.4. Potential ecological risk of OPEs to the aquatic ecosystem of Poyang Lake

Based on the expected risk prioritization of OPEs, 27 sampling sites in Poyang Lake exhibited an ecological risk of OPEs ($RQ > 0.01$) contamination to aquatic organisms (Fig. S14a), with the highest risks observed in the *Pak Sha Chau* ($RQ = 1.91$) and *Master Temple* ($RQ = 1.09$). Compared with previous research in Poyang Lake ($RQ < 0.1$), the ecological risk of OPEs in this study showed a higher risk for aquatic organisms [29]. The observed differences between these studies were induced by their differential predicted no-effect concentration sources, which this study was derived from the USEPA ECOTOX database and Chinese technical guidelines, including acute toxicity and chronic toxicity, while the previous study mainly focused on acute toxicity [29,33]. In addition, TDCIPP showed a medium risk ($RQ = 0.99$) to aquatic organisms that may be attributed to its higher contribution rate to the concentrations of $\sum OPEs$, and TPHP had a low risk ($RQ = 0.07$) for aquatic ecosystems in Poyang Lake (Fig. S14b). Other OPEs posed no ecological risk to aquatic organisms in Poyang Lake (Fig. S14b). A previous review noted that TPHP and TDCIPP might pose a moderate risk to aquatic ecosystems, such as those in Europe and China [33]. Previous results found for the margin of safety showed that TDCIPP posed an ecological risk of developmental and growth toxicity [70]. Although CDP had a low ecological risk in 27 sampling sites in Poyang Lake, no risk was measured by the expected risk prioritization method due to its lower concentration in water and lower contribution rate to the total concentration of OPEs (Figs. S3a, S14b, and S15). Due to the lack of data regarding the toxicological information of OPEs to aquatic organisms, there are great differences and deficiencies in ecological risk assessments, hindering effective risk management of OPEs.

4. Conclusion

OPEs are ubiquitous in various environmental media of Poyang Lake, extending even to biological matrices such as feathers. This study indicates that WT and DO can drive the distribution of OPEs

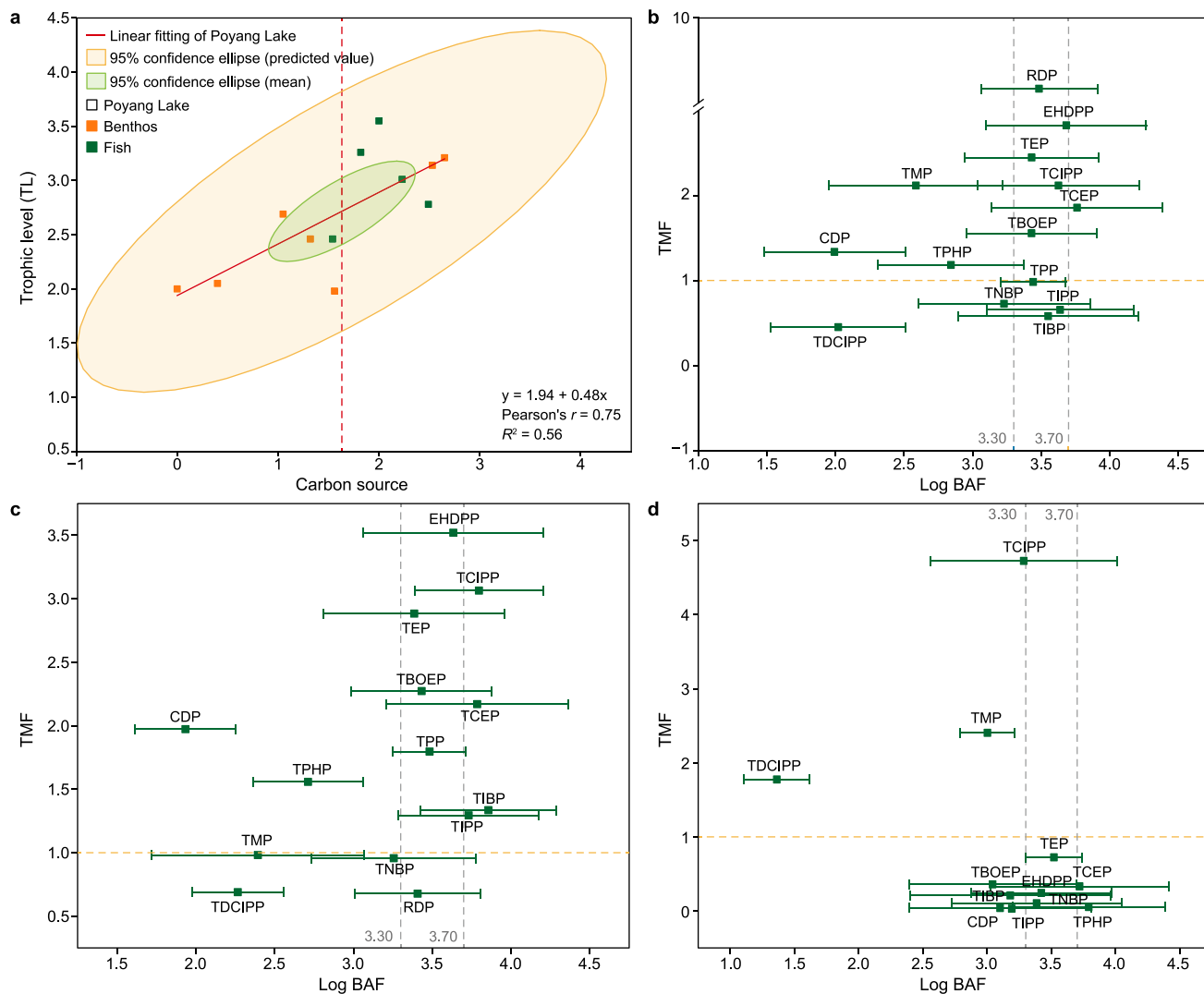


Fig. 5. Bioaccumulation and biomagnification characteristics of OPEs in aquatic organisms. **a.** Correlation analysis of carbon source and trophic level for aquatic organisms in Poyang Lake. The vertical red dotted line represented the mean carbon source values for the food web of Poyang Lake. **b–d.** Differential biomagnification characteristics of OPEs for all aquatic organisms (**b**), benthos (**c**), and wild fish (**d**). TMF >1 indicated trophic magnification in aquatic organisms. 3.30 < log BAF <3.70 indicated potential bioaccumulation, while log BAF >3.70 indicated stronger bioaccumulation.

in the water and sediment of Poyang Lake. Additionally, DO and pH are identified as driving factors influencing OPEs concentrations in plankton and benthic invertebrates. However, the mode of action of these driving factors is still unknown. Although higher OPEs concentrations were detected in wild fish than in benthic invertebrates and plankton, benthic invertebrates tended to accumulate OPEs compared to wild fish based on the analysis of BAFs and TMFs. This difference is attributed to differences in the metabolism of different OPEs in organisms, which remains largely unknown and should be further studied. Dietary intake may be the primary route for wild fish accumulating OPEs rather than respiratory intake. In assessing ecological risks, the cumulative risk of OPEs (\sum OPEs) in Poyang Lake is deemed concerning, as it surpasses the threshold for low risk. This heightened risk is largely attributed to a higher risk of TDCIPP to aquatic ecosystems and its higher contribution rate to the total concentration of OPEs. Due to the lack of data regarding the toxicological information of OPEs to aquatic organisms, there are great differences and deficiencies in ecological risk assessments, hindering effective risk management of OPEs. Meanwhile, there remains a need to compare the distribution and bioaccumulation

characteristics of OPEs between sites with normal climatic conditions and those under extreme conditions, such as high temperatures and droughts, as targeted in this study.

CRediT authorship contribution statement

Zhenfei Yan: Conceptualization, Methodology, Formal Analysis, Data Curation, Writing - Original Draft. **Chenglian Feng:** Conceptualization, Methodology, Investigation, Funding Acquisition, Resources. **Yiping Xu:** Validation, Investigation, Writing - Review & Editing. **Jindong Wang:** Methodology, Data Curation. **Nannan Huang:** Methodology, Validation. **Xiaowei Jin:** Validation, Visualization. **Fengchang Wu:** Project Administration, Resources. **Yingchen Bai:** Project Administration.

Declaration of competing interest

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

Acknowledgements

This research was funded by the National Natural Science Foundation of China (42277274), Postgraduate Research & Practice Innovation Program of Jiangsu Province (422003256), Beijing Natural Science Foundation (8222077), National Key Research and Development Program of China (2021YFC3200104).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ese.2024.100401>.

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