Supplementary materials

A comparative study on the bioaccumulation and trophic transfer of organophosphate esters in marine versus riverine food webs

Sixu Liu[a], Baolin Liu[a, *], Yong Yu[b, *], Junjie Li[a], Xinyu Ma[a]

[a] College of Chemistry, Changchun Normal University, Changchun 130032, China

[b] Research Center of Regional Development and Environment, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun 130102, China

*Corresponding author: Prof. Baolin Liu

E-mail: liubl@ccsfu.edu.cn

*Corresponding author: Prof. Yong Yu

E-mail: yuyong@iga.ac.cn

Text S1 Instrumental conditions for determination of OPEs

8 OPEs were determined using an Agilent 7890A-5977B GC-MS (Agilent Technologies, Santa Clara, CA, USA) operated using a DB-5ms quartz capillary column (60 m×0.25 mm×0.25μm). High-purity helium (purity ≥ 99.999%) was selected as the carrier gas with a flowing speed of 1.2 mL/min. The injector temperature was set to 260 ℃ and the injection volume was 1 μL using split injection (10:1). The column temperature was initially set to 60℃ and subsequently rose to 280 ℃ at 5 ℃/min and held for 10 min. The solvent delay time was 10 min. The temperatures of ion source, quadrupole and transmission line were 230 ℃, 150 ℃ and 260 ℃, respectively.

Text S2 Detection of the abundances of nitrogen stable isotope

All biological samples were washed with Milli-Q® water. The muscles were selected as the samples for fish and invertebrates, and all the biological individuals were taken as the samples for phytoplankton. The powdered sample was obtained after freeze-dried at -80℃ in vacuum. 0.1 g of biological sample was weighed into a vial, in which 10 mL of methanol was added. The mixture was oscillated for 24 h to remove the lipid from the biological samples. After removing the lipid, the sample was dried at 80 ℃ and stabilized for 4 h. Subsequently, 0.5 mg of biological sample was accurately weighed into a tip cup for instrumental analysis. The isotopic compositions of nitrogen in the organisms were determined using an isotope ratio mass spectrometer (Delta Plus, Thermo Finigan, USA). The stable nitrogen isotope abundances ($\delta^{15}N$) are calculated in equation (1):

$$\delta^{15}N(‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000 \qquad (1)$$

where R_{sample} and $R_{standard}$ represent $^{15}N/^{14}N$ in the sample and standard, respectively.

Text S3 The calculation of BAF and BSAF

BAF (L/kg) and BSAF were calculated using the following equations (2) and (3):

$$BAF_{ww} = \frac{C_{organism}}{C_{water}} \times 1000 \qquad (2)$$

$$BSAF_{ww} = \frac{C_{organism}}{C_{sediment}} \qquad (3)$$

where $C_{organism}$, C_{water} and $C_{sediment}$ denote the concentrations of OPEs in organisms (ng/g wet weight, ww), water (ng/L) and sediment (ng/g ww).

Considering the impact of biological lipid, BAF and BSAF were normalized with lipid content to make the data comparable (OECD, 2012), which were calculated by equations (4) and (5):

$$BAF_{lw} = \frac{BAF_{ww}}{L_{organism}} \qquad (4)$$

$$BSAF_{lw} = \frac{BSAF_{ww}}{L_{organism}} \qquad (5)$$

where BAF_{lw} (L/kg) and $BSAF_{lw}$ denote lipid-normalized BAF and BSAF, respectively. $L_{organism}$ is the lipid content of organism.

Reference

OCED. 2012. OCED guideline for testing of chemicals 305. Bioaccumulation in fish: Aqueous and dietary exposure. Organization for Economic Co-operation and development. http://www.pbtprofiler.net/criteria.asp

Text S4 The calculation of trophic level and trophic magnification factor

The isotopic compositions of nitrogen ($\delta^{15}N$) in the organisms were used to calculate the trophic level (TL) of each species, which was shown in equation (6):

$$TL_{consumer} = 2 + \frac{\delta^{15}N_{consumer} - \delta^{15}N_{reference}}{\Delta\delta^{15}N} \qquad (6)$$

where $\Delta\delta^{15}N$ is the concentration factor of adjacent TLs (3.4‰) (Goutte et al., 2020). The primary producers are *Mactra veneriformis* with TL=2 in Liaodong Bay and *Viviparus chui* with TL=2 in Songhua River. Subsequently, TL and logarithm of lipid-normalized concentration of OPEs (ng/g lipid weight, lw) were analyzed to obtain the regression equation (7):

$$\log C_{organism\ lw} = a + b \times TL \qquad (7)$$

The trophic magnification factor (TMF) of OPEs was obtained by equation (8) (Qadeer et al., 2019):

$$TMF = 10^{b} \qquad (8)$$

where TMF<1 indicates biodilution of OPEs, while TMF>1 suggests biomagnification of OPEs in aquatic food web.

References:

Goutte, A., Alliot, F., Budzinski, H., Simonnet-Laprade, C., Santos, R., Lachaux, V., Maciejewski, K., Le Menach, K., Labadie, P., 2020. Trophic Transfer of Micropollutants and Their Metabolites in an Urban Riverine Food Web. Environ. Sci. Technol. 54, 8043-8050. https://doi.org/10.1021/acs.est.0c01411

Qadeer, A., Liu, M., Yang, J., Liu, X., Khalil, S.K., Huang, Y., Habibullah-Al-Mamun, M., Gao, D., Yang, Y., 2019. Trophodynamics and parabolic behaviors of polycyclic aromatic hydrocarbons in an urbanized lake food web, Shanghai. Ecotoxicol. Environ. Saf. 178, 17-24. https://doi.org/10.1016/j.ecoenv.2019.04.003

Text S5 Health risk assessment

The consumption of aquatic food is the main route of exposure to OPEs by human. The estimated daily intake (EDI) (mg/(kg·d)) was calculated by equation (9):

$$EDI = \frac{C \times IR}{BW} \times 10^{-6} \qquad (9)$$

C is the concentration of OPEs in aquatic products (ng/g wet weight, ww). IR represents the consumption rate of organisms (g/d), which is 50 g/d and 142.2 g/d for child and adult, respectively (Leung et al., 2000; US EPA, 2000). BW is the body weight, which is set at 15 kg and 60 kg for child and adult, respectively (Cheung et al., 2007; US EPA, 1997).

Hazard quotient (HQ) is defined as the ratio of EDI of reference doses (RfD) for each OPE congener, which is calculated by equation (10).

$$HQ = \frac{EDI}{RfD} \qquad (10)$$

where RfD is the reference dose of OPEs, which is shown in **Table S3**. HQ is used to estimate the potential risks of human exposed to OPEs through the consumption of aquatic organisms. HQ ≤ 1 indicates that OPEs have no obvious health risk to human, whereas HQ >1 suggests that OPEs pose a potential risk of to human health. The health risk index of 8 OPEs is calculated by the total hazard quotient (THQ) using equation (11):

$$THQ = \sum_{i=1}^{n} HQ_i \qquad (11)$$

where i represents OPE homologue; n is the number of selected OPEs.

The carcinogenic risk by three carcinogenic OPEs including TCEP, TNBP and TEHP can be estimated by incremental lifetime cancer risk (ILCR) using equation (12):

$$ILCR = \frac{C \times IR \times EF \times ED \times CSF}{BW \times AT} \times 10^{-6} \qquad (12)$$

where EF is the exposure frequency (365 d/a); ED is exposure duration (70 a) (Zhang et al., 2020). AT is average exposure time (25550 d) (Zhang et al., 2020). CSF is the oral cancer slope factor ((kg·d)/mg) of TCEP, TNBP and TEHP with a value of 0.02, 0.009 and 0.0032, respectively (Li et al., 2018). The value of ILCR less than 1×10^{-6} indicates a negligible carcinogenic risk; the value of ILCR ranging from 1×10^{-6} to 1×10^{-4} suggests the potential carcinogenic risk; the value of ILCR greater than 1×10^{-4} shows a high carcinogenic risk.

References

Cheung, K.C., Leung, H.M., Kong, K.Y., Wong, M.H., 2007. Residual levels of DDTs and PAHs in freshwater and marine fish from Hong Kong markets and their health risk assessment. Chemosphere 66, 460–468. https://doi.org/10.1016/j.chemosphere.2006.06.008

Leung, S.S.F., Chan, S.M., Lui, S., Lee, W.T.K., Davies, D.P., 2000. Growth and nutrition of Hong Kong children aged 0–7 years. J. Paediatr. Child Health 36, 56–65. https://doi.org/10.1046/j.1440-1754.2000.00441.x

US EPA, 1997. US EPA. Exposure Factors Handbook. Environmental Protection Agency. https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=12464

US EPA, 2000. US EPA. Guidance for Assessing Chemical Contaminant, Data for Use in Fish Advisories, Vol 1: Fish Sampling and Analysis. 3rd ed. https://www.researchgate.net/publication/263062176_National_Guidance_Guidance_for_Assessing_Chemical_Contaminant_Data_for_Use_In_Fish_Advisories

Zhang, C., Li, Y., Wang, C., Feng, Z., Hao, Z., Yu, W., Wang, T., Zou, X., 2020. Polycyclic aromatic hydrocarbons (PAHs) in marine organisms from two fishing grounds, South Yellow Sea, China: Bioaccumulation and human health risk assessment. Mar. Pollut. Bull. 153, 110995. https://doi.org/10.1016/j.marpolbul.2020.110995

Li, J., Zhang, Z., Ma, L., Zhang, Y., Niu, Z., 2018. Implementation of USEPA RfD and SFO for improved risk assessment of organophosphate esters (organophosphate flame retardants and plasticizers). Environ. Int. 114, 21-26. https://doi.org/10.1016/j.envint.2018.02.027

Text S6 Fugacity Model

The migration of OPEs is driven by fugacity gradients between organisms of varying trophic levels. Fugacity tends to be equalized across all biological units under equilibrium conditions, based on which the fugacity formula (13) is derived to characterize OPE accumulation equilibrium in marine organisms.

$$f_w \times D_w + f_A \times D_A + f_R \times D_R = f_B \times (D_w + D_E + D_M + D_G) \qquad (13)$$

Here, f_W, f_A and f_B represent OPE fugacity in water, food sources and biological tissues. D_W, D_A, D_E, D_G and D_M are the transfer parameters for respiration, ingestion, excretion, growth and metabolism. f_R and D_R correspond to in-vivo OPE fugacity and its biodegradation coefficient. Definitions of all parameters in equation (13) are given as follows:

$$D_T = D_W + D_E + D_M + D_G \quad (14) \qquad A = \frac{D_A}{D_T} \quad (15) \qquad R = \frac{D_R}{D_T} \quad (16)$$

Equation (13) can be simplified into equation (17):

$$f_B = f_W \times W + f_A \times A + f_R \times R \qquad (17)$$

where f_W, f_A and f_R refer to fugacity factors of three exposure pathways including water, food and parent materials. $f_A \times A$ and $f_R \times R$ denote the pollutant loads accumulated in biota via their respective exposure routes. Given that benthic animals depend on pore water for their respiratory processes, $f_W \times W$ should be modified to $W \times (X_W \times f_W + X_S \times f_S)$, where f_S is the fugacity factor of contaminant in pore water. X_W and X_S denote the proportions of the two respiratory routes. Generalizing the individual-level fugacity equation to food web systems yields the fugacity model for trophic level *i*, as shown in equation (18):

$$f_i - \sum A_{ji} \times f_j = W_i \times (X_{iW} \times f_W + X_{is} \times f_s) + R_i \times f_{iR} \qquad (18)$$

Accordingly, the fugacity model characterizing OPEs transfer across various trophic levels within the marine food web is formulated as the matrix Equation (19):

$$\begin{bmatrix} 1-A_{11} & -A_{21} & \dots & -A_{n1} \\ -A_{12} & 1-A_{22} & \dots & -A_{n2} \\ \dots & \dots & \dots & \dots \\ -A_{1n} & -A_{2n} & \dots & 1-A_{nm} \end{bmatrix} \begin{pmatrix} f_1 \\ f_2 \\ \dots \\ f_n \end{pmatrix} = \begin{pmatrix} W_1 \times (X_{1W} \times f_W + X_{1S} \times f_S) \\ W_2 \times (X_{2W} \times f_W + X_{2S} \times f_S) \\ \dots \\ W_n \times (X_{nW} \times f_W + X_{nS} \times f_S) \end{pmatrix} + \begin{pmatrix} R_1 \times f_{1R} \\ R_2 \times f_{2R} \\ \dots \\ R_n \times f_{nR} \end{pmatrix} \quad (19)$$

Equation (19) is used to obtain OPE fugacity in biota across all trophic levels, followed by concentration estimation with Equation (20):

$$C_i = f_i \times Z_i \qquad (20)$$

where Z_i represents the fugacity capacity of OPEs in organisms at each trophic level. The OPE ingestion flux of the *i*-th biological functional group via the *j*-th pathway can be quantified using Equation (21).

$$FLX_{ij} = f_{ij} \times D_{ij} \qquad (21)$$

where D_{ij} is the fugacity parameter. The values of Z_i and D_{ij} can be calculated using equation (19). The half-lives (d) of 8 OPEs are 0.471, 0.542, 0.467, 0.521, 0.492, 0.571, 5.14 and 3.07 for TCEP, TCIPP, TDCIPP, TPHP, TNBP, TBOEP, TEHP and TPP, respectively. The density (kg/m^3) and concentrations (g/m^3) of sediment are 4.50×10^5 and 1500, and those of suspended solids are 1.25 and 1500, respectively (Tang et al., 2019).

Tang, B., Poma, G., Bastiaensen, M., Yin, S.-S., Luo, X.-J., Mai, B.-X., Covaci, A., 2019. Bioconcentration and biotransformation of organophosphorus flame retardants (PFRs) in common carp (Cyprinus carpio). Environ. Inter. 126, 512-522. https://doi.org/10.1016/j.envint.2019.02.063

Table S1 Name and biological information of organisms in Liaodong Bay

Species	site	n	Length (cm)	Weight (g)	Lipid contents (%)
Mactra veneriformis	A, B	20	3.65±0.432	20.6±2.34	2.70±0.241
Dosinia laminata	B	12	4.05±0.560	37.6±2.11	3.21±0.162
Alvenius ojianus	A	9	7.31±0.122	106±6.27	3.29±0.213
Pampus argenteus	A, B	15	20.4±1.16	112±0.281	7.44±0.424
Arius sinensis	B	17	21.9±3.17	51.4±8.24	8.27±0.392
Cynoglossus semilaevis	A, B	12	34.0±2.95	312±2.48	7.07±0.110
Hexagrammos indicus	A, B	20	43.2±0.362	468±1.45	8.67±0.742
Octopus ocellatus	A	12	22.1±2.42	40.6±5.28	3.12±0.131
Haliotis discus hannai	A, B	23	9.01±2.32	58.3±0.913	4.95±0.474
Trachinotus ovatus	A, B	6	34.5±2.56	675±0.743	10.3±0.132
Scomberomorus niphonius	B	22	43.7±0.153	578±1.65	9.07±0.272
Oratosquilla woodmasoni	A	14	21.4±5.02	30.9±4.28	5.21±0.315
Ostrea gigas Thunberg	B	13	14.0±1.05	251±1.35	5.77±0.232
Rapana rapiformis	A	9	8.05±1.23	90.3±10.2	5.01±0.157
Portunus trituberculatus	A	11	27.4±0.232	140±14.7	4.00±0.253
Ammodytes personatus	B	20	12.5±1.10	5.52±0.653	4.42±0.227
Lophius litulon	A, B	20	52.7±1.43	1887±9.79	7.70±0.375

Table S2 Name and biological information of organisms in Songhua River

Species	site	n	Length (cm)	Weight (g)	Lipid contents (%)
Leuciscus waleckii	C	16	39.9±2.43	257±5.54	4.06±1.48
Carassius auratus	D	10	9.52±0.541	38.6±3.13	7.26±0.542
Leuciscus baicalensis	C, D	17	13.3±0.144	31.8±3.27	8.94±0.413
Barbatula nuda	C, D	14	5.67±1.16	12.9±0.285	7.50±0.753
Culter alburnus	C, D	12	13.9±0.178	41.3±1.24	9.05±0.457
Pseudobagrus ussuriensis	C, D	18	47.9±5.91	281±2.48	8.80±1.28
Pelteobagrus fulvidraco	C, D	17	15.4±0.623	41.3±1.89	6.26±1.74
Siniperca chuatsi	C, D	10	14.1±3.43	55.4±4.92	7.08±1.28
Hypophthalmichthys molitrix	C, D	12	20.8±3.71	80.3±2.81	8.2±0.473
Acanthorhodeus chankaensis	C	14	3.45±0.565	8.28±0.742	11.7±2.18
Eriocheir sinensis	D	13	19.8±0.0952	80.8±0.765	9.07±5.76
Dytiscidae	D	24	3.34±1.02	6.91±0.382	5.18±0.421
Cristaria plicata	D	12	38.0±1.95	367±7.75	7.78±6.12
Viviparus chui	C	11	2.33±1.06	7.45±2.39	10.9±0.655
Potamogeton crispus	C, D	17	/	28.4±9.89	0.531±0.0579
Spirogyra	C, D	14	/	19.5±5.76	0.592±0.0213
Ceratophyllum demersum	C, D	12	/	23.7±3.84	0.525±0.0787

Table S3 MS parameters, limits of detection (LODs), limits of quantification (LOQs) of 8 OPEs

OPEs	Abbreviation	Retention time (min)	Characteristic ion	LODs (ng/g)	LOQs (ng/g)	RfD (mg/(kg·d))		$logK_{ow}$[3]
						Values	References	
tris(2-chloroethyl) phosphate	TCEP	30.75	205, 223, 249	0.234	0.779	0.022	[1]	1.63
tris(2-chloroisopropyl) phosphate	TCIPP	31.52	99, 125, 157	0.00605	0.0202	0.008	[2]	2.89
tri(1,3-dichloro-2-propyl) phosphate	TDCIPP	41.58	99, 191, 381	0.119	0.396	0.015	[1]	3.65
tris(2-butoxyethyl)phosphate	TBOEP	42.58	125, 199, 299	0.0345	0.115	0.015	[1]	3.00
tributyl phosphate	TNBP	28.07	99, 155, 211	0.00533	0.0178	0.024	[1]	3.82
tri-n-propyl phosphate	TPP	21.61	99, 141, 183	0.00469	0.0156	na		2.67
tris(2-ethylhexyl)phosphate	TEHP	43.50	99, 211, 268	0.0118	0.0394	0.035	[1]	9.49
triphenyl phosphate	TPHP	42.68	215, 325, 326	0.00408	0.0136	0.07	[1]	4.70

na means data is not available

References

[1] Gu, L., Hu, B., Fu, Y., Zhou, W., Li, X., Huang, K., Zhang, Q., Fu, J., Zhang, H., Zhang, A., Fu, J., Jiang, G., 2023. Occurrence and risk assessment of organophosphate esters in global aquatic products. Water Res. 240, 120083. https://doi.org/10.1016/j.watres.2023.120083

[2] Zhang, X., Zou, W., Mu, L., Chen, Y., Ren, X., Hu, X., Zhou, Q., 2016. Rice ingestion is a major pathway for human exposure to organophosphate flame retardants (OPFRs) in China. J. Hazard. Mater. 318, 686-693. https://doi.org/10.1016/j.jhazmat.2016.07.055

[3] Li, X., Zhao, N., Fu, J., Liu, Y., Zhang, W., Dong, S., Wang, P., Su, X., Fu, J., 2020. Organophosphate Diesters (Di-OPEs) Play a Critical Role in Understanding Global Organophosphate Esters (OPEs) in Fishmeal. Environ. Sci. Technol. 54, 12130-12141. https://doi.org/10.1021/acs.est.0c03274

Table S4 Food web model in LDB[1]

	1	2	3	4	5	6
Species	Small mollusks	Small crustaceans	Large crustaceans	Small fishes living in middle-upper layer of seawater	Demersal fishes	Benthic predators
1	0	0.15	0.3	0.2	0.35	0.2
2	0.05	0.05	0.2	0.25	0.35	0.4
3	0	0	0	0	0	0.05
4	0	0	0.05	0.1	0.15	0.15
5	0	0	0	0	0	0.15
6	0	0	0	0	0.15	0

Reference

[1] Tong, L., Tang, Q., Pauly, D., 2000. A preliminary approach on mass-balance ecopath model of the Bohai Sea. Chinese Journal of Applied Ecology 11, 435-440.

Table S5 Parameters of biological properties used for fugacity modeling

Species	Small mollusks	Small crustaceans	Large crustaceans	Demersal fishes	Small fishes living in middle-upper layer of seawater	Benthic predators
Volume (cm^3) [1]	0.128	0.211	5.19	14.7	14	70.7
Lipid content	0.0753	0.0724	0.0396	0.0848	0.11	0.854
Growth rate (/d)[1]	0.0188	0.0219	0.00548	0.00649	0.00575	0.00219
Feeding rate (/d)[1]	0.0751	0.0822	0.0192	0.0216	0.0238	0.0126
Ratio of respiration in overlying water to the total respiration [1-3]	0.5	0.6	0.8	1	1	0.75
Ratio of respiration in pore water to the total respiration [1-3]	0.5	0.4	0.2	0	0	0.25
Absorption factor of intestinal tract from water[4]	5.3×10-8	5.3×10-8	5.3×10-8	5.3×10-8	5.3×10-8	5.3×10-8
Absorption factor of intestinal tract from lipid[4]	3	3	1.5	1.5	1.5	1.5

[1] Tong, L., Tang, Q., Pauly, D., 2000. A preliminary approach on mass balance ecopath model of the Bohai Sea. Chinese journal of Applied Ecology 11, 435-440.
[2] Deng, J., Meng, T., Ren, S., 1988a.The fish species composition, abundance and distribution in the Bohai Sea. Marine Fisheries Research 9, 11-90.
[3] Deng, J., Zhu, J., Chen, J., 1988b. Main invertebrates and their fishery biology in the Bohai Sea. Marine Fisheries Research 9, 91-120.
[4] Campfens, J., Mackay, D., 1997. Fugacity-based model of PCB bioaccumulation in complex aquatic food webs. Environ. Sci. Technol. 31, 577-583. https://doi.org/10.1021/es960478w

Table S6 Logarithmic BAF_{ww} (L/kg, wet weight, ww) of OPEs in the organisms from Liaodong Bay

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Median value of fish	**0.996**	**0.231**	**1.05**	**1.15**	**0.879**	**0.844**	**0.532**	**1.95**
Pampus argenteus	0.847	-0.202	1.50	1.63	0.675	1.75	0.451	1.82
Arius sinensis	0.985	-0.224	0.870	1.10	0.969	1.56	0.413	1.92
Cynoglossus semilaevis	1.12	0.166	0.862	0.972	0.914	0.480	0.506	1.94
Hexagrammos indicus	0.927	-0.143	0.750	0.945	0.799	/	0.230	1.98
Trachinotus ovatus	1.00	0.479	1.46	0.891	1.27	1.07	0.789	1.79
Scomberomorus niphonius	0.939	0.409	1.05	1.62	0.802	2.32	0.361	1.96
Ammodytes personatus	0.996	0.236	1.31	1.17	1.04	0.609	0.607	2.04
Lophius litulon	0.996	0.510	1.05	1.20	0.899	0.889	0.790	1.81
Median value of benthos	**0.902**	**-0.007**	**0.882**	**0.937**	**0.741**	**0.532**	**0.506**	**1.89**
Mactra veneriformis	0.904	-0.240	1.45	0.723	0.468	1.06	0.654	1.88
Dosinia laminata	1.01	0.114	0.859	0.962	1.10	0.201	0.739	2.12
Alvenius ojianus	0.715	-0.260	0.567	0.916	0.523	-0.0491	0.336	2.02
Octopus ocellatus	0.692	-0.217	0.922	0.575	0.382	0.304	0.103	1.55
Haliotis discus hannai	0.998	-0.262	1.23	1.20	0.687	1.59	0.624	1.94
Ostrea gigas Thunberg	0.942	0.132	0.845	0.810	1.01	0.923	0.617	2.18
Rapana rapiformis	0.830	0.260	0.972	1.10	0.910	0.869	0.672	1.98
Oratosquilla woodmasoni	0.665	0.263	0.968	1.01	0.637	0.258	0.427	1.86
Portunus trituberculatus	0.959	-0.281	0.940	0.988	0.691	0.439	0.401	1.82
Median value of all the species	**0.942**	**0.114**	**0.968**	**0.988**	**0.802**	**0.879**	**0.506**	**1.94**

Table S7 Logarithmic BAF_{lw} (L/kg, lipid weight, lw) of OPEs in the organisms from Liaodong Bay

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Median value of fish	**2.09**	**1.35**	**2.11**	**2.25**	**2.04**	**2.00**	**1.64**	**3.07**
Pampus argenteus	1.98	0.911	2.63	2.75	1.82	2.88	1.56	2.96
Arius sinensis	2.07	0.856	1.96	2.17	2.05	2.64	1.49	2.99
Cynoglossus semilaevis	2.27	1.31	2.01	2.12	2.07	1.64	1.66	3.09
Hexagrammos indicus	1.99	0.905	1.81	2.00	1.86	0.746	1.32	3.04
Trachinotus ovatus	1.99	1.46	2.45	1.88	2.25	2.07	1.77	2.78
Scomberomorus niphonius	1.98	1.45	2.10	2.66	1.85	3.36	1.40	3.00
Ammodytes personatus	2.34	1.60	2.66	2.53	2.39	1.96	1.96	3.38
Lophius litulon	2.11	1.62	2.17	2.32	2.02	2.00	1.90	2.93
Median value of benthos	**2.27**	**1.36**	**2.33**	**2.30**	**2.10**	**1.87**	**1.90**	**3.28**
Mactra veneriformis	2.50	1.31	3.04	2.28	2.01	2.61	2.25	3.43
Dosinia laminata	2.54	1.59	2.33	2.43	2.57	1.70	2.23	3.69
Alvenius ojianus	2.18	1.21	2.06	2.41	2.00	1.32	1.81	3.51
Octopus ocellatus	2.20	1.29	2.43	2.09	1.89	1.06	1.61	3.05
Haliotis discus hannai	2.30	1.04	2.54	2.51	1.99	2.89	1.93	3.25
Ostrea gigas Thunberg	2.18	1.37	2.08	2.04	2.25	2.16	1.85	3.42
Rapana rapiformis	2.13	1.56	2.27	2.40	2.21	2.17	1.97	3.28
Oratosquilla woodmasoni	1.95	1.56	2.25	2.29	1.92	1.54	1.72	3.14
Portunus trituberculatus	2.37	1.11	2.34	2.38	2.10	1.84	1.80	3.23
Median value of all the species	**2.18**	**1.31**	**2.27**	**2.32**	**2.02**	**2.00**	**1.80**	**3.14**

Table S8 Logarithmic BAF_{ww} (L/kg, wet weight, ww) of OPEs in the organisms from Songhua River

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Median value of fish	**1.96**	**0.410**	**1.89**	**1.52**	**0.360**	**2.24**	**1.03**	**1.57**
Leuciscus waleckii	2.00	/	1.95	1.92	0.240	2.24	1.91	1.57
Carassius auratus	1.99	/	1.51	1.52	-0.0900	2.05	0.945	/
Leuciscus baicalensis	2.00	1.03	2.29	2.11	0.708	1.61	1.65	0.728
Barbatula nuda	1.97	/	/	/	/	/	/	/
Culter alburnus	1.95	/	1.54	0.922	0.0750	2.52	/	/
Pseudobagrus ussuriensis	1.90	0.905	1.72	1.43	0.373	2.14	0.634	1.16
Pelteobagrus fulvidraco	1.97	0.0480	2.52	1.38	0.320	2.07	1.43	1.60
Siniperca chuatsi	1.96	/	1.48	/	0.457	2.39	0.846	2.70
Hypophthalmichthys molitrix	1.87	/	2.49	/	/	1.63	/	1.88
Acanthorhodeus chankaensis	1.81	-0.250	2.16	1.20	0.615	2.54	0.880	1.95
Median value of benthos	**1.59**	**0.651**	**2.74**	**1.71**	**0.458**	**1.32**	**1.08**	**2.70**
Eriocheir sinensis	1.15	/	2.70	0.280	1.31	1.85	/	2.70
Dytiscidae	1.08	/	2.59	0.180	/	1.78	1.05	2.50
Cristaria plicata	1.70	/	2.90	/	0.368	/	1.09	2.73
Viviparus chui	1.33	0.651	2.71	1.72	0.646	1.33	0.741	2.76
Median value of phytoplankton	**0.167**	**1.13**	**1.73**	**1.85**	**0.371**	**2.32**	**1.66**	**2.68**
Potamogeton crispus	0.130	1.13	1.88	1.95	-0.0310	2.54	1.82	2.23
Spirogyra	0.310	1.20	0.947	1.85	0.337	2.29	1.66	2.71
Ceratophyllum demersum	-0.434	1.06	2.19	1.67	0.461	1.79	1.65	2.66
Median value of all the species	**1.87**	**0.967**	**2.17**	**1.52**	**0.370**	**2.07**	**1.09**	**2.36**

"/" indicates that OPE congeners were not detected in the species, or their concentrations were below the corresponding LODs.

Table S9 Logarithmic BAF_{lw} (L/kg, lipid weight, lw) of OPEs in the organisms from Songhua River

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Median value of fish	**3.06**	**1.39**	**2.94**	**2.63**	**1.52**	**3.35**	**2.07**	**2.82**
Leuciscus waleckii	3.25	/	3.20	3.16	1.49	3.49	3.16	2.82
Carassius auratus	3.10	/	2.62	2.63	1.02	3.16	2.06	/
Leuciscus baicalensis	3.07	2.10	3.36	3.18	1.77	2.67	2.72	1.79
Barbatula nuda	3.08	/	/	/	/	/	/	/
Culter alburnus	2.96	/	2.56	1.94	1.10	3.54	/	/
Pseudobagrus ussuriensis	3.02	2.02	2.83	2.55	1.49	3.25	1.75	2.28
Pelteobagrus fulvidraco	3.07	1.15	3.62	2.48	1.42	3.17	2.53	2.70
Siniperca chuatsi	3.04	/	2.56	/	1.54	3.46	1.93	3.78
Hypophthalmichthys molitrix	3.04	/	3.56	/	/	2.69	/	2.94
Acanthorhodeus chankaensis	2.79	0.610	3.02	2.06	1.47	3.40	1.74	2.81
Median value of benthos	**2.32**	**1.59**	**3.53**	**2.65**	**1.27**	**2.26**	**1.61**	**3.48**
Eriocheir sinensis	2.64	/	3.53	/	1.11	2.14	1.98	3.53
Dytiscidae	2.85	/	3.76	2.30	1.43	/	2.33	3.84
Cristaria plicata	2.26	/	2.97	/	0.44	/	1.17	2.81
Viviparus chui	2.01	1.59	3.65	2.66	1.59	2.27	1.68	3.70
Median value of phytoplankton	**2.41**	**3.36**	**4.00**	**4.08**	**2.65**	**4.53**	**3.92**	**4.93**
Potamogeton crispus	2.41	3.40	4.16	4.23	2.24	4.81	4.10	4.51
Spirogyra	2.54	3.36	3.17	4.08	2.56	4.52	3.89	4.94
Ceratophyllum demersum	1.83	3.23	4.46	3.93	2.73	3.51	3.92	4.93
Median values of all the species	**2.96**	**2.02**	**3.28**	**2.64**	**1.49**	**3.32**	**2.19**	**3.48**

"/" indicates that OPE congeners were not detected in the species, or their concentrations were below the corresponding LODs.

Table S10 The estimated log BAF_{lw} values (L/kg lw) for 8 OPEs in different organs of fish from LDB

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Muscle	2.09	1.35	2.11	2.25	2.04	2.00	1.64	3.07
Liver	2.38	1.65	4.22	5.32	4.40	3.30	1.96	3.41
Kidney	2.38	1.88	4.50	5.73	8.47	3.54	2.13	3.75
Gill	2.38	1.50	3.52	5.93	4.41	3.08	1.48	2.61

Notes: The log BAF_{lw} values for 8 OPEs in muscle were determined in this study. The correlation coefficients among muscle, liver, kidney, and gill were derived from Bekele et al. (2021). Based on these coefficients, the log BAF values for 8 OPEs in liver, kidney and gill of fish were estimated.

Bekele, T. G., Zhao, H., Wang, Q., 2021. Tissue distribution and bioaccumulation of organophosphate esters in wild marine fish from Laizhou Bay, North China: Implications of human exposure via fish consumption. J. Hazard. Mater. 401, 123410. https://doi.org/10.1016/j.jhazmat.2020.123410

Table S11 The estimated log BAF_{lw} values (L/kg lw) for 4 OPEs in different organs of fish from SHR

	TCIPP	TPHP	TNBP	TPP
Muscle	1.39	2.63	1.52	2.82
Liver	3.58	50.9	24.8	455
Intestine	0.79	3.19	5.86	11.9
Brain	3.3	27.9	15.4	75.6
Gill	1.08	47.2	13.8	5.98

Notes: The log BAF_{lw} values for 4 OPEs in muscle were determined in this study. The correlation coefficients among muscle, liver, intestine, brain, and gill were derived from data on *Carassius auratus* in Da et al. (2024). Based on these coefficients, the log BAF values for 4 OPEs in muscle, liver, intestine, brain, and gill of fish were estimated.

Da, S., Wang, J., 2024. Occurrence, Bioaccumulation, and Risk Assessment of Organophosphate Esters in Rivers Receiving Different Effluents. Toxics 12, 612. https://doi.org/10.3390/toxics12080612

Table S12 $BSAF_{ww}$ of OPEs in the organisms from Liaodong Bay

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Median value of fish	**5.01**	**3.97**	**3.57**	**1.49**	**6.27**	**5.26**	**10.3**	**3.17**
Arius sinensis	4.95	2.19	3.61	1.63	6.90	33.4	8.21	2.99
Cynoglossus semilaevis	6.74	5.33	3.53	1.33	6.67	4.08	12.4	3.54
Hexagrammos indicus	4.31	2.61	2.72	1.14	4.67	0.413	5.33	3.35
Lophius litulon	5.06	11.7	5.45	2.06	5.87	6.43	19.3	2.28
Median value of benthos	**4.09**	**2.08**	**13.5**	**0.686**	**2.17**	**9.51**	**14.1**	**2.71**
Mactra veneriformis	5.26	4.70	3.49	1.18	9.44	1.32	17.1	4.72
Dosinia laminata	2.80	1.99	1.82	1.10	2.74	0.559	11.0	3.72
Alvenius ojianus	2.51	2.31	4.03	0.489	1.81	1.68	3.98	1.23
Octopus ocellatus	5.41	14.5	8.57	4.40	3.64	77.8	18.2	5.60
Haliotis discus hannai	4.47	6.26	3.39	0.888	7.62	6.99	13.1	5.36
Ostrea gigas Thunberg	3.53	6.68	4.89	1.65	6.11	8.36	15.3	3.35
Rapana rapiformis	2.63	6.68	4.80	1.36	3.32	1.50	8.40	2.57
Oratosquilla woodmasoni	4.66	2.51	5.94	1.28	4.02	2.36	10.0	2.35
Portunus trituberculatus	4.09	2.08	13.5	0.686	2.17	9.51	14.1	2.71
Median value of all the species	**4.47**	**4.70**	**4.03**	**1.28**	**4.67**	**4.08**	**12.4**	**3.35**

Table S13 $BSAF_{lw}$ of OPEs in the organisms from Liaodong Bay

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Median value of fish	**65.4**	**57.5**	**48.7**	**16.8**	**61.1**	**70.5**	**136**	**34.1**
Arius sinensis	60.4	26.2	44.9	19.2	82.6	394	99.2	35.0
Cynoglossus semilaevis	95.6	74.8	50.1	19.0	94.8	58.3	178	49.9
Hexagrammos indicus	50.1	29.1	31.0	13.0	54.1	4.62	66.4	38.2
Lophius litulon	65.5	152	71.8	26.9	77.4	83.3	248	30.1
Median value of benthos	**95.3**	**84.8**	**103**	**25.6**	**93.9**	**62.1**	**247**	**66.8**
Mactra veneriformis	161	74.7	527	24.5	76.1	340	559	94.9
Dosinia laminata	177	141	102	34.9	277	41.4	529	146
Alvenius ojianus	82.3	59.0	58.0	35.4	82.9	17.4	332	116
Octopus ocellatus	80.3	73.8	130	15.8	58.1	54.4	127	39.5
Haliotis discus hannai	110	298	174	87.7	73.9	1551	373	115
Ostrea gigas Thunberg	77.5	108	58.9	15.4	131	121	228	93.3
Rapana rapiformis	70.8	133	97.3	33.2	122	170	303	66.6
Oratosquilla woodmasoni	50.4	132	92.6	26.2	62.9	29.1	166	49.5
Portunus trituberculatus	119	62.6	150	31.6	102	60.0	253	60.1
Median value of all the species	**80.3**	**74.9**	**92.6**	**26.2**	**82.6**	**60.0**	**248**	**60.1**

Table S14 $BSAF_{ww}$ of OPEs in the organisms from Songhua River

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Median value of fish	**7.11**	**0.0221**	**0.377**	**0.227**	**0.108**	**2.03**	**0.0767**	**0.786**
Carassius auratus	8.05	/	0.0820	0.291	0.0855	1.76	0.0741	/
Barbatula nuda	7.79	/	/	/	/	/	/	/
Pseudobagrus ussuriensis	6.57	0.159	0.137	0.240	0.108	2.18	0.0362	0.0954
Pelteobagrus fulvidraco	7.65	0.0221	4.08	0.214	0.120	1.88	0.228	0.586
Siniperca chuatsi	4.12	/	7.60	/	0.0769	/	0.126	3.84
Acanthorhodeus chankaensis	5.38	0.0111	0.377	0.140	0.262	5.44	0.0767	0.987
Median value of benthos	**3.27**	**0.0887**	**1.40**	**0.457**	**0.127**	**0.333**	**0.101**	**3.24**
Eriocheir sinensis	5.79	/	1.26	/	0.0838	0.323	0.119	3.25
Dytiscidae	4.93	/	0.810	0.0988	0.0667	/	0.101	2.51
Cristaria plicata	4.10	/	2.01	/	0.103	/	0.103	3.59
Viviparus chui	1.77	0.088	1.29	0.462	0.195	0.340	0.0469	3.80
Median values of all the species	**5.58**	**0.0550**	**1.26**	**0.227**	**0.103**	**1.82**	**0.101**	**2.88**

"/" indicates that OPE congeners were not detected in the species, or their concentrations were below the corresponding LODs.

Table S15 $BSAF_{lw}$ of OPEs in the organisms from Songhua River

	TCEP	TCIPP	TDCIPP	TPHP	TNBP	TBOEP	TEHP	TPP
Median value of fish	**87.6**	**0.278**	**1.30**	**2.69**	**1.51**	**33.4**	**0.864**	**7.18**
Carassius auratus	104	/	1.07	3.79	1.11	22.9	0.965	/
Barbatula nuda	98.6	/	/	/	/	/	/	/
Pseudobagrus ussuriensis	85.8	2.08	1.80	3.13	1.41	28.4	0.473	1.25
Pelteobagrus fulvidraco	96.1	0.278	51.3	2.69	1.51	23.6	2.87	7.37
Siniperca chuatsi	91.2	/	0.923	/	1.51	46.1	0.771	40.3
Acanthorhodeus chankaensis	38.9	0.0810	2.73	1.02	1.90	39.3	0.555	7.14
Median value of benthos	**10.5**	**0.774**	**8.55**	**3.99**	**0.881**	**2.91**	**0.299**	**19.8**
Eriocheir sinensis	39.3	/	8.57	/	0.568	2.19	0.808	22.0
Dytiscidae	88.2	/	14.5	1.77	1.19	/	1.82	45.0
Cristaria plicata	4.88	/	2.39	/	0.123	/	0.117	4.27
Viviparus chui	15.5	0.774	11.3	4.03	1.71	2.97	0.409	33.2
Median values of all the species	**87.0**	**0.526**	**2.73**	**2.91**	**1.41**	**23.6**	**0.771**	**14.7**

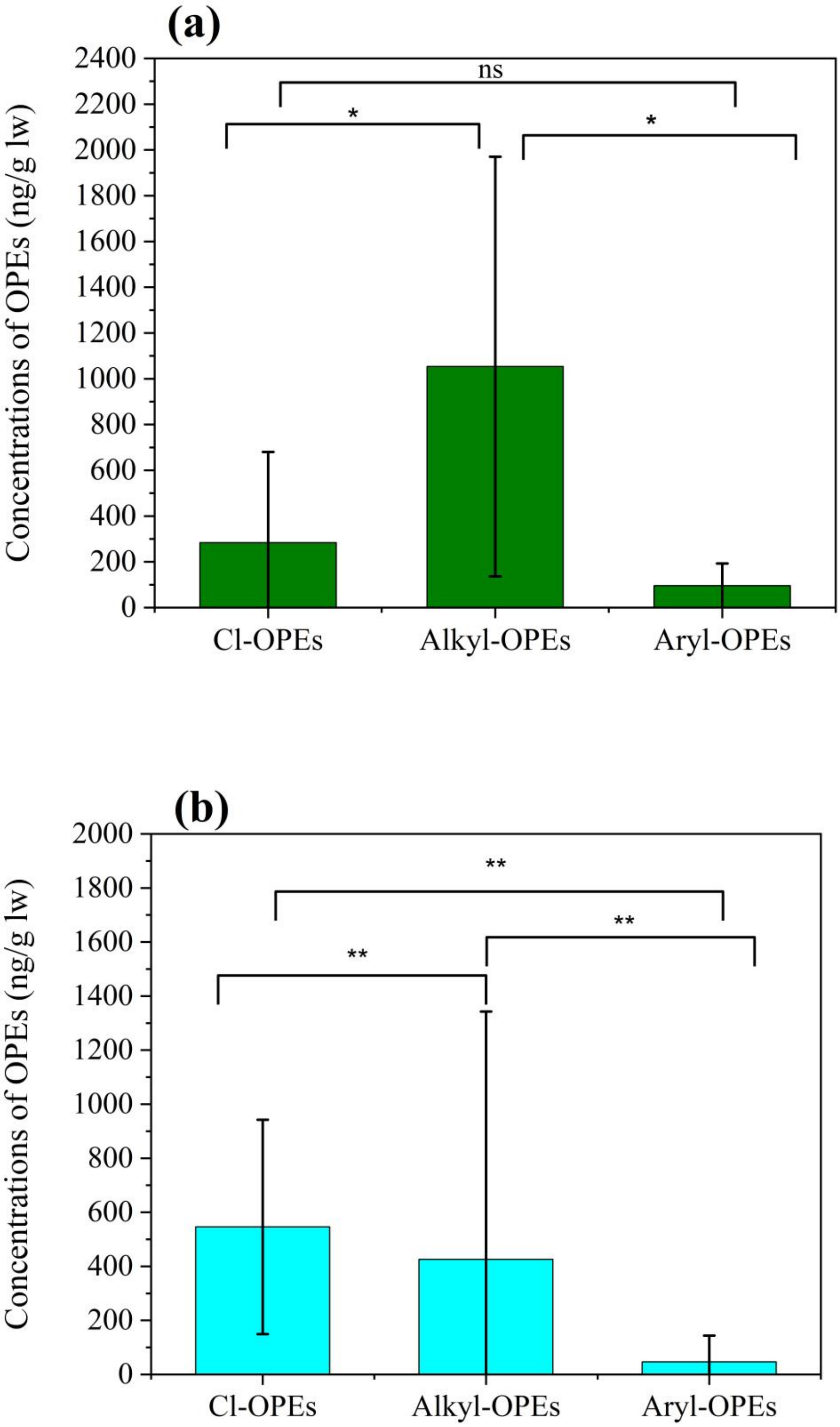


Fig. S1 Comparison of concentrations of Cl-OPEs, alkyl-OPEs and aryl-OPEs in marine organisms in LDB (a) and SHR (b) (* represents p<0.05, ** represents p<0.01)

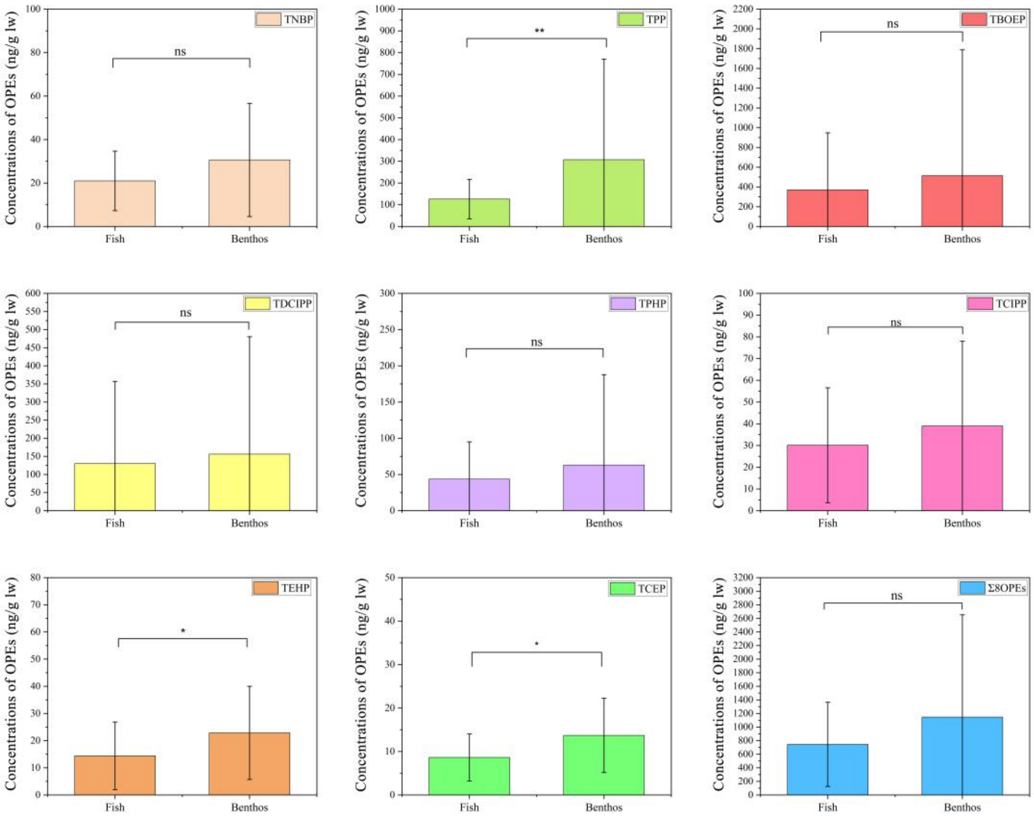


Fig. S2 Comparison of concentrations of 8 OPEs as well as Σ_8OPEs in the two groups (benthos and fish) in Liaodong Bay

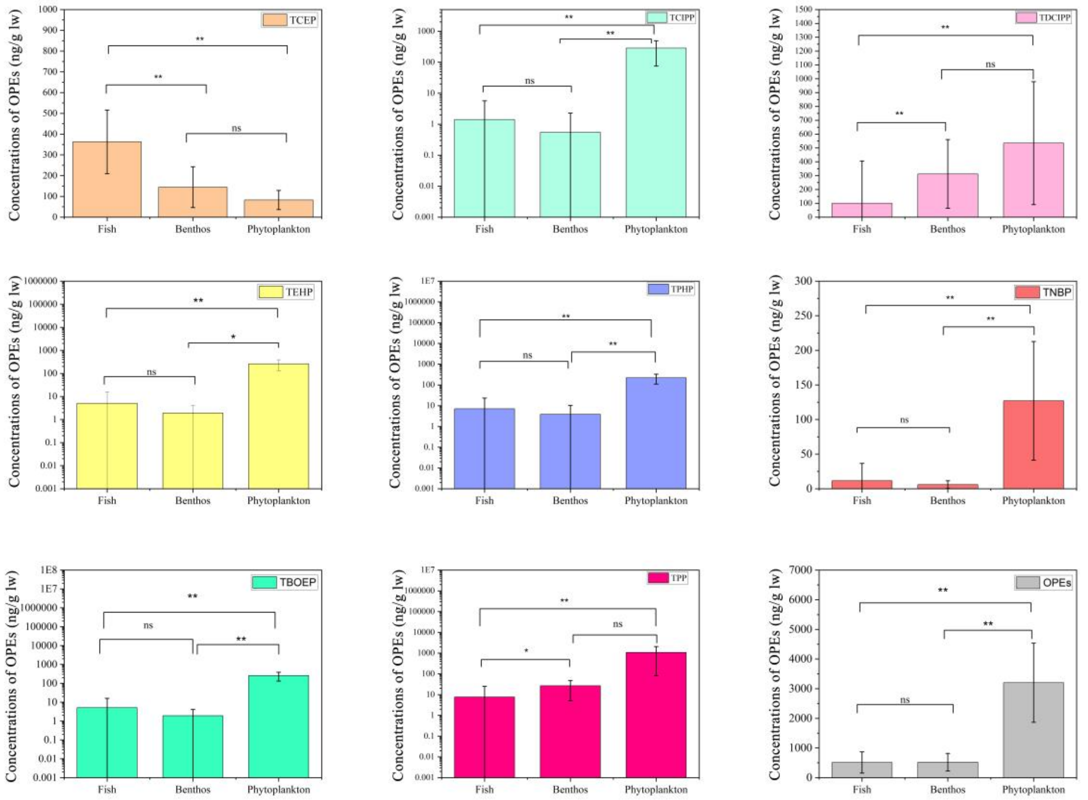


Fig. S3 Comparison of concentrations of 8 OPEs as well as Σ$_8$OPEs in the three groups (phytoplankton, benthos and fish) in Songhua River

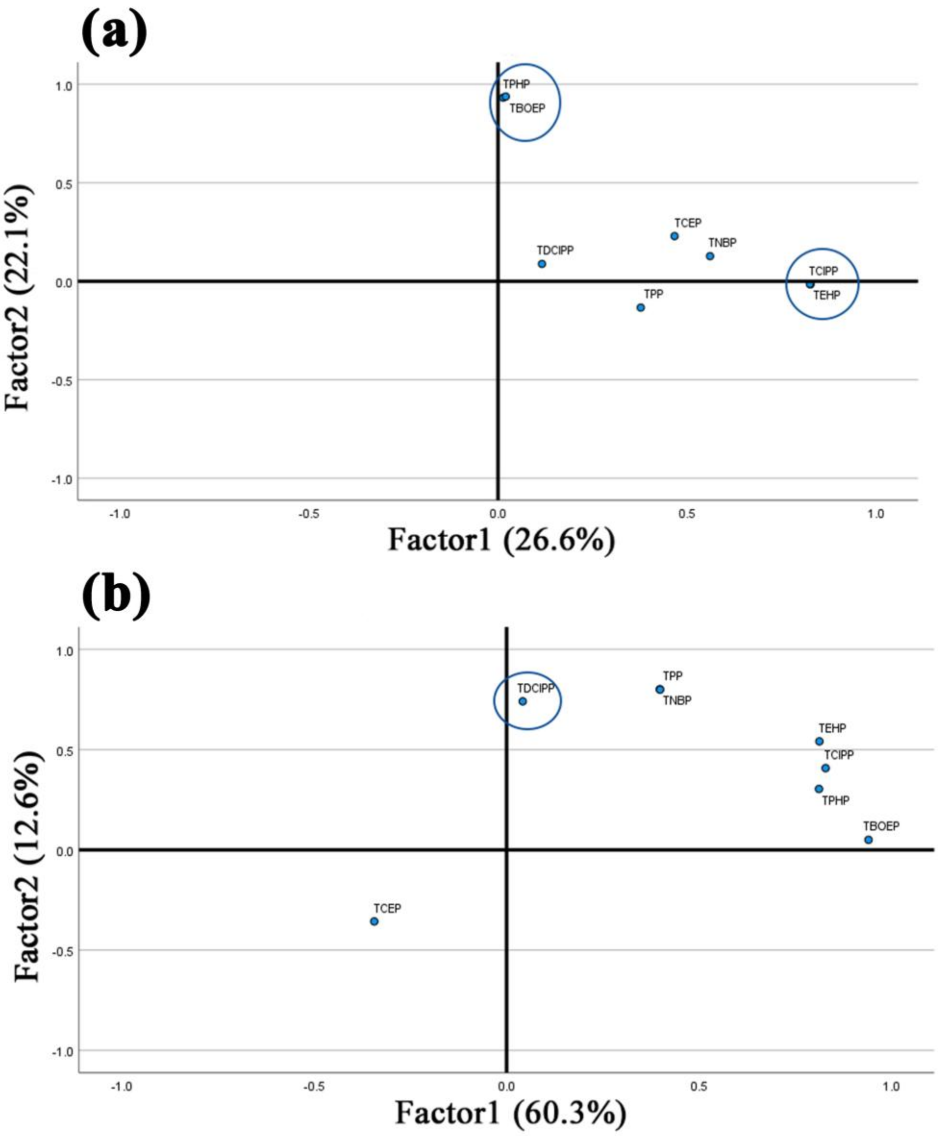


Fig. S4 Principal component analysis (PCA) ordination plots of OPE profiles in aquatic organisms from LDB (a) and SHR (b).

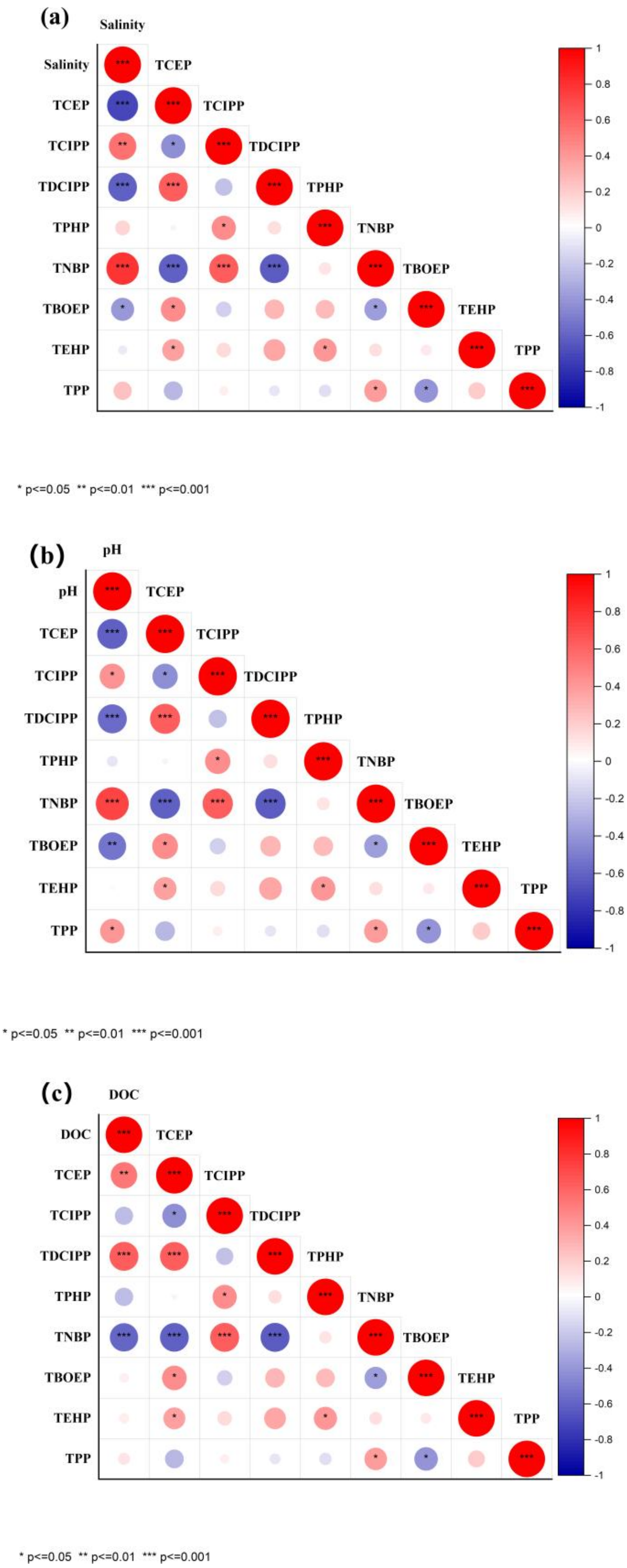
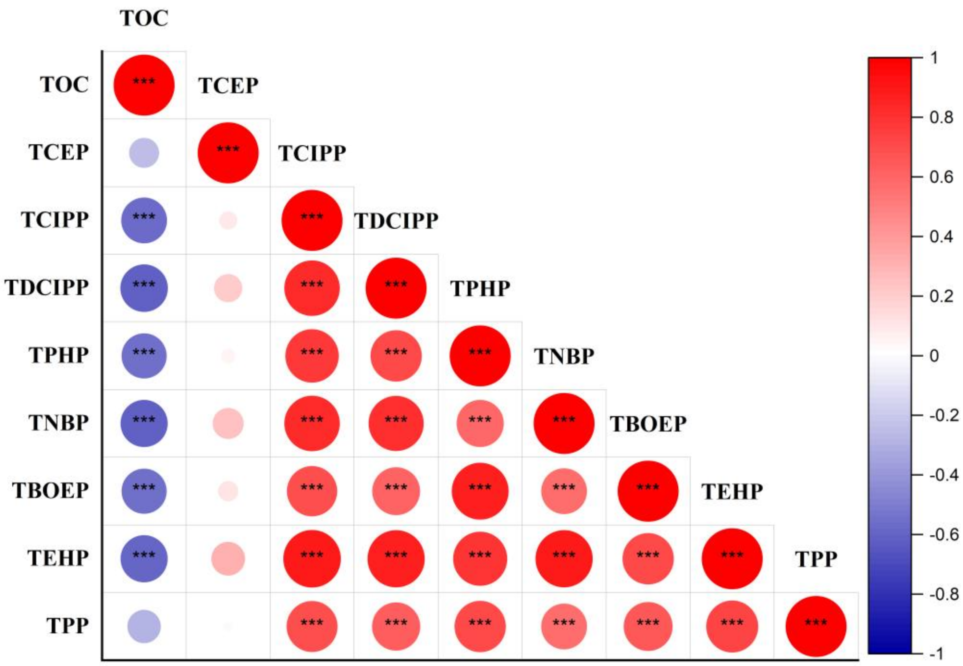


Fig. S5 The correlations of salinity (a) pH (b), and DOC (c) with log BAF values of OPEs in the two water bodies.



* p<=0.05 ** p<=0.01 *** p<=0.001

Fig. S6 The correlation of TOC with BSAF of OPEs in the two water bodies.

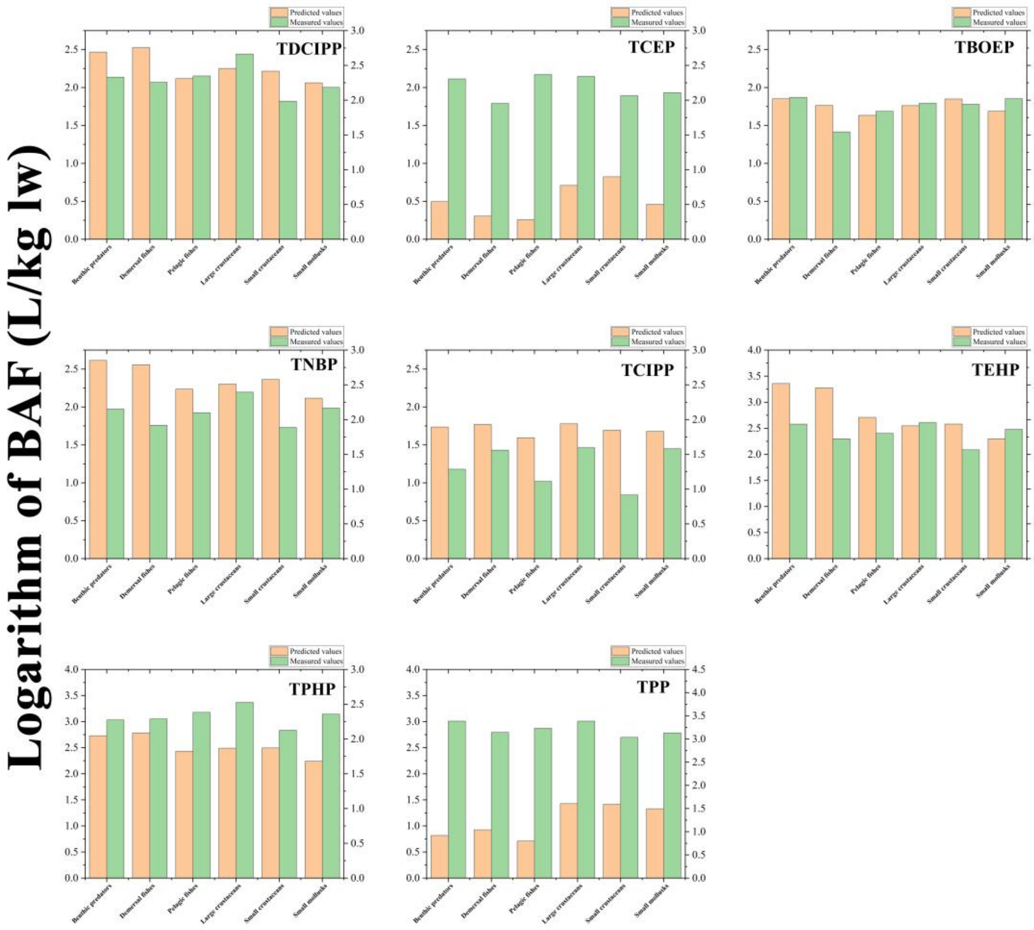


Fig. S7 Comparison of predicted and measured log-transformed BAF_{lw} of eight OPEs across different trophic levels in the marine food web.

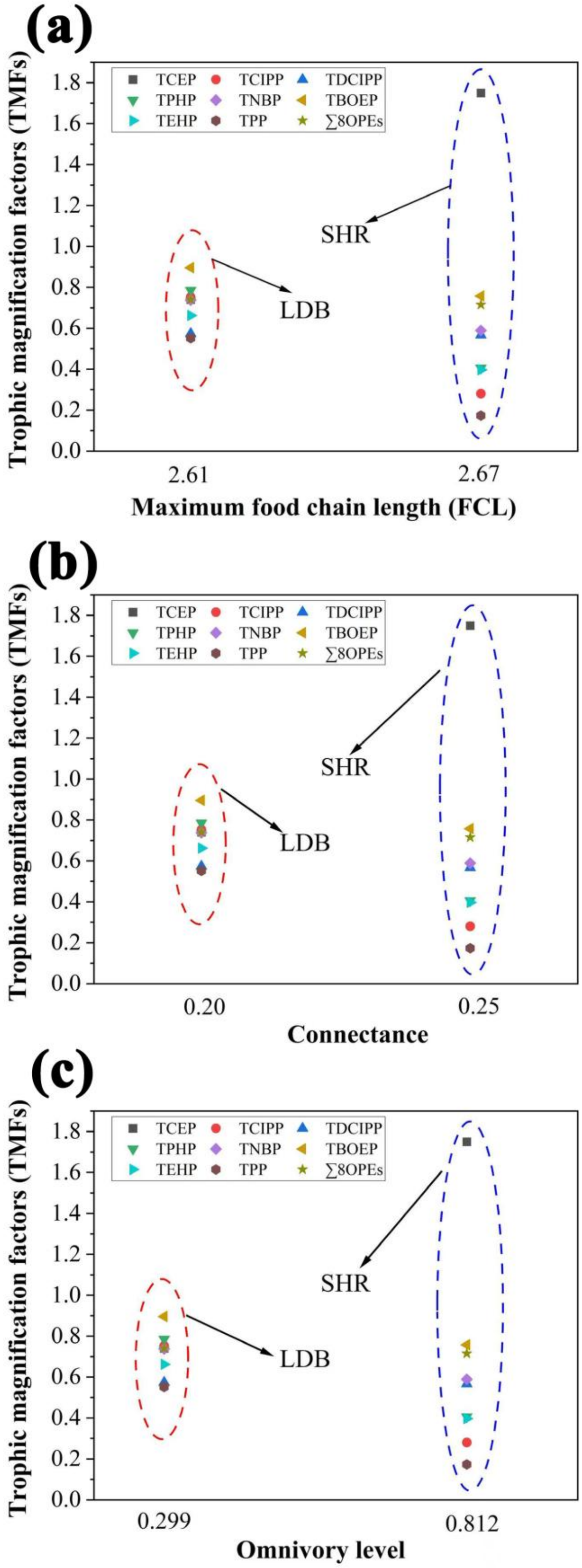


Fig. S8 Distribution of TMFs for eight individual OPEs and Σ_8OPEs in relation to FCL, connectance, and omnivory level between LDB and SHR.

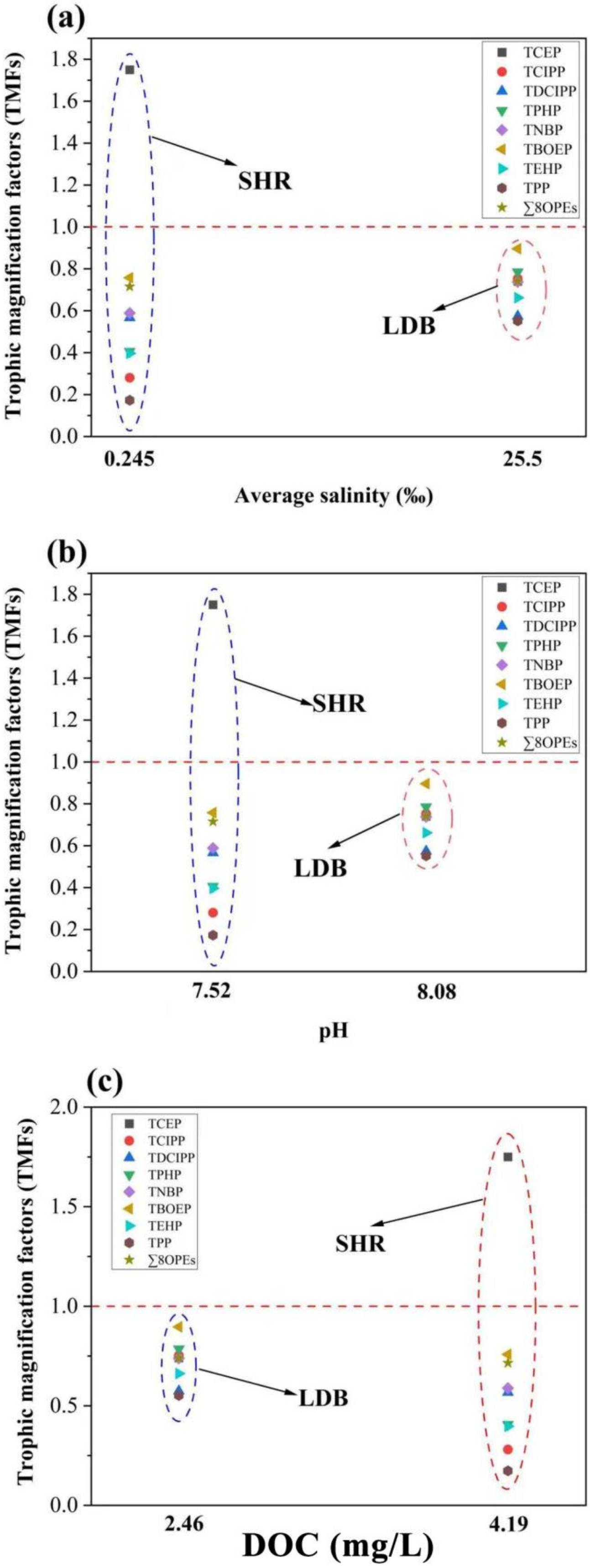


Fig. S9 Variations in TMFs of OPEs and Σ_8OPEs along gradients of salinity(a), pH (b) and DOC (c) in the studied aquatic ecosystems.