



Occurrence, phase distribution, and bioaccumulation of organophosphate esters (OPEs) in mariculture farms of the Beibu Gulf, China: A health risk assessment through seafood consumption[☆]

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ABSTRACT

As emerging pollutants, the occurrence and risks of organophosphate esters (OPEs) in mariculture farms should be concerned; however, information is limited. Beibu Gulf is one of the essential mariculture zones in China. This study aimed to investigate the occurrence of OPEs in mariculture farms of the Beibu Gulf, their phase distribution and bioaccumulation among sediment, organisms (shrimp, crab, and oyster), water, and feed. Human exposure to OPEs through seafood consumption was also assessed. The total concentrations of the 11 target OPEs (\sum_{11} OPEs) in the water samples ranged 32.9–227 ng L⁻¹. It was significantly higher in water from the culture ponds (mean 122 ng L⁻¹) than in water from the estuaries and nearshore areas (mean 51.1 ng L⁻¹) (nonparametric test, $p < 0.05$). \sum_{11} OPEs in the feeds averaged 46.0 (range 21.7–84.5) ng g⁻¹ dw, which is similar to the level in the organism samples (mean 55.5, range 21.3–138 ng g⁻¹ dw) and 4.4 times higher than that in the sediment (mean 10.9, range 35–22.1 ng g⁻¹ dw). The \sum_{11} OPEs released from the feeds to the culture ponds was estimated to be 49 $\mu\text{g m}^{-2}$ per three-month period. In the aquaculture ponds, the sediment-water distribution coefficient ($\log K_{OC}$), and the bioaccumulation factors from the water ($\log \text{BWFs}$) or the feed ($\log \text{BFAFs}$) to the organisms, depend linearly on the hydrophobicity ($\log K_{OW}$) of OPEs. The $\log \text{BWFs}$ and $\log \text{BFAFs}$ increased with increasing $\log K_{OW}$ within the $\log K_{OW}$ range of 1–7. The human exposure to OPEs through consumption of shrimp, crab, and oysters from the mariculture farms does not pose a health risk at present.

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1. Introduction

Organophosphate esters (OPEs) are widely used as flame retardants in plastics, textiles, electronic equipment, furniture, and building materials (U.S EPA, 2005; van der Veen and de Boer, 2012). Nonchlorinated alkyl phosphates have also been used as plasticizers, hydraulic fluids, lacquer, antifoam agents, glues, and extractants for some metals (van der Veen and de Boer, 2012). The usage of OPEs began in the early 20th century, increased rapidly during the 1940s, and has continued for later decades (U.S EPA, 2005). With the phasing out of polybrominated diphenyl ethers

(PBDEs) during the 2000s, the global production and usage of organophosphate based flame retardants as alternative flame retardants have increased sharply. From 1992 to 2013, the global OPE consumption increased from 102,000 to 370,000 tonnes (Esch, 1997; Zhang, 2014).

Because most OPEs are added to the host materials by mixing rather than chemically bonding, they may enter the environment via volatilization to air, dissolution in water, and permeation to soils (Reemtsma et al., 2008). As some previous review literature (Reemtsma et al., 2008; van der Veen and de Boer, 2012; Wei et al., 2015) and recent studies (Cao et al., 2017; Yadav et al., 2018; Yadav et al., 2019; Yadav et al., 2017; Zhang et al., 2020; Zhong et al., 2018) reported that in the past several decades OPEs had been widely detected in dust, air, water, soil, and sediment. A few previous studies proved that OPEs migrate to the ocean via atmospheric

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deposition and riverine discharging (Bollmann et al., 2012b; Castro-Jimenez et al., 2014; Li et al., 2018; Wang et al., 2015; Wang et al., 2014b). OPEs in the ocean can accumulate in marine organisms such as fishes and mussels (Aznar-Alemayn et al., 2018; Castro et al., 2020; Kim et al., 2011; Sundkvist et al., 2010), thus pose risks to humans through the consumption of seafood (Wei et al., 2015).

Marine aquaculture provides large quantities of seafood for human consumption. While marine fishing supplies wild seafood, marine aquaculture produces farmed seafood, which could be more contaminated. Most aquaculture farms are located in the coastal zones, where chemical pollution tends to be more severe than the open ocean because of the inputs from land-based sources (Guan et al., 2009; Holmer, 2010). The commercial feed supplies used in aquaculture farms may also have elevated contaminant level relative to what fish feeds in the wild (Berntssen et al., 2010; Maule et al., 2007). Previous studies indicated that multiple pollutants (such as PCBs, PCDDs/DFs, OCPs, PBDEs, PAHs) occurred in the commercial fish feeds (Berntssen et al., 2010; Maule et al., 2007). We can infer that OPEs may also exist in the commercial fish feeds because of the contamination of feed ingredients by OPEs. Moreover, OPEs could be present as flame retardants and plasticizers in numerous materials used in mariculture practice, such as flotation equipment in cage culture, plastic net, and floating ball in aeration pumps (Aznar-Alemayn et al., 2018). OPEs such as TCEP, TDCIPP, TPHP are also added in lacquer, and TIBP is in lubricant of the aeration pumps used in mariculture farms. TIBP is also used to regulate pore size in concrete piles that are used for oyster culture (Wei et al., 2015). However, few studies have focused on the occurrence, phase distribution, bioaccumulation, and risks of OPEs in mariculture farms (Aznar-Alemayn et al., 2018; Gadelha et al., 2019).

Beibu Gulf, located in the northwest of the South China Sea, is surrounded by Leizhou Peninsula, Hainan Island, Guangxi Zhuang Autonomous Region of China, and Vietnam. It is a natural semi-enclosed bay with an area of 1.3×10^5 km² and an average water depth of 38 m. Due to its southern subtropical marine climate and vast amounts of organism and nutrients from the rivers, Beibu Gulf has become one of the most important mariculture zones in China. In 2015, the production of marine aquaculture in Guangxi was 1.14 million tonnes, which nearly doubles the amount of 0.66 million tonnes from open water fishing (The Oceanic Administration of Guangxi, 2017). There are two main culture types based on different food sources: (1) culture ponds, in which fish, shrimp, and crab are fed on commercial feed. The brackish water from estuaries and nearshore areas are the water sources of the closed culture ponds. After being brought into the ponds, the water is usually kept in the ponds for at least one culture period (3–4 months). A little new water is added periodically to make up the loss due to evaporation and leaching; parts of the water may also be replaced occasionally by new water. (2) Open culture farms located in open estuaries and shallow seas, where mainly shellfish are cultured feeding on natural phytoplankton but not artificial feeds. In the study area, the ponds were approximately 227 km² and the seafood production was 254,000 tonnes, while the open culture area was 303 km² and the production was 723,000 tonnes in 2015 (The Oceanic Administration of Guangxi, 2017). The seafood from the Beibu Gulf has been sold to various regions of China and exported to many countries. However, no previous studies were conducted on the occurrence of OPEs in the mariculture of the Beibu Gulf as well as their impacts on the local environment and residents.

The objectives of this study were to: (1) investigate the occurrence of OPEs in the feed, seawater, sediments, and seafood from mariculture farms in Beibu Gulf; (2) investigate the partitioning and bioaccumulative behavior of OPEs among the sediment, organisms, feed, and water; and (3) estimate the dietary intakes (EDI)

of OPEs through the farmed seafood and evaluate the risk of human exposure to OPEs through seafood consumption.

2. Materials and methods

2.1. Standards and reagent

Eleven OPEs were measured in this study. Based on the substitution groups, they are categorized into: 1) chlorinated phosphates, including tris(1-chloro-2-propyl) phosphates (TCIPPs, mix of three isomers), tris(2-chloroethyl) phosphate (TCEP), and tri (1,3-dichloro-2-isopropyl) phosphate (TDCIPP); 2) alkylated phosphates, including tris(2-ethylhexyl) phosphate (TEHP), tri-iso-butyl phosphate (TIBP), tri-n-butyl phosphate (TNBP), triethyl phosphate (TTP), tris(2-butoxyethyl) phosphate (TBOEP), and trihexyl phosphate (THP); and 3) phenylated phosphates, including tri-phenyl phosphate (TPHP) and tris(methylphenyl) phosphate tri-cresyl phosphates (TMPPs, mix of three isomers). All the abbreviation of OPEs were made according to previous study by Bergman et al. (2012). High purity chemical standards of these target OPEs and two deuterated recovery standards (D₂₇-TNBP and D₁₅-TPHP) were purchased from different suppliers (Supplementary Materials Table S1). The physicochemical properties of the target OPEs are summarized in Table S1.

2.2. Sample collection and pretreatment

Surface water sample were collected from 14 different sites in the Beibu Gulf in October 2015. Locations of the sampling sites are shown in Fig. 1. They included eight culture ponds (01 P, 02 P, 04 P, 05 P, 07 P, 10 P, 12 P, and 13 P), four estuaries (06 E, 08 E, 09 E, and 11 E) and two nearshore areas (03 N and 14 N). Additional sampling information is given in Table S2. Each water sample (2.5 L) was a composite of three sub-samples collected within a radius of 20 m. Each sub-sample was collected with a stainless-steel bucket and poured into a 10-Liter pre-cleaned amber glass bottle for mixing. 2.5 L mixed water was transferred to a pre-cleaned amber bottle and stored in a cooler with ice. pH and salinity of seawater was measured using portable pH meter (INESA PHB-260, Shanghai, China) and refractometer, respectively.

A total of 12 surface sediment samples were collected at the same sampling sites where the waters were collected, except 03 N and 12 P (Table S2). Each sediment sample was a composite of three subsamples, which were collected using a stainless-steel grab bucket. The top 5 cm sediment was placed into a sealed polyethylene bag and stored in a cooler with ice. After the sediments were transported into the laboratory, they were freeze-dried, ground, sieved through an 80 mesh stainless steel sieve, and stored at -20 °C in amber glass jars until extraction. Total organic carbon (TOC) content of the sediment was determined using an elemental analyzer (Elementar Vario Macro cube, Germany), as described in Text S1.

Table S3 summarizes the information of collected organism samples. Eight composite shrimp (*Litopenaeus vannamei*) samples, each was consisted of 5–12 individual shrimps, were obtained from the eight culture ponds, respectively. Three composite crab (*Scylla Paramamosain*) samples, each having 2 individual crabs, were collected in ponds 01 P, 04 P and 07 P, respectively. Four oyster (*Crassostrea rivularis* Gould) samples, each contained 3–5 individual oysters, were collected in the four estuaries, respectively. All organism samples were sealed in polyethylene bags and stored in a cooler with ice. The weight and length of individual organisms were recorded after they were transported to the laboratory. Then the organism sub-samples were dissected individually: the muscles of shrimp and oyster were selected, and crabs were divided into

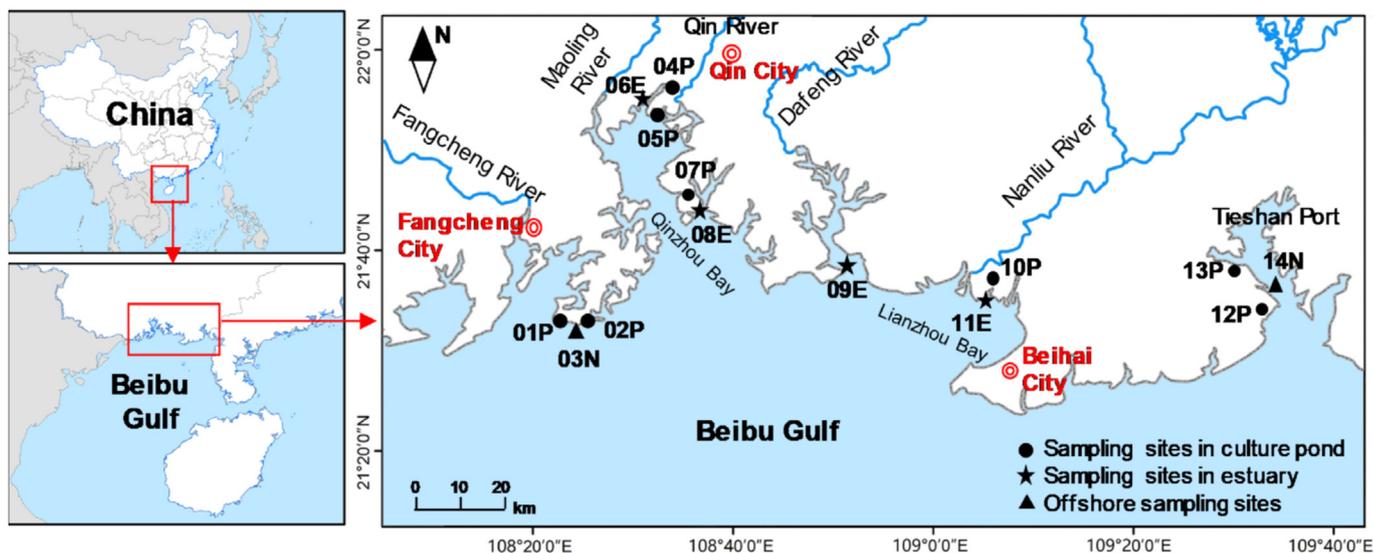


Fig. 1. Map of sampling sites in the mariculture farms of the Beibu Gulf.

three parts: crab leg muscle (CL), crab ventral muscle (CV), and crab roe (CR). The organism sub-samples of the same type from the same site were combined to form a composite sample. There were 8, 3, and 4 composite samples for shrimp, crab, and oyster, respectively (Table S3). They were freeze-dried, homogenized and stored at $-20\text{ }^{\circ}\text{C}$ in amber glass jars until extraction. The moisture contents of the composite organism samples were calculated based on the weight loss after freeze-drying. The lipid contents of individual composite organism samples were measured gravimetrically after OPE extraction.

Four commercial shrimp compound feed samples were available in two sampling sites (04 P and 07 P). These feeds were produced by two companies belonging to one Feeds Group in Guangdong Province, China. Two feed samples are for young shrimp and the other two are for adult shrimp. They were sampled into sealed polyethylene bags, separately. Then they were freeze-dried, ground, sieved through an 80 mesh stainless steel sieve, and stored at $-20\text{ }^{\circ}\text{C}$ until extraction.

2.3. Sample extraction and instrumental analysis

Detailed procedures of sample extraction and instrumental analysis are described in Supplementary Text S2. These methods were optimized based on those previously established (Liu et al., 2016; Zeng et al., 2014; Zeng et al., 2015).

Briefly, for water sample, 1 L water was added 20 ng of $\text{D}_{27}\text{-TNBP}$ and $\text{D}_{15}\text{-TPHP}$ as recovery standards after it was filtered through a glass fiber filter (GF/F, $0.7\text{ }\mu\text{m}$, Whatman, United Kingdom). An Oasis hydrophile-lipophile balance (HLB) cartridge (6 mL, 500 mg, Waters, United States) was used for solid-phase extraction of OPEs in the water samples. Then the target OPEs were eluted with 15 mL ethyl acetate. The eluent was reduced to approximately 20 μL under a gentle nitrogen flow, and then transferred to a 2-mL amber vial using ethyl acetate and kept at $-20\text{ }^{\circ}\text{C}$ until analysis. Before instrumental analysis, the extract was reduced to approximately 0.5 mL by nitrogen purge, and 200 ng hexamethylbenzene was added as an internal standard.

The sediment sample (20 g dry weight) was extracted by Soxhlet extraction with dichloromethane for 48 h. The organism (1 g dry weight) and feed (5 g dry weight) samples were extracted by Soxhlet extraction with acetone/n-hexane mixed solution (1:1, v:v),

respectively. Before extraction, 20 ng of $\text{D}_{27}\text{-TNBP}$ and $\text{D}_{15}\text{-TPHP}$ as recovery standards were added into each sample. For sediment samples, copper granules were added to the round bottom flask before extraction to remove the elemental sulphur present in samples. For each composite organism sample, about one-quarter of the extract was taken for lipid content determination. Each sample extract was concentrated by the rotary evaporator (Heidolph 4000, Germany) and was solvent exchanged to 0.5 mL hexane. The extract was then passed through Envi-Florisil SPE cartridge (1 g, 6 mL, SUPELCO, USA). The first fraction was eluted with 20 mL dichloromethane/n-hexane (8:2, v:v) mixed solvent. The second fraction that contained target OPEs was eluted with 20 mL ethyl acetate, and concentrated under nitrogen to 0.5 mL. Then, 200 ng internal standard (hexamethylbenzene) was added.

The instrumental analysis of OPEs was performed with Agilent 7890 B gas chromatograph coupled to an Agilent 7000C triple quadrupole mass spectrometry (GC-MS/MS, Agilent Technologies, Palo Alto, USA). The detailed GC and MS/MS parameters for the target OPEs, the recovery standards, and the internal standards are shown in Text S2 and Table S4.

2.4. Quality control

In analytical method development, we measured the recoveries of individual OPEs in seawater, sediment, and organism (shrimp muscle), and they ranged from 75% to 110%. The recoveries of $\text{D}_{27}\text{-TNBP}$ and $\text{D}_{15}\text{-TPHP}$ in all field samples averaged 86.4%–93.6% and 83.4%–105%, respectively (Table S5). Instrumental detection limits (IDLs) were defined as three times the signal-to-noise (S/N) ratio, and instrumental quantification limits (IQLs) were defined as ten times the S/N. The method detection limits (MDLs) and method quantification limits (MQLs) were defined as IDLs and IQLs divided the volume or weight of samples, respectively. The MQLs of the 11 OPEs ranged from 0.052 to 1.61 ng L^{-1} for water, from 0.002 to 0.065 ng g^{-1} dw for sediments, 0.052–1.61 ng g^{-1} dw for organism samples, and 0.01–0.32 ng g^{-1} dw for feeds (Table S6). In procedural blanks, five OPEs (TCEP, TIBP, TNBP, TBOEP, TMPPs) were below the IDLs, while the other six OPEs were detected with concentrations ranging from $0.099 \pm 0.039\text{ ng (procedural blank sample)}^{-1}$ (TPTP) to $0.214 \pm 0.088\text{ ng (procedural blank sample)}^{-1}$ (TPHP). The concentrations of target OPEs reported here were after

subtraction of those in blanks, but were not adjusted using the recoveries of the recovery standards.

2.5. Calculations of distribution coefficients and bioaccumulation factors

The distribution coefficients (K_d , L kg⁻¹) and organic carbon normalized distribution coefficients (K_{OC} , L kg⁻¹) of OPEs between water and sediment were calculated by Equations (1) and (2), respectively:

$$K_d = \frac{C_{\text{sediment}}}{C_{\text{water}}} \times 1000 \quad (1)$$

$$K_{OC} = K_d / \text{TOC} \quad (2)$$

where C_{sediment} and C_{water} are the concentrations of OPEs in sediment (ng g⁻¹ dw) and water (ng L⁻¹), respectively. The values of MDL were used in the cases of "not detected", and 1/2 of MQL was used if a measured concentration was lower than the MQL. TOC in Equation (2) is the dimensionless organic carbon fraction of sediment.

To better understand the extent of bioaccumulation of OPEs, biota-water accumulation factor (BWAFF) and biota-feed accumulation factor (BFAFF) were calculated for individual OPE in the cultured aquatic organisms according to Equations (3) and (4), respectively:

$$BWAFF = \frac{C_{\text{biota-ww}}}{C_{\text{water}}} \times 1000 \quad (3)$$

$$BFAFF = \frac{C_{\text{biota-dw}}}{C_{\text{feed}}} \quad (4)$$

where the BWAFF is in L kg⁻¹; $C_{\text{biota-ww}}$ (ng g⁻¹ ww) and $C_{\text{biota-dw}}$ (ng g⁻¹ dw) are the concentrations of individual OPEs in an organism sample based on wet weight (ww) or dry weight (dw); C_{water} is the concentration of individual OPEs in a water sample (ng L⁻¹); and C_{feed} is the concentration of individual OPEs in a feed sample (ng g⁻¹ dw). In this study, the BFAFFs were calculated using the concentrations of OPEs in the cultured organisms (shrimp and crap) and the average concentration of OPEs in the feed samples. Only the OPEs with detection rates of more than 70% are discussed below.

2.6. Statistical analysis

The Shapiro–Wilk test was used to test the normality of grouped data. When the data are normally distributed, independent sample *t*-test (IBM SPSS Statistics 24.0) was applied to various variables to examine the statistical significance of the differences between sub-groups; otherwise, a non-parametric test was used. A *p*-value of <0.05 was regarded as significant, whereas *p* < 0.01 was considered highly significant.

3. Results and discussion

3.1. Occurrence and concentrations of OPEs

In this study, all the 11 target OPEs were detected in the sediment and organism samples, while ten and nine OPEs were detected in the seawater and feed samples, respectively (Table 1 and Tables S7–S9). Seven to nine of the target OPEs had detection frequency of 100% in the four types of samples, indicating the extensive occurrence of OPEs in the mariculture farms of Beibu Gulf. The average \sum_{11} OPEs (total concentrations of 11 OPEs) in

different samples are compared in Fig. 2-A and 2-B, and the average relative abundance of individual OPEs in Fig. 2-C.

Seawater: \sum_{11} OPEs in the cultured ponds seawater ranged from 47.1 to 227 ng L⁻¹ (median 116 ng L⁻¹) and averaged 122 ± 59.4 ng L⁻¹ (Fig. 2-A). It is lower than the concentrations found in some European mariculture farms near urban areas, such as those reported from Portugal (\sum_7 OPEs: 547 ± 437 ng L⁻¹) and UK (\sum_7 OPEs: 275 ± 34.9 ng L⁻¹), but higher than those away from urban shores (\sum_7 OPEs: 0.43–90 ng L⁻¹) (Aznar-Alemay et al., 2018).

The \sum_{11} OPEs in the open seawater from estuaries and nearshore areas ranged from 32.9 to 71.3 ng L⁻¹ (median 50.0 ng L⁻¹) and averaged 51.1 ± 15.5 ng L⁻¹ (Fig. 2-A). It is lower than the concentrations reported from many other estuaries or coastal seawaters (Table S10), such as the Bohai Sea (Wang et al., 2015) and the Pearl River Delta (Wang et al., 2014a) in China, the zone adjacent the North Sea in Germany (Bollmann et al., 2012a); San Francisco Bay of the United States (Sutton et al., 2019); and Canal de Mira, Portugal (Gadelha et al., 2019). The region near the aquaculture farms of this work has a relatively low population density and low level of urbanization and industrialization in comparison with the developed regions in above-mentioned regions.

The average \sum_{11} OPEs was significantly higher (nonparametric test, *p* < 0.05) in the seawater from the ponds (122 ± 59.4 ng L⁻¹) than from the open estuaries and nearshore areas (51.1 ± 15.5 ng L⁻¹). Most individual OPEs that were detected in >50% of the samples, including TCEP, TMPP, TCIPPs, TDCIPP, TIBP, and TNBP, were also found to have significantly higher concentrations in the ponds than in the open sea areas (nonparametric test, *p* < 0.05). The composition of OPEs was similar between the two types of seawaters, with TMPPs, TCIPPs, TCEP, and TBOEP being the most abundant. Therefore, the effluent of the culture ponds could be among major sources of OPEs in the coastal seawater of Beibu Gulf.

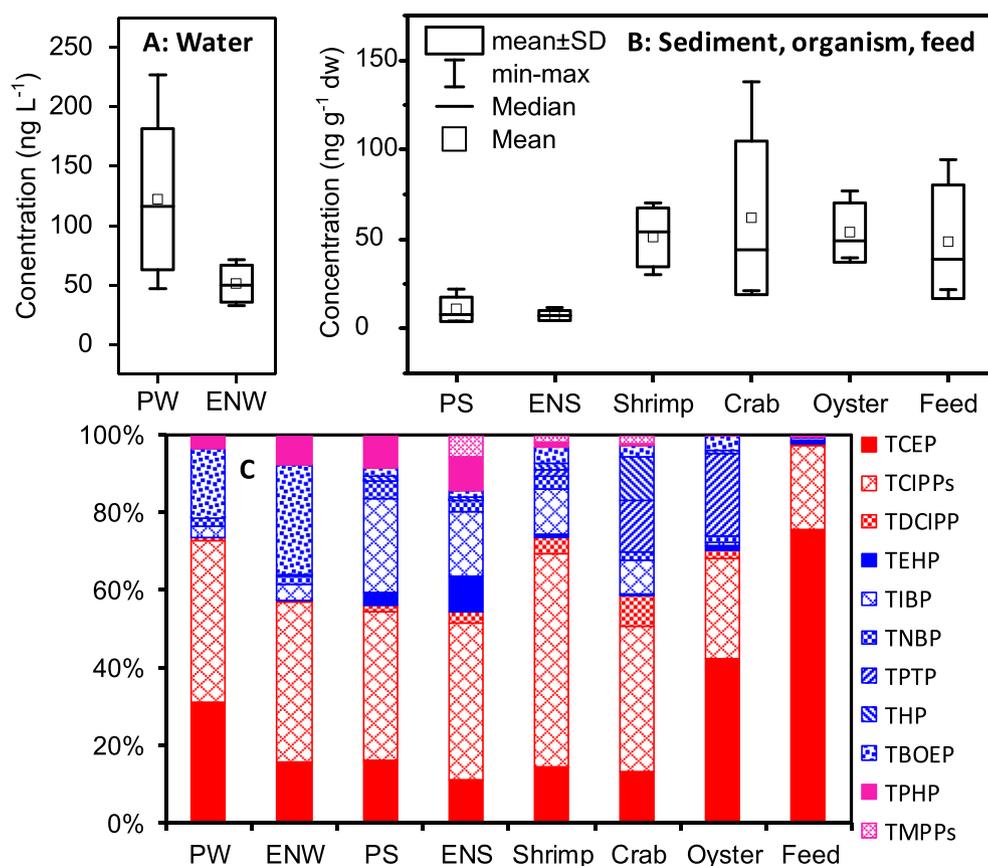
Although composition of OPEs was somewhat similar between the ponds and open seawaters, the ratio of the average concentrations of individual OPEs in ponds to those in the open sea areas, R_{OPE} (Table S7), is higher for the three chlorinated OPEs (4.70, 4.35, and 2.43) than for the alkyl and aryl OPEs (0.91–2.32). Chlorinated OPEs dominate the rapid increase in the input of OPEs to the environment since the 2000s (Cao et al., 2017), and tend to be more resistant to biodegradation than non-chlorinated ones during transport in water (Greaves and Letcher, 2017). The comparison of R_{OPE} values may also suggest that the feeds could be a major source of the OPEs in the pond water, as higher percentage of chlorinated OPEs (98%) than non-chlorinated OPEs was found in the feeds (Fig. 2-B).

The longer retention time of the culture water in the ponds appeared to result in higher concentrations of OPEs in the water. The retention times in five of the eight ponds (01 P, 02 P, 04 P, 05 P, and 07 P) ranged 3–4 months, while in the other three (10 P, 12 P, and 13 P) ranged 1–2 months. The ratios of \sum_{11} OPEs in each pond to that in the nearby estuary or nearshore sample were higher (2.3–3.8) in the five ponds with longer water retention than in the other three ponds (0.90–1.2) (Fig. 3-A). Moreover, the latter three ponds had the similar compound composition to their nearby estuaries or nearshore samples while the former five ponds presented higher (*t*-test, *p* = 0.058) percentages of chlorinated OPEs (mean $76 \pm 13\%$) than their nearby river or nearshore samples (mean $58 \pm 3.6\%$). It can be inferred that, with the culture time prolonged, the increased dosage of feed would increase the residue of OPEs in the ponds water and the percentage of chlorinated OPEs would also increase because of the relatively high percentage of chlorinated OPEs in the feeds. A rough estimation show that about 49 μg OPEs entered the shrimp ponds (water depth 1.2 m) per

Table 1

Detection rates and concentration of OPEs in seawater, sediment, and seafood collected the mariculture areas of the Beibu Gulf.

	Seawater (ng L ⁻¹ , n = 14)	Sediment (ng g ⁻¹ dw, n = 12)	Organism (ng g ⁻¹ dw, n = 19)	Feed (ng g ⁻¹ dw, n = 4)
TCEP	100%, 5.21–82.1, 13.1 ^a	100%, 0.36–2.98, 0.88	100%, 3.13–25.5, 6.91	100%, 13.1–74.4, 29.7
TCIPPs	100%, 13.9–92.5, 28.2	100%, 1.54–9.88, 2.35	100%, 5.81–58.3, 21.1	100%, 6.34–10.3, 7.56
TDCPP	100%, 0.19–1.68, 0.49	100%, 0.04–0.69, 0.09	100%, 0.19–15.2, 0.94	100%, 0.04–0.97, 0.28
TEHP	100%, 0.03–0.36, 0.14	100%, 0.06–1.71, 0.36	100%, 0.1–1.41, 0.44	100%, 0.06–0.17, 0.09
TIBP	100%, 0.63–5.68, 2.74	100%, 0.81–7.00, 1.33	100%, 0.28–17.5, 0.49	100%, 0.20–0.33, 0.22
TNBP	100%, 0.69–4.83, 1.53	100%, 0.12–1.61, 0.21	100%, 0.47–2.36, 1.37	100%, 0.19–0.45, 0.36
TPTP	43%, nd ^b –0.63, nd	67%, nd–0.01, 0.004	79%, nd–29.7, 0.31	0%, nd, nd
THP	21%, nd–0.029, nd	100%, 0.03–0.36, 0.06	100%, 0.08–24.1, 0.47	100%, 0.006–0.014, 0.008
TBOEP	100%, 5.87–34.5, 18.0	100%, 0.10–0.37, 0.16	95%, nd–3.11, 1.89	50%, nd–0.16, 0.09
TPHP	100%, 1.28–7.76, 3.99	100%, 0.38–1.81, 0.69	58%, nd–0.91, 0.15	100%, 0.06–0.28, 0.17
TMPPs	0%, nd, nd	67%, nd–1.02, 0.04	32%, nd–6.59, nd	0%, nd, nd
∑ ₁₁ OPEs	100%, 32.9–227, 68.7	100%, 4.35–22.1, 7.56	100%, 21.3–138, 50.6	100%, 21.7–84.5, 39.0

^a Detection rates, range, and mean (in bold).^b nd = not detected.**Fig. 2.** Boxplot of \sum_{11} OPEs (A and B) and composition of individual OPEs (C) in water, sediment, organism and feed samples from the mariculture farms of the Beibu Gulf. PW and PS represents water and sediment in the ponds, respectively. ENW and ENS represents water and sediment in the estuary and nearshore area, respectively.

square meter of the water surface area with the feeds during one culture period (about three months). The total inventory of \sum_{11} OPEs in the ponds, including water, sediment, and shrimp, was estimated to be 226 μg per square meter of the pond (Table S11). Therefore, the feeds may have contributed about 22% of the OPEs in the culture pond.

Sediment sample: The \sum_{11} OPEs in the sediment from the ponds and open areas ranged from 4.35 to 22.1 ng g^{-1} dw (median 7.75 ng g^{-1} dw) and from 4.51 to 11.7 ng g^{-1} dw (median 7.42 ng g^{-1} dw), respectively (Fig. 2-B). They were generally lower than those reported from developed and densely-populated areas, such as the Bohai Sea (Zhong et al., 2018); the Laizhou Bay (Wang

et al., 2017b) that is close to the Yellow River estuary in north China; the Pearl River Delta in China (Ruan et al., 2014; Zhang et al., 2018); the marine estuaries of Galicia in Spain (Cristale et al., 2013), the Palos Verdes Shelf off coast of Los Angeles, which has been impacted by wastewater treatment plant effluents (Li et al., 2019); and the Canal de Mira that is an oyster farm in Portugal (Gadelha et al., 2019) (Table S12). However, they were obviously higher than those reported from remote regions, such as from the Bering Sea to the Central Arctic Ocean (Ma et al., 2017).

Similar to the case of seawater samples, TCIPPs and TCEP had higher concentrations than other target OPEs in the sediment. However, TBOEP, which averagely contributed 35% to the \sum_{11} OPEs

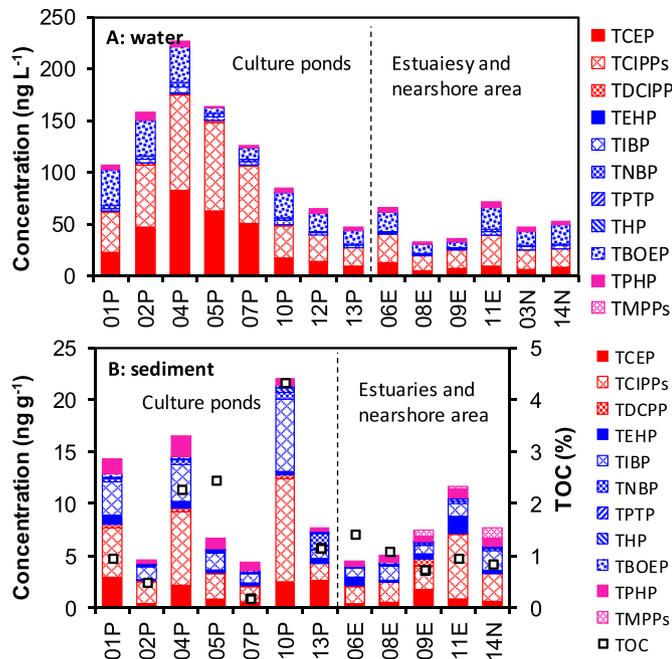


Fig. 3. Concentration profiles of OPEs in water (A) and sediment (B) samples.

in the water, only contributed 2% to \sum_{11} OPEs in the sediments; while TIBP, which contributed little to the \sum_{11} OPEs in the seawater, was the second contributors to the \sum_{11} OPEs in sediments, averaging 21%.

The average \sum_{11} OPEs was higher in the sediment from the ponds ($10.9 \pm 6.81 \text{ ng g}^{-1} \text{ dw}$) than from the open areas ($7.28 \pm 2.84 \text{ ng g}^{-1} \text{ dw}$) (Fig. 2-B, Fig. 3-B and Table S8), but the difference was not statistically significant (nonparametric test, $p > 0.05$). The average TOC contents of the sediment in the ponds ($1.69 \pm 1.44\%$) was higher than that in the open areas ($1.00 \pm 0.26\%$), although the difference was not significantly different (nonparametric test, $p > 0.05$). It is likely that some feed residues are present in the sediments of the ponds, enhancing the TOC contents. The concentrations of \sum_{11} OPEs and a few individual OPEs (TMPPs, TCIPPs, TIBP, and THP) were significantly positively related to the TOC content ($p < 0.01$) of the sediments (Table S13), indicating TOC may play an important role in the accumulation of OPEs in the sediments. However, no strong positive correlations were observed between the most K_d values of individual OPEs and TOC contents of the sediment samples (Table S14).

Organism samples: The \sum_{11} OPEs in the seafood organisms ranged from 5.13 to $39.6 \text{ ng g}^{-1} \text{ ww}$ (or 21.3 – $138 \text{ ng g}^{-1} \text{ dw}$) and averaged $14.6 \pm 10.2 \text{ ng g}^{-1} \text{ ww}$ (or $55.5 \pm 28.1 \text{ ng g}^{-1} \text{ dw}$). The average \sum_{11} OPEs in the shrimps ($12.5 \pm 3.9 \text{ ng g}^{-1} \text{ ww}$ or $50.9 \pm 16.4 \text{ ng g}^{-1} \text{ dw}$), crabs ($20.4 \pm 14.9 \text{ ng g}^{-1} \text{ ww}$ or $61.8 \pm 42.9 \text{ ng g}^{-1} \text{ dw}$), and oysters ($8.90 \pm 2.4 \text{ ng g}^{-1} \text{ ww}$ or $53.7 \pm 16.7 \text{ ng g}^{-1} \text{ dw}$) were not statistically different (Fig. 2 and Table S9). Similar to those in the water and sediments, TCIPPs and TCEP were the dominant OPEs in the organism samples. They averagely contributed $44.1 \pm 20.2\%$ and $20.4 \pm 13.5\%$ to the \sum_{11} OPEs, respectively. Among the non-halogenated OPEs, TPTP had higher concentration than others, contributing 13% and 21% to the \sum_{11} OPEs in the crab and oyster.

Feed sample: Commercial feeds are usually applied to the culture ponds to feed the shrimp or crab. In general, the major ingredients of the aquafeeds included wheat flour, soybean, corn, and fishmeal (Dong et al., 2013). The residual OPEs in the raw ingredients of the feed and packaging material (such as polypropylene woven bag)

may be sources of the OPEs in the feeds. The results in this study showed that the \sum_{11} OPEs in the feed samples were range of 21.7 – $84.5 \text{ ng g}^{-1} \text{ dw}$ (median $39.0 \text{ ng g}^{-1} \text{ dw}$) averaged $46.0 \pm 26.9 \text{ ng g}^{-1} \text{ dw}$, which is similar to the level in the organism samples (mean: $55.5 \pm 28.1 \text{ ng g}^{-1} \text{ dw}$) and 4.4 times higher than that in the pond sediment (mean: $10.9 \pm 1.7 \text{ ng g}^{-1} \text{ dw}$). The chlorinated OPEs contributed the highest proportion of the OPEs (97.8%) in the feeds. Among the three chlorinated OPEs, TCEP contributed 79.8% of \sum_{11} OPEs. Other OPEs were generally lower in the feeds than in the organisms. Compared to OPEs in the sediment, the three chlorinated OPEs had much higher concentrations than other OPEs in the feeds. Most of the feeds are ingested by organisms with the remaining settles to the sediment. The nutrients and contaminants in the feeds may release into the surrounding seawater or sediment (Avnimelech and Ritvo, 2003). Therefore, the feed could be a source of OPEs, in particular chlorinated OPEs, in the aquaculture ponds.

3.2. Partition and bioaccumulation of OPEs among sediment, organism, feed, and seawater

Generally, the calculated average $\log K_{OC}$ significantly positively correlated to the $\log K_{OW}$ of the target OPEs ($R = 0.69$, $p < 0.05$) in this study (Fig. 4A and Table S15). A similar correlation was reported in a previous study in Taihu Lake, China (Wang et al., 2018). The correlation suggests that the interactions between the hydrophobic moiety of the OPE molecules and sediment organic matter strongly influence the distribution of OPEs between sediment and water. However, it is likely that other factors are at play and nonequilibrium conditions prevail, due to the periodical water replacements and continuous input of feed residues to the sediments of this study. Most of the measured $\log K_{OC}$ of the OPEs in this study is higher than the $\log K_{OC}$ estimated by QSAR methods such as fragment contribution and molecular connectivity (Verbruggen et al., 2012), measured with soil adsorption experiment (van der Veen and de Boer, 2012), and reported from the Taihu Lake study (Wang et al., 2018) (Table S15).

The $\log BWAFs$ averaged from 1.36 (TBOEP in shrimp) to 4.25 (THP in crab), and the $\log BFAFs$ averaged from -0.78 (TCEP in shrimp) to 2.20 (THP in crab) (Fig. 4 and Table S16). Among the three aquatic organisms, oyster presented significantly ($p < 0.05$) higher accumulation potential to TCEP and TPTP than shrimp and crab. For the $BFAFs$, most of the OPEs except TCEP presented the $BFAF > 1$ ($\log BFAF > 0$), indicating that all OPEs except TCEP are bioaccumulative from the feeds.

The $\log BWAF$ or $\log BFAF$ was plotted versus $\log K_{OW}$ of OPEs in Fig. 4. For both the shrimp and crab aquaculture ponds, the correlations between $\log BFAF$ and $\log K_{OW}$ were significantly positive and linear ($R^2 = 0.84$ and 0.88 , $p < 0.01$), with TEHP ($\log K_{OW} = 9.49$, molecular weight = 435) excluded (Fig. 4-B, C). The correlations between $\log BWAF$ and $\log K_{OW}$ were also significantly positive and linear ($R^2 = 0.67$ and 0.71 , $p < 0.05$) (Fig. 4-D, E). If TEHP is included, the correlations between $\log BFAF$ and $\log K_{OW}$ were significantly parabolic ($R^2 = 0.85$ and 0.88 , $p < 0.01$) (Fig. 4-G, H). The results suggest that both $BWAFs$ and $BFAFs$ increased with increasing K_{OW} for $\log K_{OW}$ up to 7. The increases may be followed by declines at higher K_{OW} although only one data point of TEHP is available from this study. In previous studies, significant positive correlations between $\log BCFs$ and $\log K_{OW}$ were also observed in most tissues of common carp (Tang et al., 2019) and zebrafish (Wang et al., 2017a) at $\log K_{OW} < 7$. A similar trend was observed in the bioaccumulation of PCBs (Wang et al., 2007; Wu et al., 2008), i.e., the $BWAFs$ for PCBs increased with increasing K_{OW} at $\log K_{OW} < 7$ and subsequently declined with a further increase of $\log K_{OW}$. This trend could be plausibly explained by the increasing difficulty for large molecules

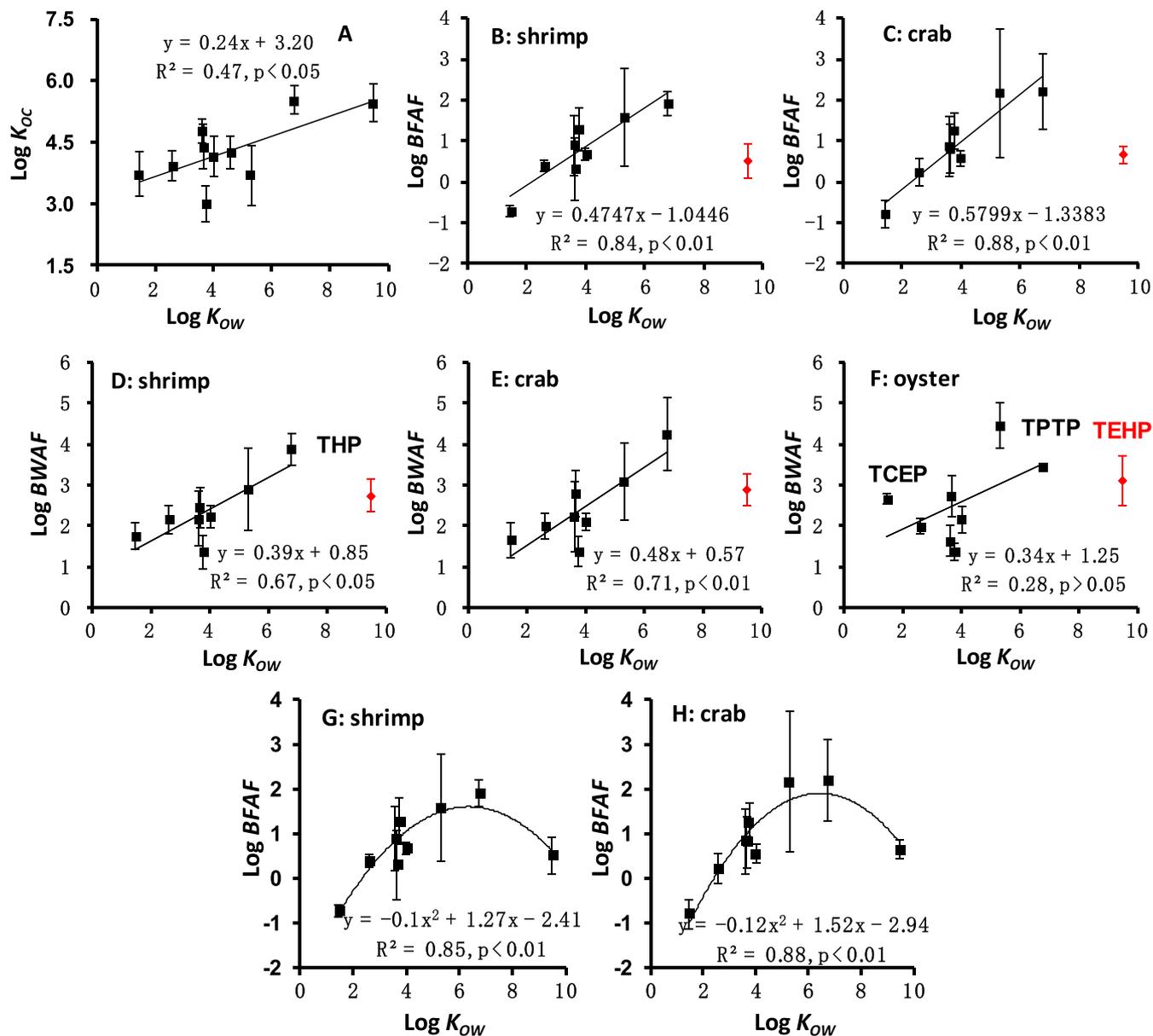


Fig. 4. The dependence of $\log K_{oc}$, $\log BWAFs$, and $\log BFAFs$ of OPEs on their $\log K_{ow}$.

to migrate across biomembranes and/or their relatively fast metabolic degradation in organisms (Wang et al., 2007).

Unlike the observations in shrimp and crab, the correlation between the $\log BWAFs$ and $\log K_{ow}$ were not significant ($p > 0.05$) in the oyster (Fig. 4-F). In particular, the $BWAFs$ of TCEP and TPTP diverged from the general trend predicted by K_{ow} . One of the possible reasons may be the fast water exchange in the estuaries, where the oysters live.

3.3. Health risk assessment through seafood consumption

Estimated dietary intakes (EDI) of OPEs were calculated for male and female of three age groups (2–5 years, 5–18 years, and >18 years) of human consumers according to the method detailed in Text S3. The 95th percentile concentration of OPEs was used to present a high exposure level. The EDI values of total OPEs for the three age groups ranged from 9.31 to 23.75 ng kg^{-1} body weight (bw) day^{-1} (Table 2 and Table S17). The youth (5–18 years) had the

highest daily intakes, followed by children (2–5 years) and adults (>18 years). Between the two genders, males had higher daily intakes than the females for both the children and youth, while the opposite was found for the adult. The highest contribution to EDIs is from the oyster, which accounted for about 50% of the total OPE intake, followed by the crab (25%) and shrimp (25%), for all the consumers. The exposures to TCIPs and TCEP are higher than other individual OPEs. The sum contribution of TCIPs and TCEP accounted for approximately 60% of total EDI of OPEs.

The estimated exposure risks of OPEs are shown in Fig. S2. The hazard quotients (HQs) were calculated for all OPEs except TIBP, TPTP, THP, and TMPPs for which the reference dose (RfD) values are not available. Among different OPEs, the three chlorinated phosphates posed comparatively higher risks. Nevertheless, the hazard quotients of the three compounds were still much below the safe threshold of 1.0. The hazard index (HI), which is the sum of HQs of the seven individual OPEs, ranged from 2.1×10^{-4} (adult male) to 5.3×10^{-4} (youth male), indicating that the risk of ingesting the

Table 2

Estimated daily dietary intakes (EDI, ng kg⁻¹ bw day⁻¹) of OPEs via seafood consumption by different age groups from south China and RfD (ng kg⁻¹ bw day⁻¹) values of OPEs.

	Children (2–5 years)		Youth (6–18 years)		Adult (>18 years)		RfD ^a
	Male	Female	Male	Female	Male	Female	
TCEP	4.44	2.82	5.74	3.79	2.25	2.47	22,000
TCIPPs	6.33	4.05	8.18	5.40	3.21	3.51	80,000
TDCIPP	0.95	0.61	1.22	0.80	0.48	0.52	15,000
TEHP	0.27	0.17	0.35	0.23	0.14	0.15	35,000
TIBP	1.15	0.74	1.48	0.98	0.58	0.64	na
TNBP	0.33	0.21	0.43	0.28	0.17	0.18	24,000
TPTP	3.04	1.94	3.92	2.58	1.54	1.67	na ^b
THP	0.80	0.51	1.02	0.66	0.39	0.42	na
TBOEP	0.67	0.43	0.87	0.57	0.34	0.37	15,000
TPHP	0.16	0.10	0.20	0.14	0.08	0.09	70,000
TMPPs	0.27	0.18	0.35	0.23	0.14	0.15	na
∑ ₁₁ OPEs	18.40	11.74	23.75	15.66	9.31	10.18	

^a RfD: reference dose, data is from Ding et al. (2018).

^b RfD value is not available.

seafood was low with regard to OPEs.

The assessment of the overall risks posed by OPEs must include other exposure pathways in addition to seafood consumption. The main human exposure routes of organophosphorus compounds include breathing, dietary intake, skin absorption, and unconscious dust intake (Ding, 2016; Ding et al., 2018). To date, the studies on dietary intake of OPEs are limited, especially on EDI via seafood. Ding (2016) reported that the median EDI of OPEs via fish for adults and toddler in eastern China were 45 and 31 ng kg⁻¹ bw day⁻¹, which are higher than the results of this study. In southwestern China, the median EDI of OPEs from rice meals for adults was reported to be 312 ng kg⁻¹ bw day⁻¹ (Zhang et al., 2016). Additional EDIs via contacting dust and drinking water were reported (Ali et al., 2012; Ding et al., 2015; He et al., 2015; Lee et al., 2016; Tajima et al., 2014). These studies demonstrated that the EDI via food was comparable to or higher than those from contacting dust and drinking water. Thus, the threat of OPEs through seafood intake should not be discounted. Most OPEs are relatively soluble in water and easily combined with protein (Zhang et al., 2016), which is rich in seafood. With the increase of production and uses of OPEs, contamination of seafood produced from mariculture farms is expected to increase. As such, future surveillance and research on OPEs in the marine environment are warranted.

4. Conclusions

The results obtained in the present study indicated that OPEs widely occurred in the feed, water, sediments, and aquatic organisms (seafood) from marine aquaculture farms in the Beibu Gulf, China. Among target OPEs, TCIPPs and TCEP were the primary contaminants. The feed is an important source of OPEs in the mariculture farms. In general, the distribution of different OPEs among sediment, water, and feed, and the bioaccumulation of organisms from water and feed were largely controlled by their hydrophobicity and molecular size. Both log BWAFs and log BFAs increased with increasing *K*_{OW} within the log *K*_{OW} range of about 1–7, and the trend is likely to reverse with log *K*_{OW} greater than 7. The assessment on the dietary risk indicated that consumption of shrimp, crab, and oysters from the marine aquaculture farms involved in this work does not pose a health risk to humans at present.

Declaration of competing interest

No conflict of interest exists in the submission of this manuscript, and the manuscript is approved by all authors for publication.

CRedit authorship contribution statement

Ruijie Zhang: Conceptualization, Investigation, Methodology, Data curation, Writing - original draft, Writing - review & editing. **Kefu Yu:** Conceptualization, Funding acquisition, Resources, Supervision. **An Li:** Writing - review & editing. **Weibin Zeng:** Data curation, Writing - original draft. **Tian Lin:** Methodology, Writing - review & editing. **Yinghui Wang:** Project administration, Resources.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.114426>.

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