



Occurrences and distribution characteristics of organophosphate ester flame retardants and plasticizers in the sediments of the Bohai and Yellow Seas, China



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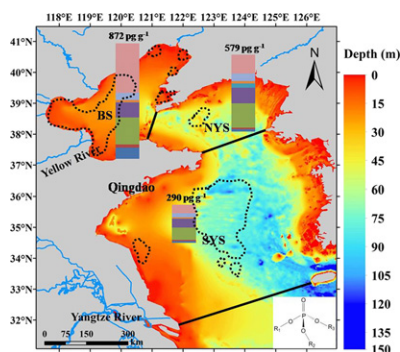
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HIGHLIGHTS

- Eight OPEs were widely detected in the sediment of the Bohai and Yellow Seas.
- TCEP and TEHP were the most dominant OPEs.
- High levels of OPEs were found in the Bohai Sea than those in the Yellow Sea.
- OPEs showed a positive correlation with TOC.
- Riverine discharge and hydrodynamic parameters influence the spatial distributions of OPEs.

GRAPHICAL ABSTRACT



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ABSTRACT

Concentrations and distribution characteristics of organophosphate esters (OPEs) in surface sediment samples were analyzed and discussed for the first time in the open Bohai Sea (BS) and Yellow Sea (YS). Three halogenated OPEs [tris-(2-chloroethyl) phosphate (TCEP), tris-(1-chloro-2-propyl) phosphate (TCPP), and tris-(1,3-dichloro-2-propyl) phosphate (TDCPP)] and five non-halogenated OPEs [tri-isobutyl phosphate (TiBP), tri-*n*-butyl phosphate (TnBP), tri-*n*-propyl phosphate (TPnP), triphenyl phosphate (TPhP) and tris-(2-ethylhexyl) phosphate (TEHP)] were detected in this region. The concentrations of eight OPEs in total (Σ_8 OPEs) ranged from 83 to 4552 pg g^{-1} dry weight (dw). The halogenated OPEs showed higher abundances than the non-halogenated ones did, with TCEP, TCPP, and TEHP the main compounds. Generally, concentrations of OPEs in the BS were higher than those in the YS. Riverine input (mainly the Changjiang Diluted Water (CDW)) and deposition effect in the mud areas might have influenced the spatial distributions of OPEs. Correlation between OPE concentrations and total organic carbon (TOC) indicated TOC was an effective indicator for the distribution of OPEs. Inventory analysis of OPEs implied that sea sediment might not be the major reservoir of these compounds.

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1. Introduction

Organophosphate esters (OPEs) are organic compounds with a phosphorus atom center that are mainly used as flame retardants and plasticizers, as well as antifoaming agents and hydraulic fluids (Wei et al., 2015). With the phasing out of brominated flame retardants (BFRs), especially polybrominated diphenyl ethers (PBDEs), in the early 21st century, production and usage of OPEs have increased significantly (Wang et al., 2015). In Western Europe, production of OPEs increased about 10% between 2001 and 2006 (Reemtsma et al., 2008). In China, usage of flame retardants reached 300,000 tons (t) in 2013, and usage of OPEs increased rapidly (Zhang, 2014). Worldwide, approximately 500,000 t of OPEs was used in 2011, and the estimated market volume of OPEs was 680,000 t in 2015 (Ou, 2011; van der Veen and de Boer, 2012).

As flame retardants, OPEs do not covalently bond to the added materials, thus they can easily leach into the environment. Additionally, OPEs are resistant to degradation, and hence can exist persistently in the environment (Liagkouridis et al., 2015; Wei et al., 2015; Zhang et al., 2016). OPEs have been ubiquitously detected in the environment and biota (Ali et al., 2012; Cao et al., 2012; Chen et al., 2012; Fromme et al., 2014; Hu et al., 2014; Mihajlovic et al., 2011; Wei et al., 2015). Even in polar regions and remote oceans, OPEs have been detected in the atmosphere, snow, and seawater (Castro-Jimenez et al., 2014; Moller et al., 2012; Sühring et al., 2016; Li et al., 2017), which indicates their long-range transportation (LRT) ability. Once pollutants such as OPEs enter seawater, they can undergo sedimentation processes by absorbing onto particles and settling down into marine sediment. From this point of view, marine sediment can be a long-term repository of these compounds (Dachs et al., 2002).

Although risk assessment of OPEs regarding human health is still in progress, carcinogenicity, neurotoxicity, teratogenicity, cytotoxicity, and metabolic toxicity of OPEs to other species are reported frequently, which indicates OPEs' potential health risks to human beings (Greaves and Letcher, 2017). For this reason, the state government of New York has prohibited the use of tris-(2-chloroethyl) phosphate (TCEP) in products for children under the age of three since 2013 (N.Y., 2011). In Washington, TCEP and tris-(1,3-dichloro-2-propyl) phosphate (TDCPP) have been banned from use in children's products and home furniture since 2014 because of their toxicity (ESHB 1294, 2013).

The Bohai Sea (BS) and the Yellow Sea (YS) are marginal seas of China. The BS is a semi-closed and inner sea with a mean depth of 18 m. It is surrounded by the Bohai Economic Rim, which consists of Liaoning, Hebei, and Shandong Provinces and the municipality of Tianjin. The BS receives large volumes of domestic sewage and industrial wastewater, which deteriorate the water quality significantly (Shen et al., 2013). For the YS, it is a marginal sea that is adjacent to the Chinese mainland (Liaoning, Shandong, and Jiangsu Provinces and the municipality of Shanghai) to the west and the Korean Peninsula to the east. The YS exchanges water with the BS to the northwest, the East China Sea (ECS) to the south, and the Western Pacific to the east via ocean currents, such as the Kuroshio Current, Subei Coastal Water (SCW), Changjiang Diluted Water (CDW), and Taiwan Warm Current (Wei et al., 2016). Meanwhile, the YS suffers from deteriorating water quality due to the dumping of huge amounts of insufficiently treated domestic sewage and industrial wastewater (Lu et al., 2013; Wang et al., 2015). Fig. 1 presents the hydrologic features (Guo et al., 2006) and mud areas (deposition zones) of the BS and YS (Saito and Yang, 1993).

Given the extensive production and usage of OPEs in China and the geographic and hydrologic features of the BS and YS, the two seas may be main reservoirs of these compounds. Zhong et al. (2017) recently reported high concentrations and the distribution patterns of seven OPEs in the seawaters of the BS and YS. However, there are few reports on these substances in the sediments of the BS and YS. Therefore, the concentrations and distributions of OPEs in these marine sediments should be investigated to better understand the environmental behaviors of

these important pollutants. In this work, 49 surface sediment samples from the BS and YS were collected and analyzed to (i) investigate the concentrations, compositions, and distribution patterns of OPEs in the marine sediments of the BS and YS; (ii) explore the factors influencing the spatial distributions of OPEs; and (iii) derive inventories of OPEs in the BS and YS.

2. Materials and methods

2.1. Sample collection

In September 2010, during a research cruise campaign, 49 surface sediment samples (top 2 cm) were collected from the BS and YS with a stainless steel box corer. All the collected samples were instantly stored at $-20\text{ }^{\circ}\text{C}$ before freeze-drying. The locations of all the sampling sites are shown in Fig. 2.

2.2. Chemicals and materials

The native standards, including TCEP, tris-(1-chloro-2-propyl) phosphate (TCPP), TDCPP, tri-isobutyl phosphate (TiBP), tri-*n*-butyl phosphate (TnBP), triphenyl phosphate (TPHP), tripentyl phosphate (TPeP) and tris-(2-ethylhexyl) phosphate (TEHP) were supplied by Sigma-Aldrich. Deuterated surrogate standards, e.g. d_{27} -TnBP (99%), d_{15} -TPHP (99%) and d_{12} -TCEP (99%) were purchased from Sigma-Aldrich. Acetone, *n*-hexane (purity >99%) and dichloromethane (DCM) were obtained from LGC Standards (Wesel, Germany).

Neutral silica gel (0.1–0.2 mm; Macherey-Nagel, Düren, Germany) and anhydrous sodium sulfate (purity 99%; Merck, Darmstadt, Germany) were cleaned with dichloromethane (DCM) using a Soxhlet extractor for 24 h, and then baked at $450\text{ }^{\circ}\text{C}$ for 12 h. All organic solvents used were of analytical grade, and redistilled using a glass system. Laboratory glassware was baked at $450\text{ }^{\circ}\text{C}$ for 12 h, and then rinsed with acetone and *n*-hexane.

2.3. Sample extraction and fractionation

Sediment samples (10 g) were packed in extraction thimbles; spiked with $20\text{ }\mu\text{L}$ of $500\text{ }\mu\text{g }\mu\text{L}^{-1}$ of d_{27} -TnBP, d_{15} -TPHP, and d_{12} -TCEP as surrogate standards; and extracted with DCM for 18 h at a flow rate of 5 mL min^{-1} using a Soxhlet extractor. The extracts were evaporated to 1–2 mL using hexane as the keeper and further cleaned on a silica column (2.5 g, 10% water deactivated) on which 3 g anhydrous granulated sodium sulfate was added. The extract was purified via elution with 20 mL hexane (Fraction 1) and 20 mL acetone/DCM (V/V = 1:1) (Fraction 2). Fraction 2 was concentrated down to $150\text{ }\mu\text{L}$ by a roto-evaporator and nitrogen blower. Then, $10\text{ }\mu\text{L}$ of $50\text{ }\mu\text{g }^{13}\text{C}_6\text{-PCB-208}$ (Wellington Laboratories, Canada) was added as the injection standard.

2.4. Instrumental analysis

The analytical method for the determination of OPEs has been described elsewhere (Ma et al., 2017). In the current study, the samples were analyzed using a gas chromatograph Agilent 7890A GC coupled to a triple quadrupole mass spectrometer Agilent 7010 MS (GC-MS/MS) equipped with a programmed temperature vaporizer (PTV) injector (Agilent Technologies, USA). The MS transfer line and the high sensitivity electron impact ionization source (HSEI) were held at $280\text{ }^{\circ}\text{C}$ and $230\text{ }^{\circ}\text{C}$, respectively. The MS/MS was operated in multiple reaction monitoring (MRM) mode. The collision cell gases were nitrogen (1.5 mL min^{-1}) and helium (2.25 mL min^{-1}). Analytes were separated on a HP-5 ms Ultra Inert capillary column ($30\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$ film thickness; J&W Scientific and Agilent Technologies, CA). One microliter of the sample was injected in pulsed splitless mode following an inlet temperature program of: $50\text{ }^{\circ}\text{C}$ for 0.2 min, increased to $300\text{ }^{\circ}\text{C}$ at $300\text{ }^{\circ}\text{C min}^{-1}$, and then held for 20 min. High purity helium

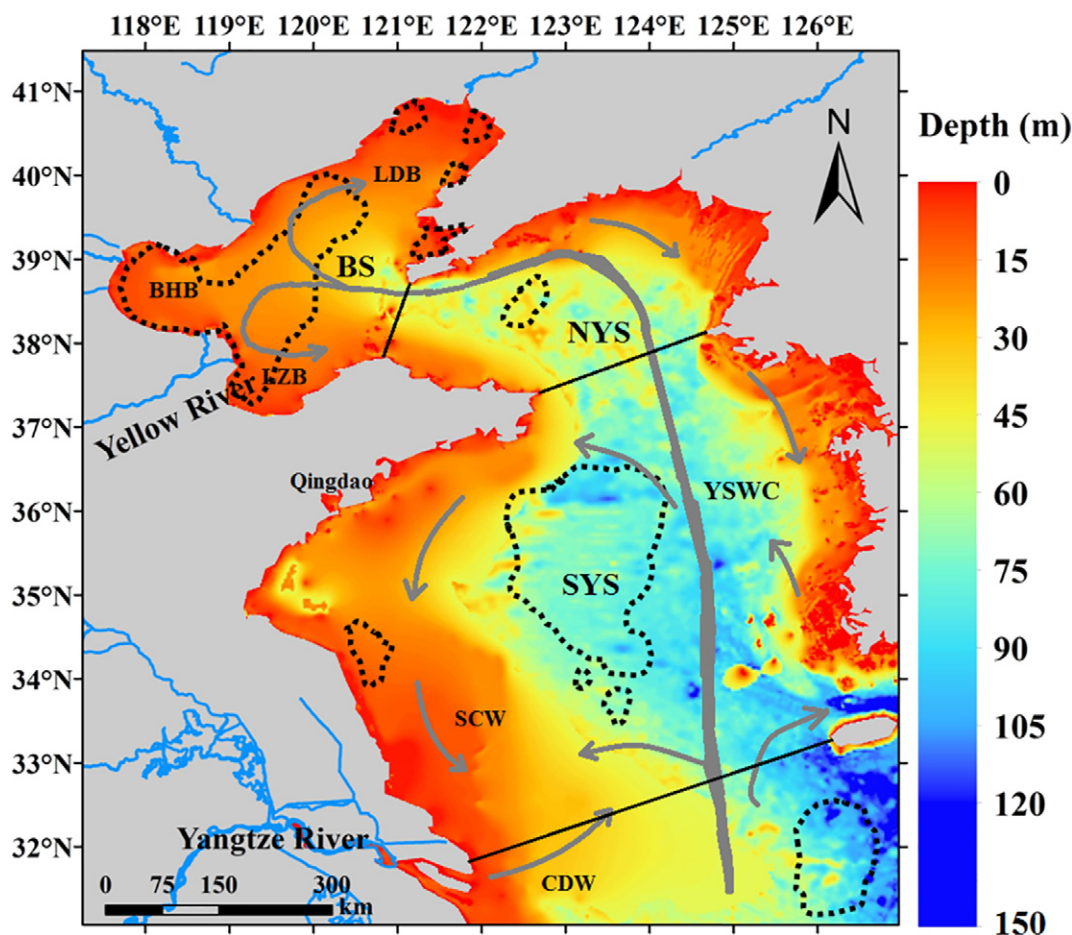


Fig. 1. Mud areas and hydrological information of the Bohai Sea (BS) and the Yellow Sea (YS). Dashed black lines enclose the mud areas (deposition zones) in the BS and YS. Colored bar shows the water depth of the BS and YS. Black straight lines show the boundaries of the BS, Northern Yellow Sea (NYS), and Southern Yellow Sea (SYS). Gray curved line shows the ocean currents in the BS and YS. SCW: Subei Coastal Water; CDW: Changjiang Diluted Water; YSWC: Yellow Sea Warm Current. LZB: Laizhou Bay; BHB: Bohai Bay; LDB: Liaodong Bay. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(99.999%) was used as the carrier gas. The GC oven temperature was held at 50 °C for 2 min; increased to 80 °C at 20 °C min⁻¹, then 250 °C at 5 °C min⁻¹, and finally 300 °C at 15 °C min⁻¹; and then held for 10 min. The ions selected for quantification and quantization are listed in Table S1. MassHunter Quantitative Analysis software (version B05.00, Agilent Technologies, USA) was used for data processing.

Quantization was performed using the internal calibration method based on a 10-point calibration curve for individual OPEs. The response factors were derived from the calibration curves (10-points) made for the response ratio between target compounds (0.0–0.5 ng μL⁻¹) and surrogate standards (0.1 ng μL⁻¹).

2.5. Quality control and quality assurance

The recovery rates of the selected OPEs for the sample preparation procedure, including Soxhlet extraction, rotation evaporation, and nitrogen evaporation, were checked by spiking the extract sediments with 50 ng standard mixture. The recoveries were from 63 ± 12% to 117 ± 16% for the eight OPEs selected. Moreover, extraction efficiency was checked via twofold extraction for five particle samples, which showed that the proportion of the eight OPEs in the first extraction ranged from 91 ± 6% for TDCPP to 99 ± 0.2% for TCEP. Five procedural blanks were extracted together with the samples. The mean concentrations of OPEs in the blanks ranged from 0.4 ± 0.2 pg g⁻¹ (TnBP) to 34 ± 6 pg g⁻¹ (TCPPs). The method detection limits (MDLs) were derived from the procedural blanks and quantified as the mean field blanks plus three times the standard deviation (3σ) of the field blanks. The

MDLs ranged from 1 pg g⁻¹ (TPeP) to 52 pg g⁻¹ (TCPPs) for 10 g sediment. All the concentrations of OPEs presented in this study were corrected for the recoveries and blanks.

3. Results and discussion

3.1. Concentrations and compositions of OPEs in the sediments

As shown in Table 1, the concentrations of the eight OPEs in total (Σ_8 OPEs) in the surface sediments ranged from 83 to 4552 pg g⁻¹ dry weight (dw), with a geometric mean (GM) concentration of 516 pg g⁻¹ dw. Generally, TCPP, TCEP, and TEHP were the main OPEs in the surface sediments, and the halogenated OPEs were more abundant than the non-halogenated ones. For the halogenated OPEs, TCEP was the dominant OPE, contributing 21 ± 14% to the Σ_8 OPEs. Individual TCEP concentrations ranged from 7 to 671 pg g⁻¹ dw, with a GM of 127 pg g⁻¹ dw. TCPP (ranged from 29 to 1521 pg g⁻¹ dw) was the second highest halogenated OPE per concentration, with a GM of 83 pg g⁻¹ dw. For the non-halogenated OPEs, TEHP was the dominant compound, contributing 27 ± 16% to the Σ_8 OPEs. Individual TEHP concentrations ranged from 8 to 3445 pg g⁻¹ dw, with a GM concentration of 113 pg g⁻¹ dw. Following TEHP, TPhP (ranged from 7 to 209 pg g⁻¹ dw) was the second most abundant compound of the non-halogenated OPEs, with a GM concentration of 40 pg g⁻¹ dw. Excluding TPeP (detection rate: 69%), all the OPEs analyzed showed 100% detection rates.

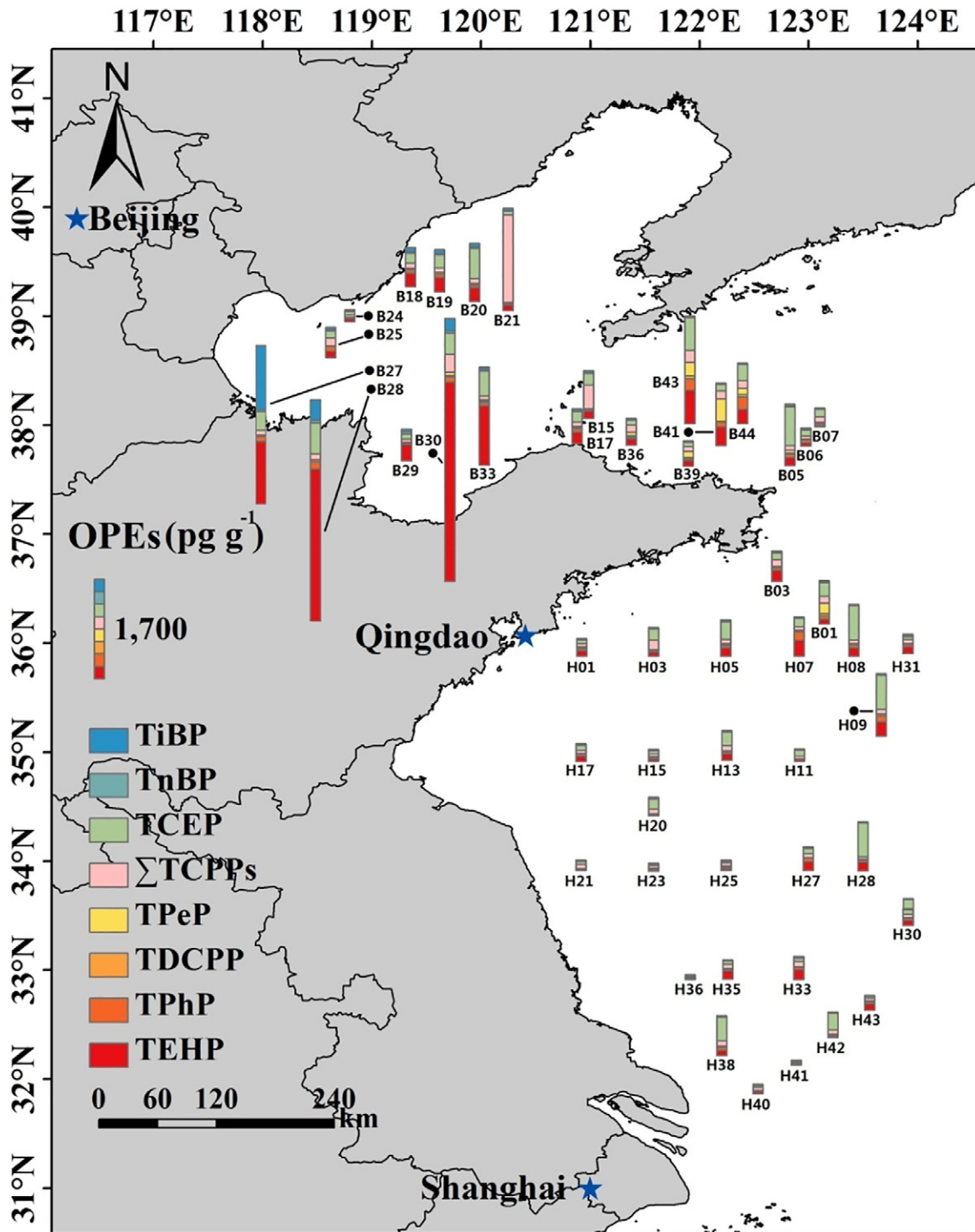


Fig. 2. Locations of sampling sites and concentrations and distributions of the total and individual organophosphate esters (OPEs).

As shown in Fig. 3, the compositions of OPEs in some sites showed unique features. For sites B29, B30, and B33 in the mouth of Laizhou Bay (LZB) and B28 on the southern edge of the mouth of Bohai Bay (BHB), TEHP was the predominating compound and accounted for >50% of the Σ_8 OPE compositions. Meanwhile, in the western part of the mouth of Liaodong Bay (LDB), the percentages of TCEP, TDCPP, and TiBP obviously increased and the percentage composition of TCEP was at a level comparable with or higher than that of TEHP. This indicates different OPE sources for LZB, BHB, and LDB. According to Wang et al. (2015), OPEs in LZB, BHB, and LDB mainly come from rivers draining into these bays. Therefore, the composition differences of

OPEs in the bay mouth areas might reflect, at least partially, the composition differences in riverine OPE inputs.

In the Northern Yellow Sea (NYS), especially at B39, B41, B43, and B44, an obvious feature of OPE composition was that the percentage of TPeP rose significantly. At B41, TPeP was the predominant OPE and even surpassed the percentages of TCEP and TEHP. Based on the obvious increase in compositions of TPeP, certain sources may exist for this compound. According to Yang and Liu (2007), the sediment of this area mainly comes from the Yellow River and is transported through the Bohai Strait. However, the low TPeP composition for the BS (Figs. 2 and 3) implied the compound might not come from the BS. Given that

Table 1
Statistics of OPEs in the Bohai and Yellow Seas ($n = 49$).

| Study regions | Values (pg g^{-1}) | Halogenated OPEs | | | Non-halogenated OPEs | | | | | Total |
|---------------|-------------------------------|------------------|------|-------|----------------------|------|------|------|------|-------|
| | | TCCP | TCEP | TDCPP | TiBP | TnBP | TPeP | TEHP | TPhP | |
| BS & YS | Maximum | 1521 | 671 | 54 | 1109 | 54 | 387 | 3445 | 209 | 4552 |
| | Minimum | 29 | 7 | 2 | 8 | 4 | <MDL | 8 | 7 | 83 |
| | Geometric mean | 83 | 127 | 12 | 23 | 12 | 2 | 113 | 40 | 516 |
| BS | Maximum | 1521 | 537 | 34 | 1109 | 54 | 55 | 3445 | 128 | 4552 |
| | Minimum | 39 | 52 | 4 | 28 | 9 | <MDL | 51 | 22 | 205 |
| | Geometric mean | 113 | 202 | 18 | 85 | 24 | 2 | 375 | 53 | 1137 |
| YS | Maximum | 414 | 671 | 54 | 34 | 21 | 387 | 583 | 209 | 1864 |
| | Minimum | 29 | 7 | 2 | 8 | 4 | <MDL | 8 | 7 | 83 |
| | Geometric mean | 76 | 111 | 11 | 16 | 10 | 2 | 80 | 36 | 411 |

OPEs are typical terrigenous pollutants, TPeP in this area probably comes from the Liaodong and/or Shandong Peninsulas. In the Southern Yellow Sea (SYS), H21, H23, H25, and H36 showed similar compositions. At these sites, TCCP was the dominating compound and the percentage of TnBP also was increased. According to Zhong et al. (2017), one of the largest OPE manufacturers is located in northern Jiangsu Province, China. It produces 20,000 t of OPEs annually, with TCCP its main product. That is to say, an increase of TCCP in the OPE composition for these sites might be attributed to the input of that OPE manufacturer.

From the North Pacific to the Arctic Ocean, OPEs were investigated by Ma et al. (2017), and the concentrations of seven OPEs in total (Σ_7 OPEs) (TCEP, TCCP, TDCPP, TiBP, TnBP, TPeP, and TPhP) ranged from 159 to 4658 pg g^{-1} , with a mean concentration of 872 pg g^{-1} dw. Similar to our study, the halogenated OPEs had higher concentrations than the non-halogenated ones, and TCEP was also the predominant compound, contributing $54 \pm 18\%$ to the total OPEs, with a highest concentration of 3903 pg g^{-1} dw. However, TiBP in their study was the predominant non-halogenated OPE. This can be explained by the fact that they did not analyze the extremely hydrophobic TEHP, which has a log K_{ow} value of 9.49. Actually, for the Schwechat River, TEHP was not detected in the river water, whereas a high level of this compound (140,000 pg g^{-1}) was detected in the sediment (Martinez-Carballo et al., 2007). Even in the BS and YS, TEHP was not detected in the seawater (Zhong et al., 2017) whereas high concentrations of this compound were detected in the sediment in the current study. This can be explained by the fact that TEHP has high hydrophobicity, thus is liable to be absorbed onto suspended particulate matter and then prone to deposition in the sediment (Reemtsma et al., 2008; Wei et al., 2015).

3.2. Spatial distribution of OPEs in the sediments and its influencing factors

Fig. 2 shows the overall distribution pattern of OPEs in the BS and YS. Generally, the concentrations of the Σ_8 OPEs in the BS were higher than

those in the YS ($p < 0.01$). As shown in Fig. 2 and Table 1, the concentrations of the Σ_8 OPEs ranged from 205 to 4552 pg g^{-1} dw, with a GM of 1137 pg g^{-1} dw in the BS. However, in the YS, the concentrations of the Σ_8 OPEs ranged from 83 to 1864 pg g^{-1} dw, with a GM of 411 pg g^{-1} dw. For individual OPEs, all the compounds, except for TPeP, showed similar patterns to that of the Σ_8 OPEs, i.e., higher concentrations occurred in the BS. The TPeP concentrations in the YS (ranged from <MDL to 387 pg g^{-1} dw) were higher than those in the BS (ranged from <MDL to 55 pg g^{-1} dw). This implied that additional input of TPeP (which might come from the Liaodong and/or Shandong Peninsulas) might exist in the YS, as mentioned in Section 3.1. Higher concentrations of the Σ_8 OPEs and individual OPEs in the BS might result from the higher number of pollution sources in the BS and the poorer water exchange capacity of the BS (Zhang et al., 2013). Yet, Zhong et al. (2017) reported similar OPE distribution patterns in the water phases of the BS and YS. Details about the OPE concentrations are listed in Table S2 in the supporting information.

For the individual sites, B30 in the mouth of LZB showed the highest concentration (4552 pg g^{-1} dw) of the Σ_8 OPEs among all the sites. In the mouth of BHB, B27 and B28 also showed high concentrations, whereas their neighboring sites (B24 and B25 in the north part of the mouth of BHB) showed relatively low Σ_8 OPE concentrations. In the mouth of LDB (B18, B19, B20, and B21), from the west to the east, the concentrations of the Σ_8 OPEs showed a descending trend. Furthermore, almost all the sites with high OPE concentrations in the BS resided in the mud areas (sediment deposition zone) (Figs. 1 and 2). Generally, high concentration of OPEs in the bay mouths might indicate serious pollution in LZB, BHB, and LDB.

Like the patterns for the BS, both in the NYS and SYS, most of the high concentrations occurred in the mud areas or their adjacent regions (Figs. 1 and 2). For example, B43 showed the highest Σ_8 OPE concentration among all the sites in the NYS and its location was adjacent to the central mud area of the NYS (no sediment samples were collected in

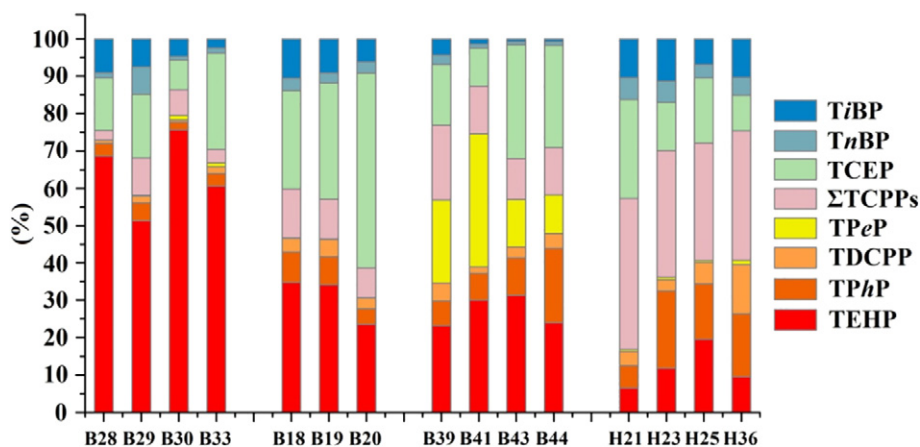


Fig. 3. Composition profiles of the investigated organophosphate esters (OPEs) in the surface sediments of several individual sites.

the mud area of the NYS). Similarly, in the SYS, for some transects (transect: H01, H03, H05, H07, and H08; transect: H21, H23, H25, H27, and H28), sites residing in the mud areas showed higher concentrations than their neighboring sites did (concentrations of H05, H07, and H08 were higher than those of H01 and H03; concentrations of H21, H27, and H28 were higher than those of H23 and H25). This phenomenon can be explained by the fact that hydrophobic organic pollutants (dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexanes (HCHs)) can be co-transported with suspended particles and deposited in the mud areas of the BS and YS (Hu et al., 2011). In our study, most of the OPEs (log K_{ow} values ranged from 1.44 to 9.49 for the OPEs studied in this work) had log K_{ow} values comparable with or higher than those of DDT (log K_{ow} = 6.90) and HCHs (log K_{ow} values ranged from 3.72 to 4.14 for the most common isomers) (Rani et al., 2017; Wang et al., 2015). That is to say, OPEs might present comparable or higher particle affinity and might also be liable to finally depositing in the mud areas.

Exceptionally, though H38 does not reside in the mud area, it still presented a higher Σ_8 OPE concentration than those in its neighboring sites (H35, H36, H40, and H41). This might be attributed to the input of the Changjiang Diluted Water (CDW). The CDW prevails during summer and presents a tongue-shaped and northeastward extension (Wei et al., 2016) under which H38 resides. Together with the CDW, many substances derived from the Yangtze River (particles and pollutants) are trapped and settle down to the sediment (Hu et al., 2011), which might result in the higher Σ_8 OPE concentration for H38. Taken together, riverine substance input and deposition effect of mud areas might be the main factors that influenced the distributions of OPEs in the sediments.

Additionally, a distribution pattern of TOC-normalized OPE concentrations is presented in Fig. S1 in the supporting information. Compared with Fig. 2, a high contribution of OPEs to the south Yellow Sea from the Yangtze River discharge can be distinguished, and a high load of OPEs in the nearshore region compared to the offshore region was also highlighted.

3.3. Correlation between OPEs and total organic carbon (TOC)

TOC is an important parameter for assessing the environmental status of aquatic ecosystems in marine and estuarine sediments (Hu et al., 2008). In this study, the TOC of 45 sites (Table S2; data for sites B25, H21, H35, and H43 was not obtained) was analyzed, and a positive correlation between OPEs and TOC was found ($n = 45, p < 0.01$). This result implied that TOC might be used as a tool for the estimation of organic pollutants (Li et al., 2016) such as OPEs. However, in the BS only, poor correlation was found between TOC and OPEs, whereas, in the YS, positive correlation between the two was still present (see details in Table S3). A reasonable explanation of this pattern might be that, in the BS, spatially limited or defined sources of OPEs near the coast existed. These sources might disrupt the correlation between OPEs and TOC. Rivers draining into the BS might be among the sources of

high concentrations of OPEs (up to 1,548,640 $\mu\text{g L}^{-1}$ in the water phase) (Wang et al., 2015), though concentrations in the sediment and suspended particles of these rivers were not reported. The high level of OPEs detected at site B33 might result from the input of the adjacent Jiehe River (808,080 $\mu\text{g L}^{-1}$, water phase) (Wang et al., 2015), which also emphasized the importance of riverine input, as mentioned in Section 3.2. Additionally, landfills and sewage outfalls in the coastal areas may also be one of the sources (Zhong et al., 2017). In this study, high concentrations of OPEs were detected at sites B27 and B28, which were adjacent to a pollutant discharge zone (SOA, 2016). For these two sites, which are located in the mud areas, apart from the deposition effect of OPEs mentioned in Section 3.2, point sources (the pollutant discharge zone) might be another factor that resulted in the high concentrations. For B28 was closer to the pollutant discharge zone and showed higher OPE concentrations than those of B27, which is a typical pattern for point sources.

3.4. Inventories of OPEs in the BS and YS

Given the frequently detected concentrations of OPEs in the surface sediments of the BS and YS, mass inventories regarding this area could be derived. Because the average sedimentation rates in the BS and YS were estimated as 0.31 cm a^{-1} (Li et al., 2002), the 2 cm of top sediment captured would reflect the OPE inputs since 2004, during which usage of BFRs in East Asian countries began to decrease and was gradually replaced by usage of OPE flame retardants (Ou, 2011).

The calculation method used was as previously reported (Jonsson et al., 2003), and detailed information regarding such is provided in the supporting information. As shown in Table 2, the inventories of the Σ_8 OPEs ranged from 474 to 26,000 kg, with a GM of 2499 kg. For the halogenated OPEs, TCEP was estimated to range from 38 to 3833 kg, with a GM of 727 kg, whereas the inventories of non-halogenated TEHP were estimated to range from 46 to 19,680 kg, with a GM of 648 kg. Compared with the amount of OPE usage in China (Ou, 2011), input of OPEs to the sediment still only accounted for a small proportion. Meanwhile, the estimated burden of OPEs in the seawaters of the BS and YS was about 396,604 kg (see calculation method in the supporting information), which was much higher than that of the sediment OPEs. According to Ma et al. (2017), the inventories of the Σ_7 OPEs (as mentioned in Section 3.1) ranged from 17,000 to 292,000 kg, with an average value of 78,000 kg (Table 2), in the Central Arctic Ocean Basin (area: $4.489 \times 10^6 \text{ km}^2$), which also accounted for a small proportion of the OPE production/usage volumes in the United States and Europe. Taken together, the sea sediments of the BS, YS, and Central Arctic Ocean Basin might not be the only reservoirs of OPEs for their corresponding regions.

However, in the Great Lakes (Lakes Superior, Michigan, and Ontario; total area: $1.58 \times 10^5 \text{ km}^2$), the average inventory of the seven OPEs that were also analyzed in the present study was 22,497 kg (Cao et al., 2017) (Table 2). In Lake Michigan, 17 tons of OPEs resided in the lake

Table 2
Estimation results of the inventories of OPEs in the sediments of the Bohai and Yellow Seas and those reported in other studies.

| Studied regions | Values (kg) | Halogenated OPEs | | | Non-halogenated OPEs | | | | | Total |
|---|----------------|------------------|---------|-------|----------------------|--------|------|--------|------|---------|
| | | TCPP | TCEP | TDCPP | TiBP | TnBP | TPeP | TEHP | TPhP | |
| BS & YS ^a | Maximum | 8689 | 38,339 | 3089 | 63,359 | 3099 | 2211 | 19,680 | 1194 | 26,000 |
| | Minimum | 166 | 38 | 11 | 45 | 23 | 3 | 46 | 40 | 474 |
| | Geometric mean | 476 | 727 | 93 | 130 | 70 | 13 | 648 | 2256 | 2499 |
| The Central Arctic Ocean Basin ^b | Maximum | 26,000 | 219,000 | 9200 | 16,000 | 12,000 | 4600 | – | 5900 | 292,000 |
| | Minimum | 570 | 12,000 | 0 | 3600 | 1100 | 0 | – | 0 | 17,000 |
| | Average | 7300 | 5400 | 1700 | 7800 | 4000 | 930 | – | 1600 | 78,000 |
| The Great Lakes ^c | Average | 3040 | 906 | 1237 | 7357 | 5446 | – | 1087 | 3424 | 22,497 |

–: not analyzed in the cited studies. BS: the Bohai Sea; YS: the Yellow Sea.

^a Data from this study.

^b Data from Ma et al. (2017).

^c Data from Cao et al. (2017).

sediment, which accounted for approximately 25% of the total burden (63 tons) (Cao et al., 2017). This phenomenon reflected the different OPE distributions in the water and corresponding sediment in seas and freshwater lakes.

4. Conclusion

This study focused on the concentrations, compositions, and distributions of OPEs in the sediments of the BS and YS. High concentrations of OPEs were detected, with TCEP and TEHP being the dominant compounds of halogenated and non-halogenated OPEs, respectively. For the extensively reported carcinogenicity, neurotoxicity, teratogenicity, cytotoxicity, and metabolic toxicity to organisms and human beings, high concentrations of OPEs in certain coastal regions might pose threats to marine organisms, especially benthic ones. Actions should be taken to alleviate OPE pollution in these areas, and more attention should be paid to the potential environmental risks of OPEs. Riverine input and transportation and deposition of suspended particles in mud areas might be the main factors that influence the distribution patterns of OPEs in marine sediment. Positive correlation between TOC and OPEs in the whole region implied a common source of TOC and organic pollutants. However, the deviation of TOC and OPEs in the BS implied limited or defined sources of OPEs near the coast. The input of OPEs calculated for the sediments only accounted for a small proportion of OPE usage in China. This indicated that sea sediment might not be the main reservoir of OPEs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2017.09.272>.

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