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

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25 **Abstract**

26 Concentrations and distribution characteristics of organophosphate esters (OPEs) in surface
27 sediment samples were analyzed and discussed for the first time in the open Bohai Sea (BS) and
28 the Yellow Sea (YS). Three halogenated OPEs (Tris-(2-chloroethyl) phosphate (TCEP),
29 Tris-(1-chloro-2-propyl) phosphate (TCPP) and Tris-(dichloroisopropyl) phosphate (TDCPP)) and
30 five non-halogenated OPEs (Tri-*iso*-butyl phosphate (TiBP), Tri-*n*-butyl phosphate (TnBP),
31 Tripentyl phosphate (TPeP), Triphenyl phosphate (TPhP) and Tris-(2-ethylhexyl) phosphate
32 (TEHP)) were detected in this region. The concentrations of the total 8 OPEs (Σ_8 OPEs) ranged
33 from 83 to 4552 pg g⁻¹ dry weight (dw). The halogenated OPEs showed higher abundances than
34 the non-halogenated ones with TCEP, TCPP and TEHP being the main compounds. Generally,
35 concentrations of OPEs in the BS were higher than those in the YS. Riverine input (mainly the
36 Changjiang Diluted Water (CDW)) and deposition effect in the mud areas might influence the
37 spatial distributions of OPEs. Correlation between concentrations of OPEs and total organic
38 carbon (TOC) indicated TOC was an effective indicator for the distribution of OPEs. Budget
39 analysis of OPEs implied that sea sediment might not be the major reservoir of these compounds.

40

41 **Capsule:** Eight OPE congeners were widely detected in the sediment of BS and YS, and TCEP and
42 TEHP were the two dominant compounds.

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44

45 **Key words:** Tris (2-chloroethyl) phosphate (TCEP); Tris (2-ethylhexyl) phosphate (TEHP); total
46 organic carbon (TOC); budget

47 1. Introduction

48 Organophosphate esters (OPEs) are organic compounds with a phosphorus atom center and
49 are mainly used as flame retardants (mainly chlorinated OPEs) and plasticizers, as well as
50 antifoaming agents and hydraulic fluids (mainly nonhalogenated OPEs) (Wei et al., 2015). With
51 the phasing out of brominated flame retardants (BFRs), especially polybrominated diphenyl ethers
52 (PBDEs) in the early 21th century, production and usage of OPEs have increased significantly
53 (Wang et al., 2015). In the western Europe, produce of OPEs increased about 10% between 2001
54 and 2006 (Reemtsma et al., 2008). In China, usage of flame retardant reached 300,000 tons (t) in
55 2013 and usage of OPEs increased most rapidly (Zhang, 2014). Worldwide, approximately
56 500,000 t of OPEs were used in 2011 and the estimated market volume of OPEs was 680,000 t in
57 2015 (Ou, 2011; van der Veen and de Boer, 2012).

58 As flame retardants, OPEs do not covalently band to the added materials, thus they can easily
59 leach into the environment. Additionally, OPEs are resistant to be degraded and hence they can
60 exist persistently in the environment (Liagkouridis et al., 2015; Wei et al., 2015; Zhang et al.,
61 2016). OPEs have been ubiquitously detected in environment and biota (Ali et al., 2012; Cao et al.,
62 2012; Chen et al., 2012; Fromme et al., 2014; Hu et al., 2014; Mihajlovic et al., 2011; Wei et al.,
63 2015). Even in polar regions and remote oceans, OPEs were detected in atmosphere, snow and
64 seawater (Castro-Jimenez et al., 2014; Moller et al., 2012; Sühring et al., 2016; Li et al., 2017),
65 which indicates their long-range transportation (LRT) ability. Once pollutants like OPEs entered
66 into seawater, they can also undergo sedimentation processes by absorbing on particles and
67 settling down into marine sediment. From this point view, marine sediment can be seemed as
68 long-term repository of these compounds (Dachs et al., 2002).

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

76 The Bohai Sea (BS) and the Yellow sea (YS) are marginal seas of China. The BS is a
77 semi-closed and inner sea of China with a mean depth of 18 m. It is surrounded by the Bohai
78 Economic Rim which is consisted of Liaoning, Hebei, and Shandong Provinces and the Tianjin
79 municipality. BS receives large volumes of domestic sewage and industrial wastewater which
80 deteriorate the water quality significantly (Shen et al., 2013). For the YS, it is a marginal sea
81 which is adjacent to the Chinese mainland (Liaoning, Shandong, and Jiangsu Provinces and the
82 Shanghai municipality) westward and bordered Korean Peninsula to the east. The YS exchanges
83 water with the BS to the northwest, the East China Sea (ECS) to the south and the Western Pacific
84 to the east by ocean currents, such as Kuroshio Current, the Subei Coastal Water (SCW), the
85 Changjiang Diluted Water (CDW) and the Taiwan Warm Current (Wei et al., 2016). Meanwhile,
86 the YS suffers from deteriorating water quality due to dumping of huge amounts of less-treated
87 domestic sewage and industrial wastewater (Lu et al., 2013; Wang et al., 2015). Figure 1 presents
88 the hydrologic features (Guo et al., 2006) and mud areas (deposition zones) of the BS and YS
89 (Saito et al., 1994).

90 Given the extensive production and usage of OPEs in China and the geographic and

91 hydrologic features of the BS and YS, the two seas may be among the main reservoir of these
92 compounds. In a previous study, high concentrations and distribution patterns of 7 OPEs in the
93 seawater of the BS and YS was recently reported by Zhong et al. (2017). However there are very
94 limited reports on these substances in the sediment of the BS and YS. Therefore, concentrations
95 and distributions of OPEs in marine sediments should be investigated to better understand the
96 environmental behaviors of these important pollutants. In this work, 49 surface sediment samples
97 from the BS and YS were collected and analyzed to (i) investigate the concentrations,
98 compositions and distribution patterns of OPEs in marine sediment of the BS and YS; (ii) explore
99 the factors influencing the spatial distributions of OPEs; (iii) derive a budget of OPEs in the BS
100 and YS.

101 **2. Materials and methods**

102 **2.1 Sample collection**

103 Forty-nine surface sediment samples (top 2 cm) were collected from the BS and YS with a
104 stainless steel box corer in September 2010, during a research cruise campaign. All the collected
105 samples were instantly stored at -20 °C before freeze drying. Locations of all the sampling sites
106 are shown in Figure 2.

107 **2.2 Chemicals and materials**

108 The native standards, including TCEP, Tris-(1-chloro-2-propyl) phosphate (TCPP), TDCPP,
109 Tri-iso-butyl phosphate (TiBP), Tri-*n*-butyl phosphate (TnBP), Triphenyl phosphate (TPhP),
110 Tripentyl phosphate (TPeP) and Tris-(2-ethylhexyl) phosphate (TEHP) were supplied by Sigma
111 Aldrich. Deuterated surrogate standards, e.g. d27-TnBP (99%), d15-TPhP (99%) and d12-TCEP
112 (99%) were purchased from Sigma Aldrich. Acetone, *n*-hexane (purity > 99%) and

113 dichloromethane (DCM) were obtained from LGC Standards (Wesel, Germany).

114 Neutral silica gel (0.1 ~ 0.2 mm, Macherey-Nagel, Düren, Germany) and anhydrous sodium
115 sulfate (Merck purity 99%, Darmstadt, Germany) were cleaned with dichloromethane (DCM)
116 using Soxhlet extractor for 24 h, and baked at 450 °C for 12 h. All organic solvents used were of
117 analytical grade, and redistilled using glass system. Laboratory glassware was baked at 450 °C for
118 12 h, and then rinsed with acetone and *n*-hexane.

119 **2.3 Sample extraction and fractionation**

120 Sediment samples (10 g) were packed in extraction thimbles and spiked with 20 µl of 500 pg
121 µl⁻¹ of d₂₇-TnBP, d₁₅-TP \hbar P and d₁₂-TCEP as surrogate standards, extracted with DCM for 18 h at
122 a flow rate of 5 mL min⁻¹ using Soxhlet extractor. Extracts were evaporated to 1 ~ 2 mL using
123 hexane as keeper and further cleaned on a silica column (2.5 g, 10 % water deactivated) topped on
124 3 g anhydrous granulated sodium sulfate. The extract was purified by eluting with 20 mL hexane
125 (Fraction 1) and 20 mL acetone/DCM (V/V = 1:1) (Fraction 2), respectively. Fraction 2 was
126 concentrated down to 150 µL by roti-evaporation and nitrogen blower. Ten microliter of 50 pg
127 ¹³C₆-PCB-208 (Wellington Laboratories, Canada) was added as injection standard.

128 **2.4 Instrumental analysis**

129 Analytical method for the determination of OPEs with GC-MS/MS has been described
130 elsewhere (Ma et al., 2017). In detail, the samples were analyzed using a gas chromatograph
131 Agilent 7890A GC couple to a triple quadrupole mass spectrometer Agilent 7010 MS
132 (GC-MS/MS) equipped with a programmed temperature vaporizer (PTV) injector (Agilent
133 Technologies, USA). The MS transfer line and the high sensitivity electron impact ionization
134 source (HSEI) were held at 280 °C and 230 °C, respectively. The MS/MS was operated in

135 Multiple Reaction Monitoring (MRM) mode. The collision cell gases were nitrogen (1.5 mL min^{-1})
136 and helium (2.25 mLmin^{-1}). Analytes were separated on a HP-5MS Ultra Inert capillary column
137 ($30 \text{ m} \times 0.25 \text{ mm i.d.} \times 0.25 \text{ } \mu\text{m}$ film thickness, J&W Scientific and Agilent Technologies, CA).
138 One microliter of the sample was injected in the pulsed splitless mode with an inlet temperature
139 program following $50 \text{ }^\circ\text{C}$ for 0.2 min, increased to $300 \text{ }^\circ\text{C}$ at $300 \text{ }^\circ\text{C min}^{-1}$ and then held for 20
140 min. High purity helium (99.999%) was used as the carrier gas. The GC oven temperature was
141 held at $50 \text{ }^\circ\text{C}$ for 2 min, increased to $80 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C min}^{-1}$, then increased to $250 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C min}^{-1}$,
142 finally increased to $300 \text{ }^\circ\text{C}$ at $15 \text{ }^\circ\text{C min}^{-1}$, and held for 10 min. Selected ions for quantification
143 and quantization were listed in Table S1. MassHunter quantitative analysis software (version
144 B05.00, Agilent Technologies, USA) was used for data processing.

145 Quantization was performed using the internal calibration method based on 10-point
146 calibration curve for individual OPEs. The response factors were derived from the calibration
147 curves (10-points) made for response ratio between targets compounds ($0.0 \sim 0.5 \text{ ng } \mu\text{L}^{-1}$) and
148 surrogate standards ($0.1 \text{ ng } \mu\text{L}^{-1}$).

149 **2.5 Quality control and quality assurance**

150 The recovery rates of the selected OPEs for the sample preparation procedure, including
151 Soxhlet extraction, rotation evaporation, and nitrogen evaporation, were checked with spiking 50
152 ng standard mixture to extract sediments. The recoveries were from $63 \pm 12\%$ to $117 \pm 16\%$ for
153 the selected 8 OPEs. Moreover, extraction efficiency was checked with twice extraction for 5
154 particle samples, which showed that the proportion of 8 OPEs in first extraction ranged from $91 \pm$
155 6% for TDCPP to $99 \pm 0.2\%$ for TCEP. Five procedural blanks were extracted together with the
156 samples. The mean blanks of OPEs are from $0.4 \pm 0.2 \text{ pg g}^{-1}$ (TnBP) to $34 \pm 6 \text{ pg g}^{-1}$ (TCPPs). The

157 method detection limits (MDLs) were derived from the procedural blanks and quantified as mean
158 field blanks plus three times the standard deviation (3δ) of field blanks. MDLs ranged from 1 pg
159 g^{-1} (TPeP) to 52 pg g^{-1} (TCPPs) for 10 g sediment. All the concentrations of OPEs presented in
160 this study were corrected for recoveries and blanks.

161 **3. Results and Discussion**

162 **3.1 Concentrations and compositions of OPEs in sediment**

163 As shown in Table 1, concentrations of the total 8 OPEs (Σ_8 OPEs) in surface sediment ranged
164 from 83 to 4552 pg g^{-1} dry weight (dw), with a geometric mean (GM) concentration of 516 pg g^{-1}
165 dw. Generally, TCPP, TCEP and TEHP were main OPEs in surface sediment and the halogenated
166 OPEs were more abundant than the non-halogenated ones. For the halogenated OPEs, TCEP was
167 the dominant OPEs which contributed $21 \pm 14\%$ to the Σ_8 OPEs. Individual TCEP concentrations
168 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}
169 dw) was the second highest halogenated OPEs in concentration with a GM of 83 pg g^{-1} dw. For
170 the non-halogenated OPEs, TEHP was the dominant compound which contributed $27 \pm 16\%$ to the
171 Σ_8 OPEs. Individual TEHP ranged from 8 to 3445 pg g^{-1} dw with a GM concentration of 113 pg g^{-1}
172 dw. Following TEHP, TP h P (ranged from 7 to 209 pg g^{-1} dw) was the second most abundant
173 compound of the non-halogenated OPEs with a GM concentration of 39.50 pg g^{-1} dw. Except for
174 TPeP (detection rates: 69%), all the OPEs analyzed showed a 100% detection rate.

175 However, as shown in Figure 3, compositions of OPEs showed significant differences among
176 individual sites (Figure 3A) and between the BS and YS (Figure 3B) as well. For instance, TEHP
177 at B29, B30 and B33 on the Laizhou Bay (LZB) mouth and sites B27 and B28 on the south part of
178 the Bohai Bay (BHB) mouth showed extremely high percentage (which even surpassed the sum of

179 the remaining OPEs) of the total OPEs. While on the Liaodong Bay (LDB) mouth, TCPP at B21
180 also surpassed the total amount of the other OPEs. This might indicate different sediment origins
181 and/or pollution sources for those areas mentioned above (Yang et al., 2007).

182 **3.2 Spatial distribution of OPEs in sediment and its influencing factors**

183 Figure 2 showed overall distribution pattern of OPEs in the BS and YS. Generally,
184 concentrations of Σ_8 OPEs in the BS were higher than those in the YS ($p < 0.01$). As shown in
185 Figure 2 and Table 1, concentrations of the Σ_8 OPEs ranged from 205 ~ 4552 pg g^{-1} dw with a GM
186 of 1137 pg g^{-1} dw in the BS. However, in the YS, concentrations of Σ_8 OPEs ranged from 83 ~
187 1864 pg g^{-1} dw with a GM of 411 pg g^{-1} dw. For individual OPEs, most compounds showed
188 similar patterns to that of the Σ_8 OPEs, i.e., higher concentrations occurred in the BS, except for
189 TPeP. TPeP concentrations in the YS (ranged from < MDL to 387 pg g^{-1} dw) were higher than
190 those in the BS (ranged from < MDL to 55 pg g^{-1} dw). This implied that additional sources of
191 TPeP might exist in the YS. Higher concentrations of Σ_8 OPEs and individual OPEs in the BS
192 might result from the more pollution sources in the BS and the poorer water exchange capacity of
193 the BS (Zhang et al., 2013). Actually, in the BS and YS, similar OPE distribution patterns were
194 also reported in water phase (Zhong et al., 2017). Details about the OPEs concentrations were
195 listed in Table S2 in the supporting information.

196 For individual sites, B30 on the LZB mouth showed the highest concentration (4552 pg g^{-1}
197 dw) of the Σ_8 OPEs among all the sites. On the BHB mouth, B27 and B28 also showed high
198 concentrations while their neighboring sites (B24 and B25 on the south part of the BHB mouth)
199 showed relatively low Σ_8 OPEs concentrations. While on the LDB mouth (B18, B19, B20 and
200 B21), from the west to the east, concentrations of Σ_8 OPEs showed a descending trend. Actually,

201 almost all the sites with high OPE concentrations in the BS resided on the mud areas (sediment
202 deposition zone) (Figures 1 and 2). Generally, high concentration of OPEs in the bay mouths
203 might indicate serious pollutions in the LZB, BHB and LDB.

204 Like patterns in the BS, both in the North Yellow Sea (NYS) and South Yellow Sea (SYS),
205 most high concentrations occurred in mud areas or their closely adjacent regions (Figures 1 and 2)
206 as well. For example, B43 showed the highest Σ_8 OPEs concentration among all the sites in the
207 NYS and its location was closely adjacent to the central mud area of the NYS. (No sediment
208 samples were collected in the mud area of the NYS.) Similarly, in the SYS, on some transects
209 (transect H01, H03, H05, H07 and H08; transect H21, H23, H25, H27 and H28), sites reside on
210 the mud areas showed higher concentrations than their neighboring sites (concentrations of H05,
211 H07 and H08 were higher than those of the H01 and H03; concentrations of H21, H27 and H28
212 were higher than those of the H23 and H25.). This phenomenon could be explained by the fact that
213 hydrophobic organic pollutants can co-transport with suspended particles and deposit in the mud
214 areas of the BS and YS (Hu, et al., 2011). In our study, most OPEs have comparable or even
215 higher *K_{ow}* values with/than dichlorodiphenyltrichloroethanes (DDTs) and
216 hexachlorocyclohexanes (HCHs) (Rani et al., 2017; wang et al., 2015). That is to say, OPEs might
217 present comparable or even higher particle affinity and might also be liable to finally deposit in
218 the mud areas.

219 Exceptionally, though H38 does not reside on the mud area, it still presented higher Σ_8 OPEs
220 concentration than those in its neighboring sites (H35, H36, H40 and H41). This might be
221 attributed to the input of Changjiang Diluted Water (CDW). The CDW prevails during summer
222 and presents a tongue-shaped and northeastward extension (Wei et al., 2016) under which H38

223 resides. Together with the CDW, lots of Yangtze River derived substances (particles and pollutants)
224 are trapped and settle down to the sediment (Hu, et al., 2011), which might result in the higher
225 Σ_8 OPEs concentration at H38. Taken together, riverine substance input and deposition effect of
226 mud areas might be the main factors that influenced the distributions of OPEs in sediment.

227 **3.3 Correlation between OPEs and total organic carbon (TOC)**

228 TOC is important parameters for assessment of environmental status of aquatic ecosystems in
229 marine and estuarine sediments (Hu et al., 2008). In this study, TOC of 45 sites (data of sites B25,
230 H21, H35 and H43 was not obtained) were analyzed and a positive correlation between OPEs and
231 TOC was found ($n = 45, p < 0.01$). This result implied that TOC might be used as a tool for the
232 estimation of organic pollutants (Li et al., 2016) like OPEs. However, in the BS poor correlation
233 was found between TOC and OPEs while in the YS positive correlation between the two still
234 existed. A reasonable explanation of this pattern might be that in the BS spatially limited or
235 defined sources of OPEs near the coast existed. These sources might disrupt the correlation
236 between OPEs and TOC. Actually, rivers draining into the BS might be among the sources for
237 high concentrations of OPEs (up to 1548640 pg L⁻¹) (Wang et al., 2015). High level of OPEs
238 detected at site B33 might result from the input of the adjacent Jiehe River (808080 pg L⁻¹) (Wang
239 et al., 2015), which also emphasized the importance of riverine input mentioned in section 3.2.
240 Additionally, landfills and sewage outfalls in the coastal areas may also be one of the sources
241 (Zhong et al., 2017). In this study, high concentrations of OPEs were detected at sites B27 and B28,
242 which were adjacent to a pollutant discharge zone (SOA, 2016). For the two sites (B27 and B28)
243 residing on mud areas, apart from the deposition effect of OPEs mentioned in section 3.2, point
244 sources (the pollutant discharge zone) might be another factors that resulted in the high

245 concentrations. (B28 was closer to the pollutant discharge zone and showed higher OPEs
246 concentrations than those of the B27, which was a typical pattern for point sources).

247 **3.4 Budget of OPEs in the BS and YS**

248 Given the frequently detected concentrations of OPEs in the surface sediment of the BS and
249 YS, a mass budget regarding this area could be derived. Since the average sedimentation rates in
250 BS and YS were estimated to be 0.31 cm a⁻¹ (Li et al., 2002), the 2 cm top sediment captured
251 would reflect the OPEs input since 2004 in which usage of BFR in East Asia countries began to
252 decrease and was gradually replaced by OPE flame retardants (Ou, 2011).

253 The calculation method used was as previously reported (Jonsson et al., 2003) and detailed
254 information was provided in the supporting information. As shown in table 2, the budget of
255 Σ_8 OPEs ranged from 474.14 to 26000.44 kg with a GM of 2498.62 kg. For halogenated OPEs,
256 TCEP was estimated to range from 38.27 to 3833.09 kg with a GM of 726.75 kg while the budget
257 of non-halogenated TEHP was estimated to range from 45.70 to 19679.56 kg with a GM of 648.30
258 kg. Compared with the amount of OPEs usage in China (Ou, 2011), input of OPEs to the sediment
259 still only accounted for a small proportion, which indicated that sea sediment might not be the
260 only reservoir of these compounds.

261 **3.5 Comparison of OPE concentrations with other studies**

262 From North Pacific to the Arctic Ocean, OPEs were also investigated by Ma et al. (2016) and
263 the total 7 OPEs (Σ_7 OPEs) (TCEP, TCPP, TDCPP, TiBP, TnBP, TPeP and TP h P) ranged from 159
264 ~ 4658 pg g⁻¹ with a mean concentration of 872 pg g⁻¹ dw. Similar to our study, the halogenated
265 OPEs had higher concentrations than the non-halogenated ones and TCEP was also the
266 predominant compound which contributed 54± 18% to total OPEs (TCEP, TCPP, TDCPP, TiBP,

267 *TnBP*, *TPeP* and *TPhP*) with a highest concentration of 3903 $\text{pg g}^{-1}\text{dw}$. However, *TiBP* in their
268 study was the predominant non-halogenated OPEs. This can be explained by the fact that they did
269 not analyze the extremely hydrophobic TEHP which has a $\log K_{OW}$ value of 9.49. Actually, in the
270 river Schwechat, TEHP was not detected in the river water, whereas a high level of this compound
271 (140000 pg g^{-1}) was detected in the sediment of the same river (Martinez-Carballo et al., 2007).
272 Even in the BS and YS, no TEHP was detected in the seawater (Zhong et al., 2017) while high
273 concentrations of this compound were detected in this study. This can be explained by the argument
274 that because of its high hydrophobicity, TEHP are liable to be absorbed to suspended particulate
275 matter and then settled down to the sediment (Reemtsma et al., 2008; Wei et al., 2015).

276 **4. Conclusion**

277 This study focused on the concentrations, compositions and distributions of OPEs in the
278 sediment of the BS and YS. High concentrations of OPEs were detected with TCEP and TEHP
279 being the dominant compounds in halogenated and non-halogenated OPEs, respectively. This
280 implied relatively serious pollution of OPEs in this area owing to anthropogenic influence. Actions
281 should be taken to alleviate OPEs pollution in these areas and more attention should be paid to
282 potential environmental risks of OPEs to aquatic organisms. Riverine input and transport and
283 deposit with suspended particles in mud areas might be the main factors that influence the
284 distribution patterns of OPEs in the marine sediment. Positive correlation between TOC and OPEs
285 in the whole region implied a common source of TOC and organic pollutants. However, the
286 deviation of TOC and OPEs in the BS implied limited or defined sources of OPEs near the coast.
287 Input of OPEs in sediment calculated only accounted for a small proportion of OPEs usage in
288 China. This indicated that sea sediment might not be the main reservoir of OPEs.

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293 CAS (2017255).

Table1. Statistics of OPEs in the Bohai and Yellow Seas ($n=49$).

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

Table2. Estimation results of the inventories of OPEs in the sediment of the Bohai and Yellow Sea.

OPEs	halogenated OPEs			non-halogenated OPEs					total
	TCPP	TCEP	TDCPP	TiBP	TnBP	TPeP	TEHP	TPhP	
Geometric means (GMs) (kg)	476.09	726.75	93.38	129.97	69.81	12.87	648.30	225.62	2498.62
Maximum (kg)	8688.71	3833.09	308.48	6335.16	309.05	2210.74	19679.56	1193.91	26000.44
Minimum (kg)	165.66	38.27	11.43	44.56	22.85	2.86	45.70	39.99	474.14

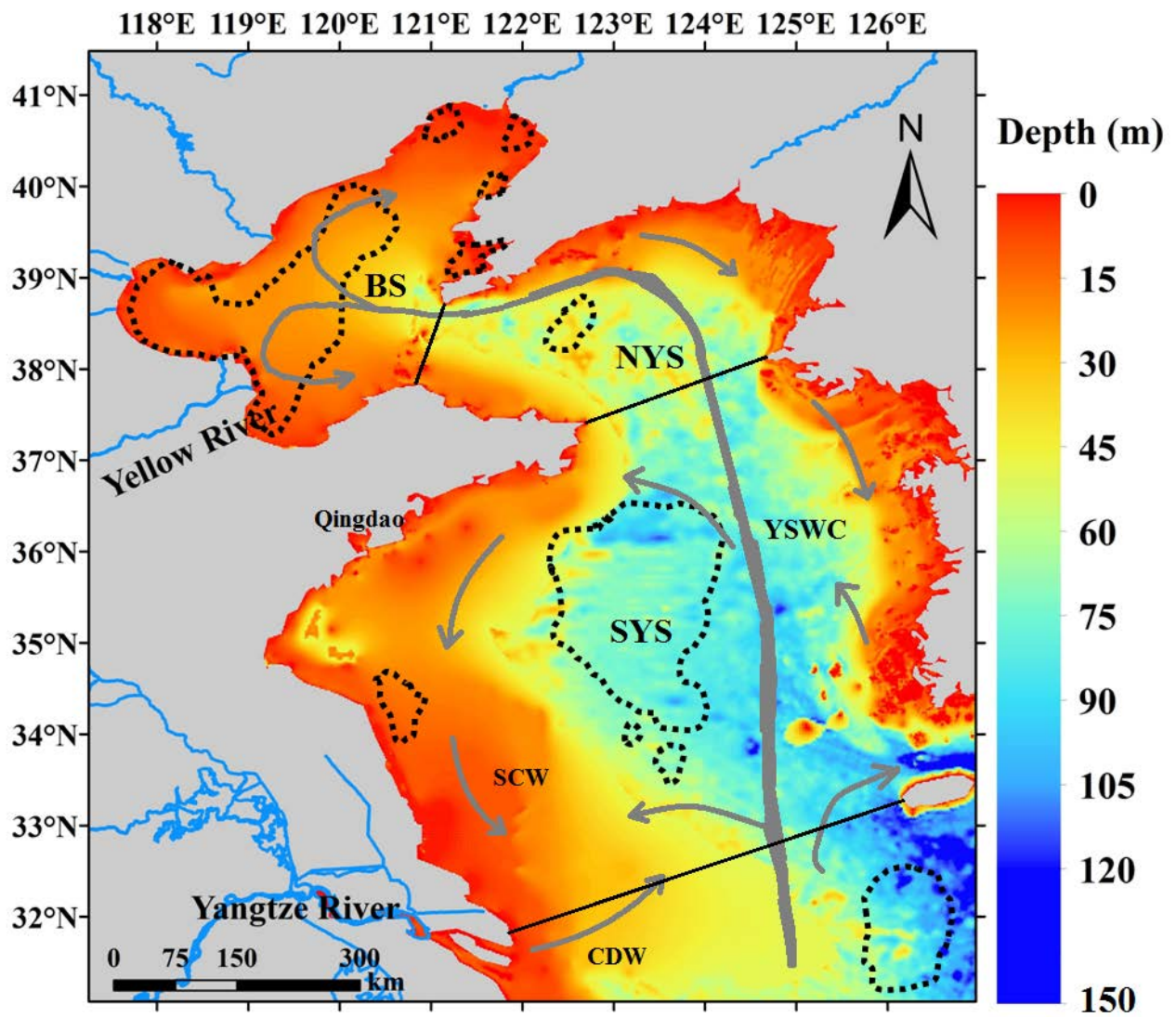


Figure 1 Clayey sediment areas and hydrological information of the Baohai Sea (BS) and the Yellow Sea (YS) (derived from Saito et al., 1994, Guo et al., 2006 and Zhong et al., 2017). Dashed blank lines enclose the regions of mud areas (deposition zones) in the BS and YS. Colored bar shows the water depth of the BS and YS. Black straight lines show the boundaries of BS, the North Yellow Sea (NYS) and the South Yellow Sea (SYS). Gray curved line shows ocean currents in the BS and YS. SCW: Subei Coastal Water; CDW: Changjiang Diluted Water; YSWC: Yellow Sea Warm Current.

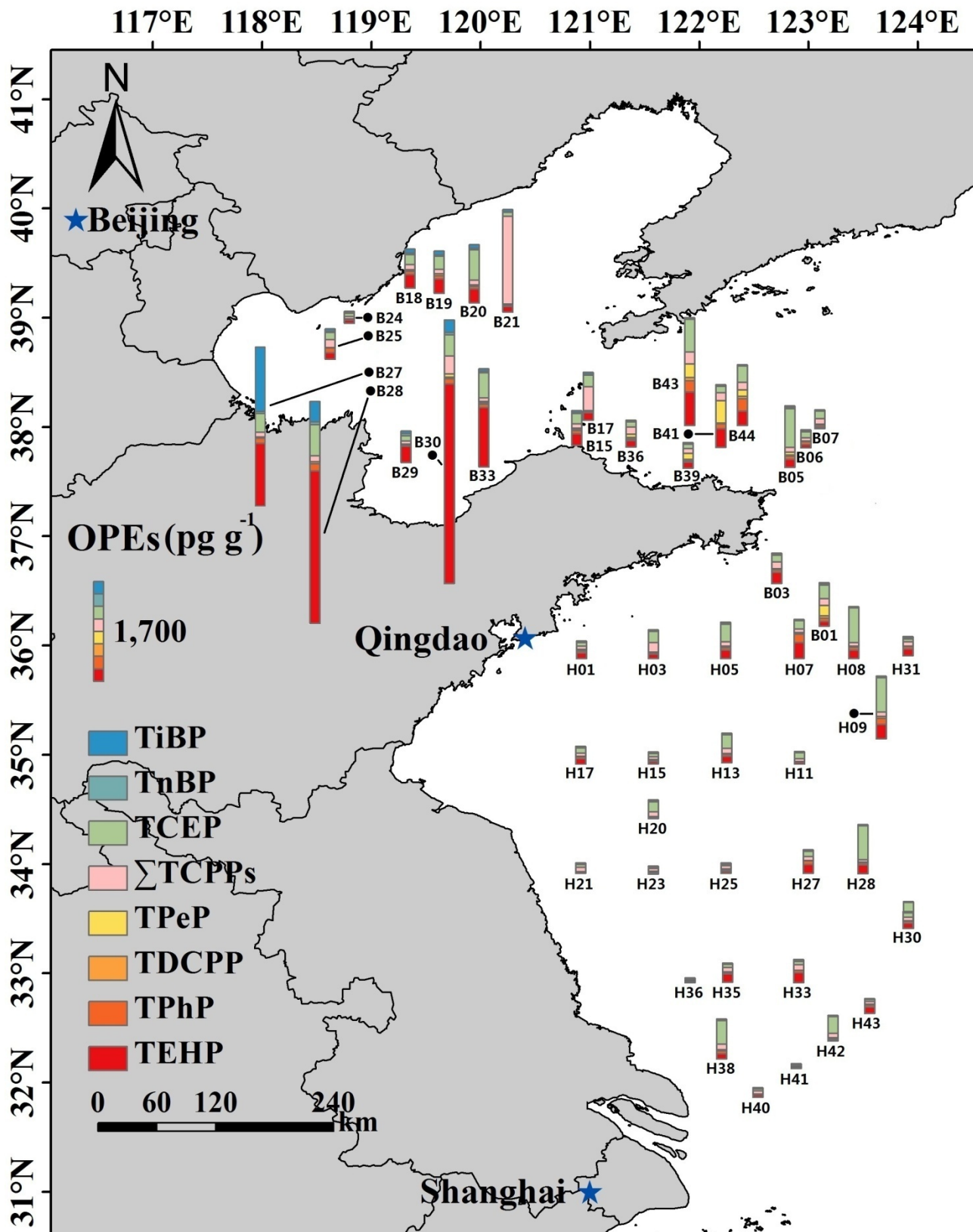


Figure 2 Locations of sampling sites and concentrations and distributions of the total and individual OPEs.

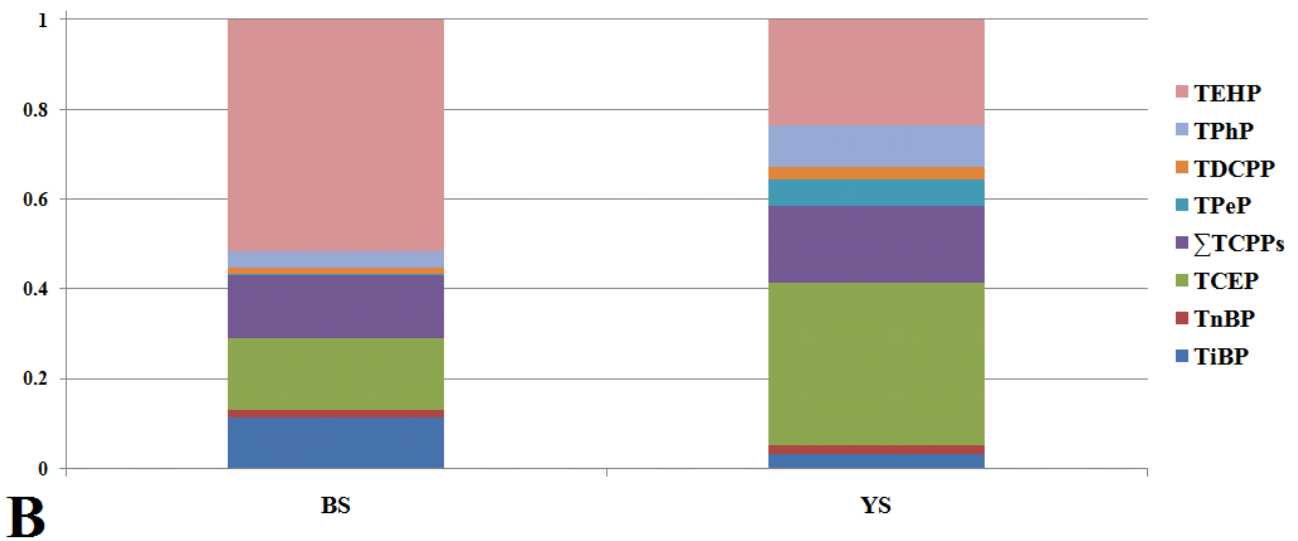
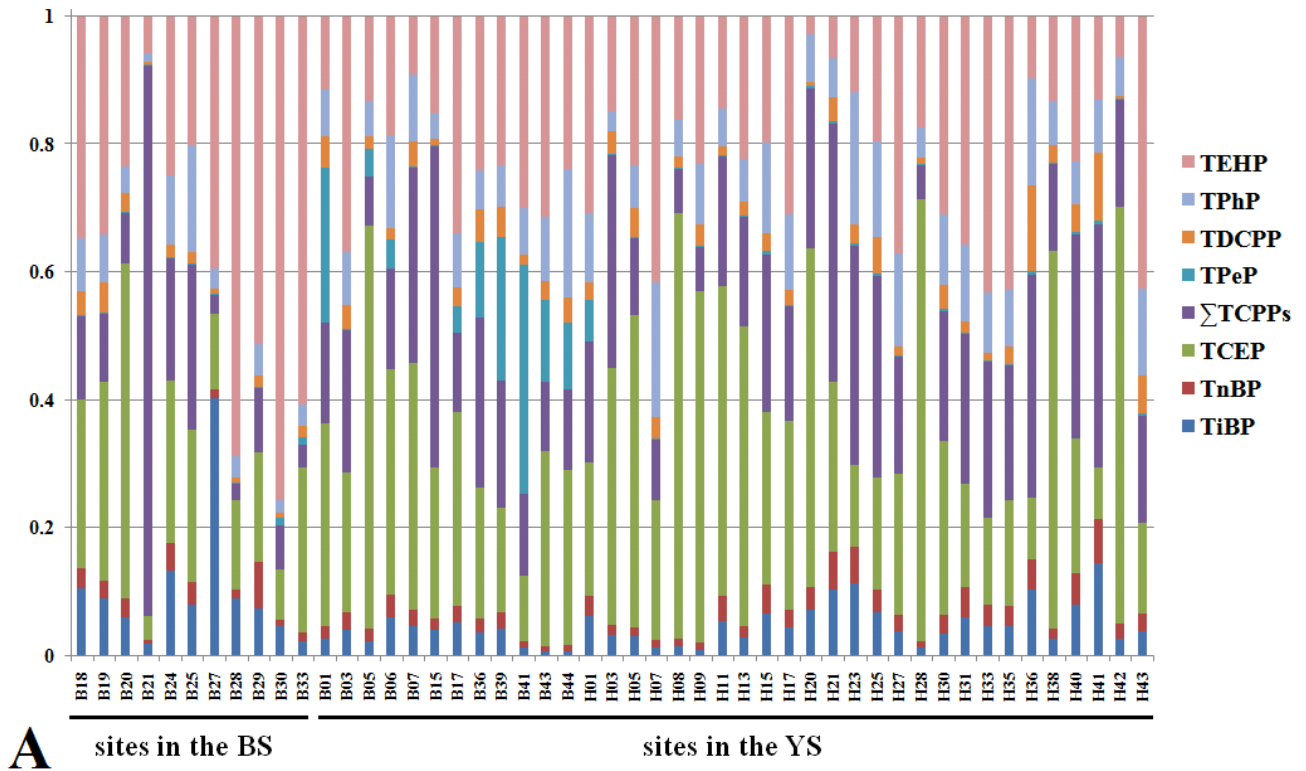


Figure 3. Composition profile of investigated OPEs in the surface sediment in the BS and YS. A: composition of OPEs for each sampling site; B: composition of OPEs for the BS and YS.

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