



# Occurrence and spatial distribution of organophosphorus flame retardants and plasticizers in the Bohai and Yellow Seas, China



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## ABSTRACT

Seawater samples from 50 sites in the BS and YS were collected to investigate the spatial distribution of 7 OPs. Concentrations of the total OPs ( $\Sigma$ OPs) in the BS and YS ranged from 8.12 ng L<sup>-1</sup> to 98.04 ng L<sup>-1</sup> with a geometric mean (GM) of 23.70 ng L<sup>-1</sup>. Tris(1-chloro-2-propyl) phosphate (TCPP) was the dominant compound, followed by tris(2-chloroethyl) phosphate (TCEP) and triphenylphosphine oxide (TPPO). The  $\Sigma$ OPs together with the most commonly detected individual OPs (TCPP, TCEP, tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tri-*iso*-butyl phosphate (TiBP), triphenyl phosphate (TPHP), and TPPO) tended to decrease from nearshore to offshore and from the surface to the bottom seawaters, indicating major land-based sources. Furthermore, the Yellow Sea Cold Water Mass (YSCWM), Changjiang Diluted Water (CDW), Taiwan Warm Current (TaWC), and Subei Coastal Water (SCW) influenced the horizontal and vertical distributions of the OPs in the study area.

## 1. Introduction

Organophosphorus flame retardants and plasticizers (OPs) have been applied in a wide range of industries for decades (Marklund et al., 2003; Reemtsma et al., 2008). Owing to their various substituent groups, OPs possess huge variations in their physicochemical properties (e.g., polarity, volatility, and solubility) (Reemtsma et al., 2008). With the prohibition and phasing out of certain brominated flame retardants (BFRs) worldwide, OPs have gradually overtaken the market share of BFRs in recent years (Stapleton et al., 2009). Commonly, non-halogenated OPs are employed as plasticizers, antifoaming agents, and additives (Marklund et al., 2003). Chlorinated OPs, such as tris(2-chloroethyl) phosphate (TCEP) and tris(1-chloro-2-propyl) phosphate (TCPP), are applied as flame retardants in floor polish, upholstery, furniture, and electronic products (Bollmann et al., 2012; Marklund et al., 2003; Salamova et al., 2014; Stapleton et al., 2009). In addition, triphenylphosphine oxide (TPPO) is widely used in the pharmaceutical industry (as an intermediate in medical synthesis) and can be applied as a ligand for metal processes (Hu et al., 2009; Wang et al., 2015).

In recent years, many studies reported the occurrence of OPs in different environmental matrices, such as air (Fromme et al., 2014;

Marklund et al., 2005; Moller et al., 2012; Staaf and Ostman, 2005), dust (Ali et al., 2012; Fromme et al., 2014; Marklund et al., 2003; Stapleton et al., 2009), water (Bacaloni et al., 2008; Bollmann et al., 2012; Hu et al., 2014; Regnery and Puttmann, 2010; Wang et al., 2015), sediment (Cao et al., 2012; Chung and Ding, 2009; Garcia-Lopez et al., 2009; Kawagoshi et al., 2002; Martinez-Carballo et al., 2007), soil (Mihajlovic et al., 2011), and biota (Chen et al., 2012; Kim et al., 2011; Ma et al., 2013; Sundkvist et al., 2010). Globally, approximately 500,000 tons (t) of OPs were used in 2011 and the amount of OPs used in 2015 reached 680,000 t (Ou, 2011; van der Veen and de Boer, 2012). In China, the usage of flame retardants reached 300,000 t in 2013 and increased rapidly (Zhang, 2014). Undoubtedly, China has become one of the largest OPs manufacturers and consumers worldwide. OPs are added into the materials physically rather than chemically, thereby they are subject to leaching into the environment through volatilization, abrasion, and dissolution (Wei et al., 2015). Liagkouridis et al. (2015) and Zhang et al. (2016) proposed the potential persistence of OPs in the environment based on software analysis and experimental evidence. Moreover, OPs can reach remote areas, such as the polar regions, through long-range atmospheric transport (LRAT) (Moller et al., 2012). Additionally, chlorinated OPs are not effectively removed

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from sewage treatment plants (Wei et al., 2015). Because of their continually increasing production and usage and, hence, emission into the environment, OPs can be categorized as “re-emerging pollutants” (Reemtsma et al., 2008; van der Veen and de Boer, 2012).

Although the risk assessments of OPs are still in progress (Wei et al., 2015), several organizations and research groups have discovered their toxicities already. In addition to the well-known carcinogenicity and neurotoxicity of certain OPs (van der Veen and de Boer, 2012), the teratogenicity of tris(1,3-dichloro-2-propyl) phosphate (TDCPP) to zebrafish (*Danio rerio*) (Dishaw et al., 2014), cytotoxicity of triphenyl phosphate (TPhP) to chicken embryonic hepatocytes (Su et al., 2014), and metabolic effects of TDCPP and TCPP on avian cells (Crump et al., 2012) have been reported. Some OPs, such as TCEP and TCPP, have been banned already from use in children's products in recent years because of their toxicity (Wang et al., 2015).

Considering the high production and consumption volumes, frequent detection rates and persistence in the environment, and possible toxicities of OPs, together with scarce knowledge on the levels and distributions of these substances in Chinese seas, efforts should be made to investigate the environmental behaviors and fates of these re-emerging pollutants. The Bohai Sea (BS) and the Yellow Sea (YS) are marginal seas of China. The BS is a semi-enclosed shallow sea (with a mean depth of 18 m and area of approximately 78,000 km<sup>2</sup>), surrounded by the Liaoning, Hebei, and Shandong Provinces and the Tianjin municipality; whereas the YS (with a mean depth of 44 m and area of approximately 380,000 km<sup>2</sup>) is more open to the west Pacific Ocean, surrounded by the Liaoning, Shandong, and Jiangsu Provinces and the Shanghai municipality to the east and the Korean Peninsula to the west (Hu et al., 2016). The BS and YS connect with each other and exchange seawater through the Bohai Strait (about 110 km in width). Influenced by the seasonal variability of East Asian monsoons, the incursion of the Kuroshio Current, and the western boundary current of the North Pacific Ocean, these two seas present complex hydrographic features (Ren et al., 2006). Meanwhile, they are suffering from deteriorating water quality and expanding areas of eutrophication and hypoxia. Huge amounts of less-treated domestic sewage and industrial wastewater are pouring into these two seas due to the rapidly urbanization and industrialization (Fang et al., 2010; Lu et al., 2013; Wang et al., 2015). Recently, high levels of OPs (mainly TCPP, TCEP, and TPPO) in 40 rivers draining into the BS have also been reported, which implies serious pollution from these compounds (Wang et al., 2015).

Aiming to analyze OPs in these coastal seas, seawater samples were collected onboard a research cruise in the summer of 2015. Firstly, 7 OPs congeners (see details in Table S1) in the seawaters of the BS and YS were analyzed. Furthermore, both horizontal and vertical distributions of these compounds were elucidated. Finally, possible sources of these compounds in the two seas were discussed.

## 2. Materials and methods

### 2.1. Chemicals

Information concerning the chemicals and analytical standards used is provided in Table S1.

### 2.2. Sampling cruise

From August 17th to September 5th 2015, 106 seawater samples were taken from 50 sites in the BS and the western YS on board the Research Vessel “*Dongfanghong 2*”. Niskin bottles coupled onto a CTD (conductivity-temperature-depth system) automated sampling device (Seabird 25, USA) was used to collect the surface and bottom seawater samples. For sites B09, H07, H09, and H11 three layers (surface, middle, and bottom) and for site H26 four layers (surface, subsurface, middle, and bottom) of seawater were collected. Fig. 1 shows the hydrological information (mainly ocean currents and water mass) (Guo

et al., 2006; Yu et al., 2006) of the BS and YS. Fig. 2 shows the geographical locations of the sampling sites.

### 2.3. Sample pretreatment

Method used to extract of OPs were followed the procedure by Rodriguez et al. (2006) with small modification. After sample collection, seawater (1 L for each sample) were filtered through 0.7 μm pore size glass microfiber filters (Whatman, GE Healthcare, Buckinghamshire, UK) and transferred into cleaned separating funnels and extracted using solid phase extraction by gravity with HLB (hydrophilic - lipophilic balance) columns (6 cm<sup>3</sup>, 200 mg). Before use, all the columns were conditioned by adding 6 mL of ethyl acetate and 6 mL of methanol and were sealed with cleaned foil and stored at -20 °C. Twenty nanograms each of surrogate (D27 TnBP, D12 TCEP, and D15 TPhP) were added on the columns in lab before boarded (Supporting information). Then, the columns were drained and eluted with 10 mL of ethyl acetate and the extracts were frozen for 24 h at -20 °C to remove water and the residual water was removed again by adding 3 g of Na<sub>2</sub>SO<sub>4</sub>. The extracts were transferred to new vials and the volume of each sample was evaporated to around 200 μL under a gentle nitrogen flow. Finally, 20 ng of polychlorinated biphenyl 208 (PCB 208) was added as an injection standard (Supporting information).

### 2.4. Quality assurance/quality control

For the spiked experiment, 100 ng each of 7 OPs congeners and 20 ng each of surrogates (D<sub>27</sub> TnBP, D<sub>12</sub> TCEP, and D<sub>15</sub> TPhP) were added on the conditioned HLB columns to evaluate the method recoveries. For method blanks, only 20 ng each of surrogates (D<sub>27</sub> TnBP, D<sub>12</sub> TCEP, and D<sub>15</sub> TPhP) were added on the conditioned HLB columns. For method recoveries and blanks, 32‰ NaCl was added into pure water to simulate the salinity of seawater. All the remaining procedures were similar to those described in sample pretreatment.

The recoveries from the spiked experiments ranged from 80 ± 9% (TPPO) to 101 ± 6% (TnBP) (*n* = 6). For the method blanks, all the compounds analyzed were detected and ranged from 12 pg L<sup>-1</sup> (TnBP) to 430 pg L<sup>-1</sup> (TPPO) (*n* = 6). The method detection limit (MDL) was defined as the method blanks plus three times of the standard deviation (3σ) of the method blanks and ranged from 30 pg L<sup>-1</sup> (TnBP) to 529 pg L<sup>-1</sup> (TPPO). Detailed information of the recoveries, means of blanks, MDL and limit of instrumental detection (LOD) (calculated at a signal-to-noise ratio of 3) are provided in Table S1. None of the concentrations of OPs in this study were corrected for recoveries and blanks (Supporting information). In all the sample pretreatment and spiked experiment, NaCl, Na<sub>2</sub>SO<sub>4</sub>, glass fiber filters and all the glassware were baked at 450 °C for 6 h before use to avoid external contamination.

### 2.5. Instrumental analysis

An Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC-MS) was used to analyze the samples. The injection was done by the automatic injector in pulsed splitless mode. The gas chromatograph was equipped with a DB-5MS column (30 m × 0.25 mm × 0.25 μm) and the heating program was as follows: 80 °C (3 min) → 8 °C min<sup>-1</sup> → 150 °C (0 min) → 5 °C min<sup>-1</sup> → 300 °C (5 min). The quadrupole was set at 150 °C and the ion source of the mass spectrometer was maintained at 230 °C and 70 eV electron impact (EI). The selected ion monitoring (SIM) mode of the mass spectrometer was chosen during the analytical procedure, and the mass-to-charge ratio of selected fragmental ions for quantification and quality assurance are listed in Table S1. Calibration curves derived from eight gradients (0, 10, 20, 50, 100, 200, 500, and 1000 pg L<sup>-1</sup>) were used to quantify the compounds of focus. All the standards and surrogates were dissolved in ethyl acetate at 2 ng μL<sup>-1</sup> as working solutions.

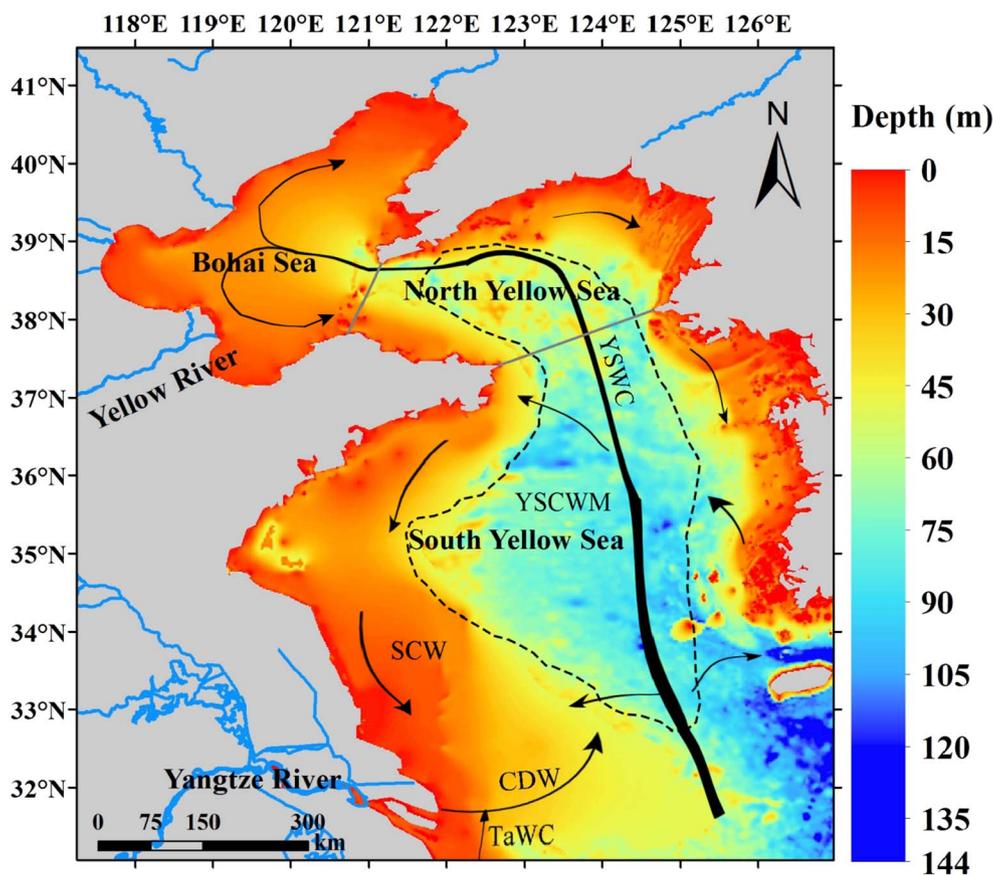


Fig. 1. Hydrological information of the Bohai and Yellow Seas (derived from Guo et al., 2006 and Yu et al., 2006). YSWC: Yellow Sea Warm Current; YSCWM: Yellow Sea Cold Water Mass; SCW: Subei Coastal Water; CDW: Changjiang Diluted Water; TaWC: Taiwan Warm Current. The two gray lines show the boundary of the Bohai Sea, the North Yellow Sea and the South Yellow Sea. The region enclosed in the dotted lines is YSCWM.

## 2.6. Data analysis

The chromatographic data were analyzed by an Agilent MSD ChemStation. Further data treatment was performed in Microsoft® Office Excel 2003, IBM® SPSS® Statistics 22 (*t*-test, ANOVA analyses and spearman analysis) and Origin® 8.5. All the interpolated graphs were generated by ordinary Kriging method (output type: prediction) in ArcGIS® 10.0.

## 3. Results and discussion

### 3.1. Concentrations of OPs

Generally, 6 (TCPP, TCEP, TDCPP, tri-iso-butyl phosphate (TiBP), TPhP, and TPPO) of 7 target compounds were detected in the offshore waters of the BS and YS. The results are summarized in Table 1 and detailed information is provided in Tables S2–S4. As presented in Table 1, chlorinated OPs were widely detected at a rate of 100% for TCPP and TCEP and 99% for TDCPP. For the five alkyl OPs (TiBP and TrnBP), only TiBP was sporadically detected in the BS. For the aryl OP, TPhP was detected in both the BS and YS. TPPO was also ubiquitous, with a detection rate of 100%.

Table S2 shows the levels and compositions of these compounds. Overall, the concentrations of these detected OPs ranged from 0.09 ng L<sup>-1</sup> (TPhP) to 31.4 ng L<sup>-1</sup> (TCPP). TCPP (GM: 9.49 ng L<sup>-1</sup>) was the dominant pollutant, followed by TCEP (GM: 6.51 ng L<sup>-1</sup>). The concentration of TDCPP, although a chlorinated OP, only possessed a GM of 0.83 ng L<sup>-1</sup>, which was one order of magnitude lower than those of TCPP and TCEP were ( $P < 0.01$ ). TiBP was detected only in several nearshore sites of the BS with a GM concentration of 0.09 ng L<sup>-1</sup>. For the aryl OP, TPhP possessed a GM concentration of 0.15 ng L<sup>-1</sup> and its concentration was only slightly higher than that of TiBP among all the detected OPs (detailed information is listed in Table S4).

Although the concentrations of the OPs in this study were comparable to those in the German Bight, North Sea (Bollmann et al., 2012), they were approximately one order of magnitude lower than those in the rivers draining into the BS were (Wang et al., 2015). However, according to Hu et al. (2014), mean concentrations of TCPP (84.12 ng L<sup>-1</sup>), TCEP (134.40 ng L<sup>-1</sup>), and TDCPP (109.30 ng L<sup>-1</sup>) in the coastal seawaters of Qingdao, Lianyungang, and Xiamen respectively were much higher than those in our study. This might be explained by the fact that their sampling sites were much closer to the coastline and therefore terrigenous sources (mainly municipal and industrial effluents of wastewater treatment plants in the nearby economic and industrial zones) (Hu et al., 2014). The composition of OPs in seawater in our study shared similarities with that in river water in the previous study by Wang et al. (2015), i.e., chlorinated OPs were major components of the ΣOPs. A correlation between TCPP and TCEP ( $n = 106$ ,  $P < 0.01$ ) was observed in the BS and YS, implying that TCPP and TCEP in the two seas might share similar pollution sources (Wang et al., 2015; Wei et al., 2015).

Our study confirms that chlorinated OPs (mainly TCPP and TCEP) are dominant OPs in the water phase, and similar to these observed in water in German Bight, North Sea (Bollmann et al., 2012); 40 rivers around the BS, China (Wang et al., 2015); urban and suburban lakes, Germany (Regnery and Puttmann, 2010); and River Aire, UK (Cristale et al., 2013); etc. This phenomenon may be partially attributed to the physicochemical properties of the chemicals. The low octanol-water partition coefficients ( $K_{OWs}$ ) and low vapor pressures ( $V_p$ s) of TCPP (log  $K_{OW} = 2.59$  and  $V_p = 2.02 \times 10^{-5}$  Torr) and TCEP (log  $K_{OW} = 1.44$  and  $V_p = 6.13 \times 10^{-2}$  Torr) make it easier for these compounds to dissolve in water and harder for them to volatilize to the atmosphere.

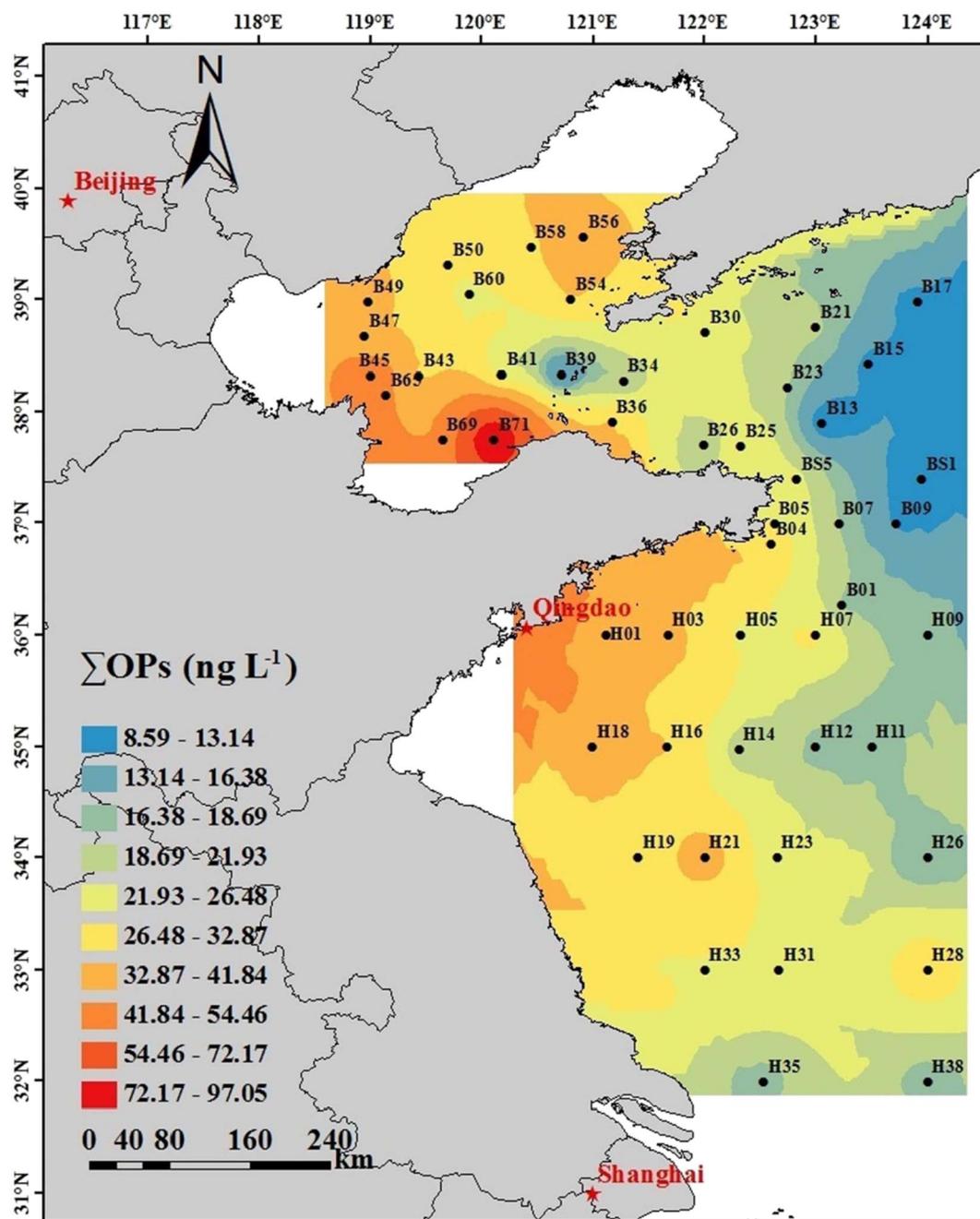


Fig. 2. Geographical locations of sampling sites and distribution of total OPs (ΣOPs) (mean concentrations of all layers for each site) in the Bohai and Yellow Seas.

**Table 1**  
Statistics of OPs in the Bohai and Yellow Seas ( $n = 106$ ).

OPs	Chlorinated OPs			Alkyl OPs		Aryl OP	TPPO
	TCPP	TCEP	TDCPP	TiBP	TnBP	TPhP	
Geometric means (GMs) ( $\text{ng L}^{-1}$ )	9.49	6.51	0.83	< MDL	< MDL	0.15	5.47
Maximum ( $\text{ng L}^{-1}$ )	31.4	29.24	3.24	11.83	< MDL	0.75	29.24
Minimum ( $\text{ng L}^{-1}$ )	2.83	2.35	< MDL	< MDL	< MDL	< MDL	1.58
Detection rates (%)	100	100	99	12	0	73	100

### 3.2. Horizontal distribution of OPs

#### 3.2.1. Higher levels of OPs in the BS than in the YS

As shown in Fig. 2 and Table S2, the concentration of ΣOPs in the BS (GM:  $33.42 \text{ ng L}^{-1}$ ) was significantly higher than in the YS (GM:  $20.95 \text{ ng L}^{-1}$ ) ( $P < 0.01$ ). The concentration of TCEP in the BS ( $9.65 \text{ ng L}^{-1}$ ) was almost twice as high as that in the YS ( $5.65 \text{ ng L}^{-1}$ ) ( $P < 0.01$ ). For TPPO, the concentration in the BS (GM:  $8.38 \text{ ng L}^{-1}$ ) was also nearly twice as high as that in the YS ( $4.69 \text{ ng L}^{-1}$ ) ( $P < 0.01$ ). It may be due to the fact that more pollution sources in the BS than in the YS and the poor water exchange ability of the BS (Zhang et al., 2013). However, the concentrations of TCPP and TDCPP (BS:  $10.79 \text{ ng L}^{-1}$  and  $1.01 \text{ ng L}^{-1}$  vs. YS:  $9.06 \text{ ng L}^{-1}$  and  $0.78 \text{ ng L}^{-1}$ , respectively) in the two seas were at a comparable level ( $P > 0.05$ ), which may indicate additional input of these two compounds in the YS. In fact, on the west coast of the southern YS, there exists one of the

largest OPs manufacturers in China, which has an annual OPs capacity of 20,000 t, while TCPP and TDCPP are the dominant products.

### 3.2.2. A descending trend from nearshore to offshore for OPs

Overall, high levels of OPs were detected at the sites that were adjacent to the coasts (Fig. 2). This may be caused by the riverine discharge and input from sewage outfalls (Zeng et al., 2015). For example, B71 exhibited the highest  $\Sigma$ OP concentration ( $97.05 \text{ ng L}^{-1}$ ) among all the sites in this study. High OP concentrations at site B71 might be partly due to the riverine input from the Jiehe River ( $514.44 \text{ kg yr}^{-1}$ , annually) (Wang et al., 2015). B65 and B45 exhibited an average concentration of  $48.75 \text{ ng L}^{-1}$ , higher than its neighboring sites (B43, B47, and B49). High OP concentrations at these sites might result from the waste dumping area (SOA, 2011) in the coastal area of Dongying city. Furthermore, in the mouth of the Laizhou Bay (LZM) (B71 and B69), the mouth of the Bohai Bay (BHM) (B45, B47, and B49), and the mouth of the Liaodong Bay (LDM) (B50, B56, and B58), relatively high levels of OPs were also detected. These three bays are parts of the Bohai Economic Rim and suffer from serious industrial and domestic wastewater pollution (Hu et al., 2011; Zhang et al., 2012; Zou et al., 2011). The average  $\Sigma$ OPs levels in these three bays follow the order of LZM ( $70.64 \text{ ng L}^{-1}$ ) > BHM ( $40.11 \text{ ng L}^{-1}$ ) > LDM ( $34.74 \text{ ng L}^{-1}$ ) > central BS (CBS,  $27.46 \text{ ng L}^{-1}$ ), whereas the distance from the shoreline to the LZM, BHM, LDM, and CBS showed an opposite trend. In addition, even for some transects (H01 – H09 and H18 – H11) of the YS, the  $\Sigma$ OPs concentration decreased with the increase in distance from the shoreline (Fig. S1). It is also a combined influence of fewer pollution sources, dilution by offshore seawater, absorption to particles and degradation effects such as hydrolysis, photolysis, and biodegradation during the transport process (Reemtsma et al., 2008; Wei et al., 2015; Zhang et al., 2013).

### 3.2.3. Influences by the Subei Coastal Water (SCW) and the Taiwan Warm Current (TaWC)

H19 and H21, located in the SCW region, had an average  $\Sigma$ OPs concentration of  $33.25 \text{ ng L}^{-1}$  and H21 had the highest  $\Sigma$ OPs concentration ( $38.13 \text{ ng L}^{-1}$ ) in the YS (Table S4). The SCW flows from the south to the north during summer (Wei et al., 2016). OPs in this area might come from, at least partially, the south coast of Jiangsu province, where many industries such as metallurgy, electronics, chemistry, and machinery are located. Meanwhile, the TaWC flows northward from the Changjiang Estuary (Wei et al., 2016) and prevails around H35, which may account for its low OPs concentrations among the nearshore sites (H01, H18, H19, H33, and H35) in the YS. This may result from the dilution effects of the Kuroshio branch, which originates from the Kuroshio Current and flows through the Taiwan Strait (Wei et al., 2016).

## 3.3. Vertical distribution of OPs

### 3.3.1. High levels of OPs in the surface layer

Generally, the concentrations of  $\Sigma$ OPs (GM:  $26.08 \text{ ng L}^{-1}$ ) in the surface layers (3 m for most sites) were higher than those in the bottom layers (13 to 77 m) (GM:  $22.47 \text{ ng L}^{-1}$ ) for ( $P < 0.01$ ) (Tables S3 and 4), though exceptions occurred at certain sites. For individual OPs, all the detected compounds (except for TPHP) showed similar vertical patterns to those of the  $\Sigma$ OPs ( $P < 0.05$ ) (Tables S3 and 4, Figs. 3, and S2). This pattern may be explained by the fact that flood season occurs during August, during which lots of freshwater together with high levels of OPs enter the seas, and the freshwater tends to stay at the surface due to their lower density than seawater. Additionally, atmospheric deposition may contribute to the higher OPs concentrations in the surface waters (Wei et al., 2015).

### 3.3.2. Influence of the Yellow Sea Cold Water Mass (YSCWM)

Another factor that might influence the vertical distribution of OPs

is the YSCWM, which occurs in summer and is located at the bottom of the central YS (Wei et al., 2016). This water mass is characterized by low temperature ( $6\text{--}12 \text{ }^\circ\text{C}$ ) and high salinity ( $31.6\text{--}33.0\%$ ) (Wei et al., 2016). Seventeen sampling sites (BS1, B01, B07, B09, B13, B23, B30, H05, H07, H09, H11, H12, H14, H16, H23, H26, and H28) were located in this area. To analyze whether this water mass could influence the vertical distribution of OPs, all YS sites were divided into two groups: those within the YSCWM (Group 1) and those outside the YSCWM (Group 2). Firstly, the  $\Sigma$ OPs concentrations in the surface and bottom layers were compared by using paired *t*-test analysis of Groups 1 and 2, respectively. The concentrations of OPs in the surface waters were significantly higher than they were in the bottom waters in both groups ( $P < 0.01$ ). Secondly, the differences in concentrations ( $\Delta C = C_{\text{surface}} - C_{\text{bottom}}$ ) between the surface and bottom waters were calculated and the  $\Delta$ Cs were compared using ANOVA analysis of Groups 1 and 2, respectively. Although the average  $\Delta$ Cs in the cold water mass (Group 1) ( $4.05 \text{ ng L}^{-1}$ ) were slightly higher than those for the other sites (Group 2) ( $3.72 \text{ ng L}^{-1}$ ), there was no statistically significant difference between the two data groups. Furthermore, seawater was collected from additional layers at sites H07, H09, H11, H26, and B09. As shown in Figs. 4 and S3, the concentrations of  $\Sigma$ OPs and individual OPs varied above and below the thermoclines and haloclines, though there were a few exceptions. This finding implied that there was less substance exchange between the surface and bottom seawaters due to the stratification effect that occurs in the YSWCM during summer. Taken together, these results indicate that the YSCWM might influence the vertical distribution of OPs to a certain extent.

### 3.3.3. Influence of large river discharge

Besides the YSCWM, the Changjiang Diluted Water (CDW) in the YS might also affect the vertical distribution of OPs. The CDW, which only prevails during summer, presents a tongue-shaped and northeastward extension on the surface water (Wei et al., 2016). H28, which locates in the YSCWM as mentioned in Section 3.3.2, sits at the front of the CDW plume. Because of its unique hydrographic features, H28 differed greatly in its  $\Sigma$ OPs concentrations between the surface ( $41.32 \text{ ng L}^{-1}$ ) and bottom ( $25.87 \text{ ng L}^{-1}$ ). This phenomenon implied large river discharge could influence areas far from the coast/estuaries and alter the distribution of OPs to a great extent.

## 3.4. Relationships between OPs distributions and salinity

It is well accepted that seawaters from the open ocean have high salinity and low pollutant concentrations, and freshwater runoff has low salinity and high pollutant concentrations (Zhang et al., 2013). In this study, a similar phenomenon was observed in the BS and YS. As mentioned above, the OPs concentration in the BS was higher than that in the YS, whereas the salinity (BS:  $30.79\%$  vs. YS:  $31.39\%$ ) of the two seas presented an opposite trend ( $P < 0.01$ ). In fact, the negative correlation between salinity and  $\Sigma$ OPs was observed in the YS ( $r_{\text{rho}} = 0.676$ ,  $n = 36$ ,  $P < 0.01$ ) and the whole region (the BS and YS) ( $r_{\text{rho}} = 0.648$ ,  $n = 50$ ,  $P < 0.01$ ) by conducting spearman analysis. Meanwhile, on the H01–H09 and H18–H11 transects of the YS, the  $\Sigma$ OPs concentration decreased with the increase of salinity as well (Fig. S1). Similarly, the vertical distribution of salinity (surface:  $30.90\%$  vs. bottom  $31.55\%$ ) showed an opposite pattern ( $P < 0.01$ ) to that of the OPs, which might imply that a higher proportion of freshwater from rivers resided at the surface, hence a high concentration of OPs occurred in the same layer. Besides the dilution effect of clean water from the open oceans, the salting out effect of organic pollutants might be another factor that resulted in the negative correlation between OPs concentrations and water salinity. According to Xie et al. (1997), solubility of organic contaminants will decrease with the increase of the salinity of seawater, which implied more OPs might separate out from the high salinity seawater and probably entered into other matrices like suspended particulate matters, sediments or atmosphere. In a word,

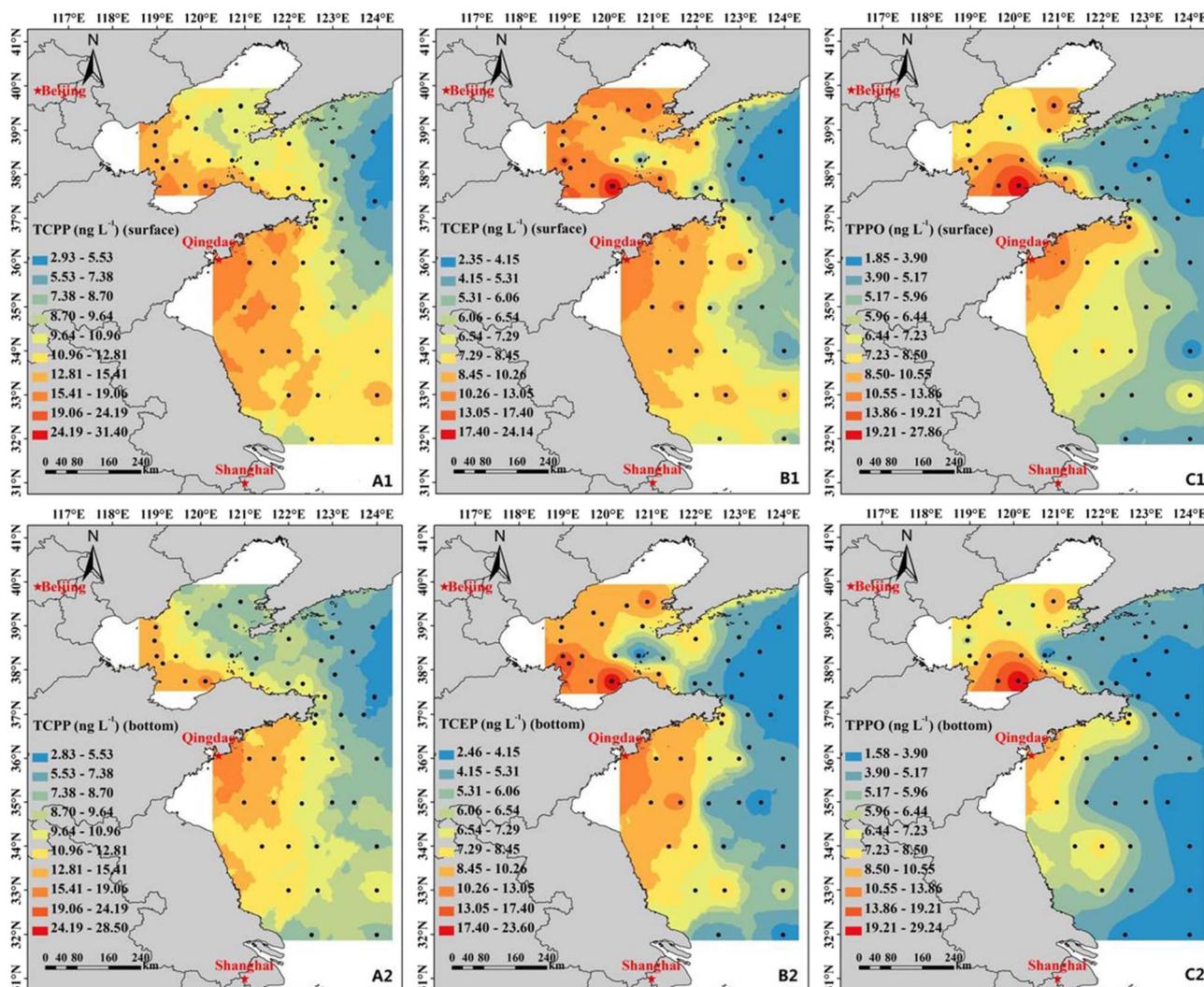


Fig. 3. Vertical distributions of TCPP (A1–A2), TCEP (B1–B2), and TPPO (C1–C2) in the Bohai and Yellow Seas.

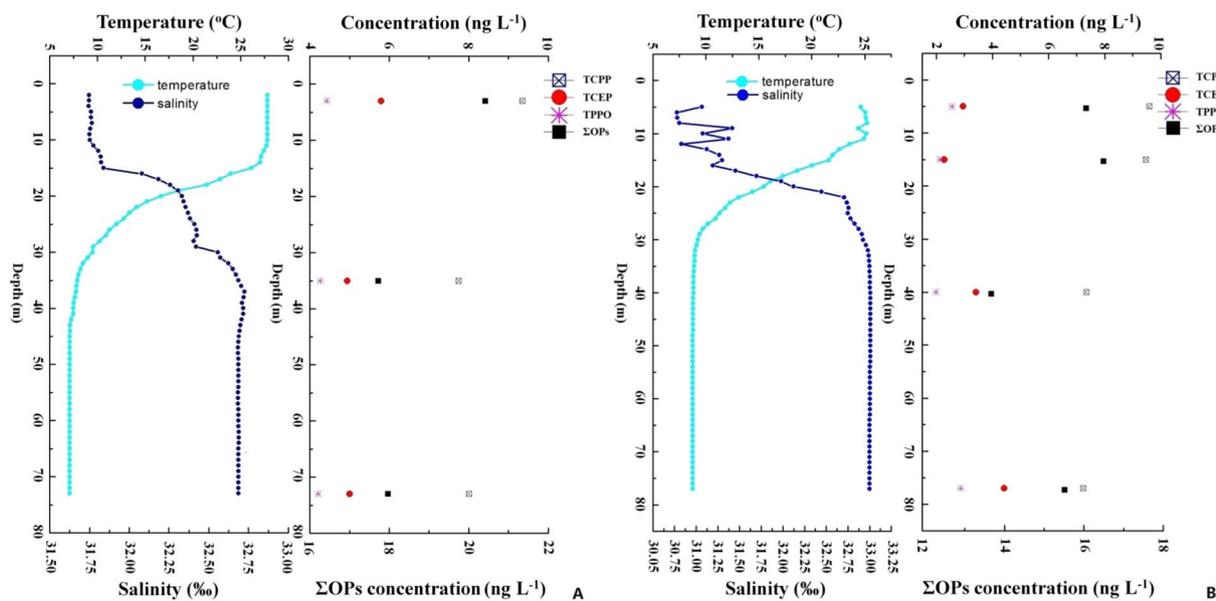


Fig. 4. Vertical distributions of the total OPs (ΣOPs) and individual OPs at sites H09 (A) and H26 (B).

salinity, which reflects the proportion of open ocean water (high salinity) to freshwater (low salinity), might be a good indicator of the distributional characteristics of pollutants such as OPs.

### 3.5. Potential sources of OPs in the sea

The distributional patterns of  $\Sigma$ OPs and individual OPs (Figs. 1, 3, and S2) present decreasing tendencies from the nearshore areas to the offshore areas, indicating that most OPs sources were from the mainland. It is widely recognized that riverine input might be one of the main terrigenous OPs sources draining to the seas (Bollmann et al., 2012; Wang et al., 2015; Wei et al., 2015). In this study, the highest concentration of  $\Sigma$ OPs was detected at site B71, which was adjacent to the highly polluted Jiehe River (Wang et al., 2015). The large difference between  $\Sigma$ OPs in the surface and bottom waters at H28 also verified this argument. Moreover, according to Bollmann et al. (2012) OPs from the River Elbe estuary to the German Bight, North Sea also showed a decreasing trend, which also emphasizes the importance of riverine input.

Landfills and sewage outfalls in the coastal areas may also be a main OPs source. Kawagoshi et al. (1999, 2002) reported high concentrations of OPs in a sea-based solid waste disposal site in the coastal area of Japan. In China, hundreds of draining outlets and dumping grounds exist along the coastline (SOA, 2016), which may contribute to the OPs in the seas. In this study, high concentrations of OPs at sites B45 and B65, which were adjacent to a pollutant discharge zone, seems to support this reasoning well.

On the other hand, atmospheric deposition may be another source. OPs could reach the aquatic and terrestrial systems through washout from the atmosphere via precipitation, which was regarded as an important entry pathway for OPs into the aquatic environment, especially in the remote lakes and open sea areas (Bacaloni et al., 2008; Wei et al., 2015). Recently, OPs flux was estimated to be 4980 kg yr<sup>-1</sup> from the atmospheric dry deposition into the South China Sea, which is comparable to the riverine input (Lai et al., 2015; Wang et al., 2015). In our study, higher concentrations of OPs in surface seawaters also may be partially attributable to direct deposition from the atmosphere. These findings confirmed the importance of atmospheric input of OPs into the seas. Therefore, aiming to assess OPs concentrations three-dimensionally, atmospheric distribution of OPs above the BS and YS should be analyzed in future studies.

## 4. Conclusions

This study showed distributional tendency of OPs in the BS and YS, i.e., the nearshore and surface seawaters possessed higher OP concentration, which indicated terrigenous sources of OPs. The chlorinated OPs (TCPP and TCEP) and TPPO were main compounds in the analyzed OPs congeners, which implied their more production and consumption in China and their persistence in the environment. Moreover, ocean current (the TaWC), coastal current (the SCW), the CDW and water mass (the YSCWM) might also influence environmental distribution of OPs, which indicated OPs distribution is a multi-factor determined process. Since relatively high OP concentrations were detected in seawaters of the BS and YS, studies about OPs in atmosphere, sediment and biota of these seas should be conducted to further elucidate the environmental behaviors and fates of OPs in this region.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marpolbul.2017.06.034>.

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