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Jinghua Zhang

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Combined effects of fronts, upwelling and the biological pump on organophosphate esters in the Changjiang (Yangtze) River estuary during summer

Jinghua Zhang[1], Yuxin Ma[1*], Yisen Zhong[1*], Rainer Lohmann[2]

[1]School of Oceanography, Shanghai Jiao Tong University, 1954 Huashan Road, 200030 Shanghai, China

[2]Graduate School of Oceanography, University of Rhode Island, 215 South Ferry Road, Narragansett, 02882 Rhode Island, United States

Corresponding Author:

Yuxin Ma (yuxin.ma@sjtu.edu.cn)

Yisen Zhong (yisen.zhong@sjtu.edu.cn)

Key Points

- Sediment inputs increased organophosphate ester concentrations in turbid bottom waters.
- The biological pump strongly affected organophosphate esters in frontal/upwelling and continental shelf regions.
- Discharge from wastewater treatment plants contributed more than 50% of organophosphate esters in the Changjiang River estuary.

Abstract:

Estuarine and coastal environments are important transport pathways and regional sinks for anthropogenic pollutants. In this study, the occurrence and transport of the continuously released organophosphate esters (OPEs) was investigated together with physical and biochemical parameters throughout the water column in the Changjiang (Yangtze) River estuary during the summer. Total dissolved and particulate OPEs showed great spatial heterogeneity, with mean concentrations of 550 ± 280 ng/L in the estuary, 110 ± 270 ng/L in the front/upwelling zone, and 410 ± 450 ng/L in the continental shelf. OPE concentrations in the estuarine bottom waters were high due to massive terrestrial/sediment inputs. In contrast, the “surface enrichment and depth depletion” of OPEs in the continental shelf was closely related to seasonal stratification. Reduced OPE concentrations were observed in the frontal/upwelling zone due to isopycnal heaving. Frontal activity and upwelling induced phytoplankton blooms in the coastal regions, which jointly contributed to elevated OPEs beneath surface water with high phytoplankton aggregation. The OPEs mainly originated from wastewater treatment plant (WWTP) discharges, industrial pollution and consumer products. These OPEs generally

posed a low ecological risk to aquatic lives, but their long-term effects cannot be ignored due to their continuous high production, usage and release.

Plain Language Summary

The environmental behavior and fate of anthropogenic contaminants, such as the continuously released organophosphate esters (OPEs), is complex in estuaries and coastal environments. In this study, the occurrence and transport of OPEs in the Changjiang River estuary was associated with different oceanographic processes, including fronts, upwelling and impacts of the biological pump. Dissolved and particulate OPEs varied greatly from the estuary to the coastal region. High OPE concentrations were found in turbid bottom waters of estuary, likely caused by massive sediment inputs. Due to summertime stratification, the OPEs showed high levels in surface seawater, but generally low concentrations in middle/bottom layers of the continental shelf. As for the transition zone between the estuary and continental shelf where fronts/upwelling coexisted, relatively low OPE concentrations were present through the water column, because of the heaving of (cleaner) bottom water masses. Relatively higher OPE concentrations were present just below the algae-rich surface water, probably caused by the settling of biogenic particles with OPEs attached. The observed OPEs were mainly from wastewater treatment plant (WWTP) discharges, industrial pollution and consumer products. The ecological risks posed by OPEs to aquatic life cannot be ignored due to the continuous exposure.

Keywords: organophosphate esters; Changjiang River estuary; frontal zone; upwelling

process; biological pump

1. INTRODUCTION

Organophosphate esters (OPEs) are a group of chemicals of emerging concern (CECs) widely applied as flame retardants and plasticizers (Blum et al., 2019; Van der Veen & de Boer, 2012). The market share of OPE flame retardants has considerably and continuously increased, especially after the international regulation of the most commonly used brominated flame retardants (BFRs), polybrominated diphenyl ethers (PBDEs), in the early 2000s (Wang et al., 2020). The increasing consumption and broad application of OPEs as additives have contributed to their high environmental mobility, mainly via release to their surroundings by leaching, abrasion and volatilization (Gravel et al., 2019). This has caused the global OPE distribution in a variety of environmental compartments including air, seawater and sediment, generally with 2-3 orders of magnitude higher concentrations than BFRs and other legacy Persistent Organic Pollutants (POPs) (Cao et al., 2017; Li et al., 2017; Schmidt et al., 2019; Wolschke et al., 2018). Moreover, some OPEs, such as tris (2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPhP), showed potential for carcinogenic and neurotoxic effects on organisms (Olivero-Verbel et al., 2022). However, there is currently no international regulation to address the increasing environmental pressure resulting from OPEs' usage and emissions.

Due to the differences in the functional groups of OPEs, their physicochemical properties, such as polarity, solubility and volatility, vary considerably. The physicochemical properties affect the environmental behavior and fate of OPEs. For

example, chlorinated OPEs (Cl-OPEs) are considered persistent and mobile pollutants due to their high water solubility and high recalcitrance to degradation (Rodgers et al., 2018), and thus are generally difficult to remove in wastewater treatment plants (WWTPs) (Zeng et al., 2015). Large quantities of Cl-OPEs are thus discharged into the aquatic environment, and their distributions are further affected by hydrodynamic processes. In contrast, some high molecular weight alkyl and aryl OPEs, with high octanol-water partition coefficient (log K_{OW} > 5), tend to be attached to particles (Fang et al., 2022). These hydrophobic non-chlorinated OPEs (non-Cl-OPEs) therefore tend to bioaccumulate in aquatic organisms and probably add additional stress to the ecosystem (Wu et al., 2021).

Estuaries and continental shelves play a crucial role in the exchange of terrigenous material between the land and open sea, and serve as important regional sinks for anthropogenic pollutants (Chen et al., 2018; Gao et al., 2015). Several studies reported on the occurrence of OPEs in the coastal environment (Fang et al., 2022; Pantelaki & Voutsa, 2021; Zhang et al., 2020), but only few described the influence of hydrological and/or biogeochemical processes on the OPE transport in these regions (Zheng et al., 2022). Hydrologically, riverine inflow carries large quantities of nutrients, terrigenous pollutants and suspended sediments into estuaries and continental shelves (Chen et al., 2006; Gao et al., 2015). Yet the fronts between oceanward freshwater and landward seawater are considered transport barriers that restrict the spreading of the waterborne materials (Dong et al., 2021). Many studies also revealed the impact of fronts on phytoplankton aggregation and blooms (Li et al., 2022; Simpson et al., 1979). Notably, the coastal upwellings bring nutrient-rich waters upward to the surface, facilitating the growth of

phytoplankton and other primary producers, and hence supporting fish stocks (Largier, 2020). Therefore, hydrodynamic processes not only regulate the physical transport of (mobile) OPEs, but the coupled biogeochemical processes may also affect the environmental behavior of OPEs. The OPEs with greater hydrophobicity typically exhibit a propensity to bind to particles originating from both marine organisms and terrestrial inputs, and then sink to deeper waters, primarily driven by the biological pump and particulate settling (He et al., 2022). Understanding the impact of these coupled hydrological-biogeochemical processes is essential for assessing the exposure risks of biota to OPEs in the estuaries and coastal regions.

The Changjiang River (Yangtze) estuary receives large quantities of terrestrial sediments, nutrients and organic pollutants discharged by WWTPs and non-point atmospheric deposition sources located in the rapidly developing watershed (Liu et al., 2007; Liu et al., 2019; Xu et al., 2018). The summer circulation off the estuary is shown in Figure 1a, including the Changjiang Diluted Water (CDW) spreading toward the northeast and the Taiwan Warm Current (TWC) originating from the Taiwan Strait (Hu & Wang, 2016). The northeastward TWC passes through the coastal area, and may be upwelled owing to the summer monsoon (Bai & Hu, 2004; Pei et al., 2009). The coexistence of river plume and upwelling complicates the ecosystem dynamics in the Changjiang River estuary. Using the physical, biogeochemical, dissolved and particulate OPEs measurements, this research aims to (i) investigate the occurrence and possible sources of dissolved and particulate OPEs; (ii) describe their hydrological and biogeochemical processes; (iii) estimate the daily mass input of dissolved and particulate OPEs, and (iv) assess the potential ecological risks posed by OPEs.

2. MATERIALS AND METHODS

2.1 Sampling

Sixty-one water samples, including both surface and subsurface waters, were collected from the Changjiang River estuary and its adjacent coastal waters of the East China Sea (ECS) on board research vessel *Zheyuke2* in July 2021 (Figure 1b). The sampling area can generally be divided into the estuary (B-C transects), the frontal/upwelling zone (sites A1-1~A1-4 & A2-1~A2-4), and the continental shelf area (sites A1-5~A1-8 & A2-5~A2-8). Approximate 1 L seawater was collected by Niskin bottles mounted on a conductivity-temperature-depth (CTD, SBE 911, Sea-Bird Co.) rosette at multiple depth levels. The samples were immediately filtered through a Whatman glass fiber filter (GF/F, 47 mm, 0.7 μm) to trap suspended particulate matter (SPM). The filtrates were then transferred into amber glass bottles and stored in a 4 °C refrigerator, while the filters were wrapped in aluminum foil and stored at -20 °C until pretreatment. The detailed sampling information is listed in Table S1.

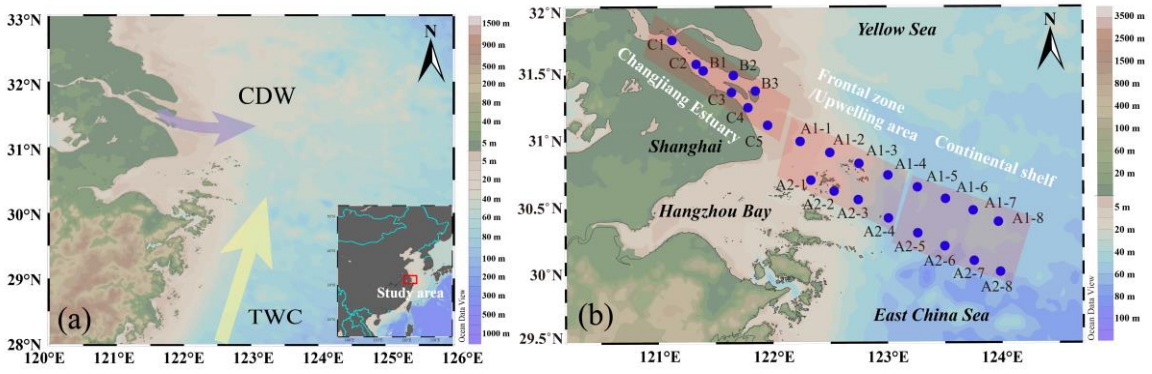

Figure 1. The schematic circulation pattern in the Changjiang River estuary: (a) Changjiang Diluted Water (CDW), Taiwan Warm Current (TWC); (b) The sampling sites in the Changjiang River estuary and its adjacent area.

2.2 Sample Analysis

The extraction and purification of filtrates were conducted following the procedures detailed prior with minor modifications (Quintana et al., 2008). The water samples were spiked with 100 ng surrogates including d_{12}-tris-(2-chloroethyl) phosphate (d_{12}-TCEP), d_{15}-triphenyl phosphate (d_{15}-TPhP) and d_{27}-tri-butyl phosphate (d_{27}-TnBP), and extracted by liquid-liquid method with 50 mL dichloromethane (DCM) three times. Colored extracts were further purified through a self-packed silica gel column (2 g anhydrous sodium sulfate loaded onto 5 g silica gel) and eluted with 20 mL DCM/acetone (v:v = 1:1). Transparent extracts were passed directly through an anhydrous sodium sulfate column to remove water. The treatments of SPM samples were modified from Wang et al. (2018), as described in Text S1. The GF/F filter samples, with 100 ng surrogates added overnight for equilibrium, were ultrasonically extracted with acetonitrile three times, then the extracts were concentrated and purified on an Oasis Prime HLB (500 mg, 6 mL, Waters, USA), and subsequently eluted with 8 mL hexane, 8 mL hexane/ethyl acetate (v:v = 1:1) and 8 mL ethyl acetate. For both filtrate and GF/F, the samples were finally concentrated and solvent-exchanged to hexane, with 100 ng p-terphenyl-d_{14} spiked as internal standard before instrumental analysis. The SPM concentrations on GF/F were measured as the difference of pre- and post-filtration weighing (Table S1). The analyses of other physical and biochemical parameters, including temperature, salinity, turbidity, photosynthetically active radiation (PAR), dissolved oxygen (DO), chlorophyll *a* (Chl *a*) and nutrients in water are described in Text S2.

2.3 Reagents and Standards

Twelve OPEs were analyzed including three Cl-OPEs (tris-(2-chloroethyl)

phosphate (TCEP), tris-(1-chloro-2-propyl) phosphate (TCPPs), tris-(1,3-dichloro-2-propyl) phosphate (TDCP)), seven alkyl-OPEs (triethyl phosphate (TEP), tri-iso-propyl phosphate (TiPrP), tri-propyl phosphate (TPrP), tri-iso-butyl phosphate (TiBP), tri-butyl phosphate (TnBP), tri-pentyl phosphate (TPeP), tris-(2-ethylhexyl) phosphate (TEHP)) and two aryl-OPEs (triphenyl phosphate (TPhP) and 2-ethylhexyl diphenyl phosphate (EHDPP)). All standards were purchased from AccuStandard (USA), except that TiPrP was obtained from Chiron (Norway) and EHDPP from Dr. Ehrenstorfer (Germany). Detailed physicochemical properties of OPEs are listed in Table S2. The targets were analyzed using a gas chromatograph coupled to a triple quadrupole mass spectrometer (GC-MS/MS, Agilent 7890B-7000D) equipped with a programmed temperature vaporizer (PTV) injector. The details for the GC-MS/MS method are given in Text S3 and Table S3. HPLC grade DCM, n-hexane, ethyl acetate and acetone were purchased from Fisher Scientific Co (USA). Guaranteed reagent anhydrous sodium sulfate and chromatographic silica gel (100-200 mesh) were supplied by Sinopharm Chemical Reagent Co., Ltd. (China).

2.4 Quality Assurance/Quality Control (QA/QC)

For QA/QC, all amber glass bottles, GF/F filters and aluminum foil were preheated at 500 °C for 5 h before use. The background values of OPEs in Niskin bottles and field blanks with Milli-Q water were below the method detection limits (MDL). To assess laboratory background contamination and analytical methods, one procedural blank and one spiked blank (Milli-Q and blank filter) were included for each batch of ten samples, during the pretreatment of seawater and filter samples (Table S4). The recoveries of surrogates were 104% ± 14% for d_{12}-TCEP, 88% ± 26% for d_{15}-TPhP, 66% ± 17% for

195 d_{27}-TnBP in dissolved water samples and 90% ± 21% for d_{12}-TCEP, 107% ± 16% for d_{15}-
196 TPhP, 65% ± 6% for d_{27}-TnBP in SPM samples. The instrumental limit of detection
197 (LOD, defined as 3 times signal-to-noise ratio (S/N)) and quantification (LOQ, defined as
198 10 times S/N) for OPEs were in the range of 0.004-1.4 ng/L and 0.015-4.7 ng/L,
199 respectively. The MDL, calculated as the mean plus three times the standard deviation
200 (SD) of blanks, were 0.34 to 5.2 ng/L for dissolved OPEs and 0.054-1.5 ng/L for
201 particulate OPEs in seawater (Table S4).

202 **2.5 Data Analysis.**

203 For each sample, OPE concentrations were MDL corrected and blank subtracted.
204 The statistical analysis and principal component analysis-multiple linear regression
205 (PCA-MLR) were performed using SPSS 24.0; EHDPP was removed from the data
206 analysis with a detection frequency lower than 60% (Text S4). The redundancy analysis
207 (RDA) was performed using the R package 'vegan' to evaluate the importance of
208 physical and ecological factors to explain the variability of OPE concentrations in
209 seawater. Before the RDA analysis, the OPE concentrations were standardized to reduce
210 the influence of abundant compounds on the results of the ordination. To check for
211 multicollinearity between explanatory variables, variance inflation factor (VIF) was set to
212 VIF<10. The permutation tests were performed to confirm the significance of RDA
213 models and explanatory factors (Monte-Carlo, 999 permutations, significance level of $p \leq$
214 0.05). The concentration of OPEs for PCA-MLR and RDA was expressed as the sum of
215 the dissolved and particulate phases. For figures, the profile of physical/biogeochemical
216 variables and OPE concentrations were produced by Ocean Data View 5.5.2; Boxplots,
217 PCA and RDA statistical analysis, and results of ecological risk assessment were

visualized by Origin 2021.

2.6 Mass Inflow Calculation

The mass inflow of OPEs from Changjiang River (F, kg/d) was calculated as:

$$F = C_i \times Q \times 10^{-9}$$

where C_i is the mean of total OPE concentrations in dissolved and particulate phase, respectively (ng/L), calculated by trapezoidal integration of OPE concentrations through the estuarine water column; and Q is the daily runoff of Changjiang River in July, 2021 (monthly runoff divided by the number of days, 117.8 billion m^3/month, http://www.cjw.gov.cn/zwzc/bmgb/kzdmb/).

2.7 Risk Assessment

A risk quotient (RQ) was calculated to assess the ecological risk of the observed OPEs in surface water of the Changjiang River estuary:

$$RQ = \frac{MEC}{PNEC} = \frac{MEC}{(LC_{50}\ or\ EC_{50})/f}$$

where *MEC* is the measured environmental concentration of OPEs; LC_{50}/EC_{50} refers to the 50% lethal/effect concentration obtained from acute toxicity tests on algae, crustaceans and fish (Verbruggen et al., 2005). *PNEC* is the predicted no-effect concentration based on LC_{50}/EC_{50}. An assessment factor (f) of 1000 was used to interpret the results inferred from intra- and interspecies susceptibility variability (Shi et al., 2020). The biological risks were categorized as no significant impact ($RQ < 0.01$), low ($0.01 < RQ < 0.1$), medium ($0.1 < RQ < 1.0$) and high ($RQ > 1.0$).

3. RESULTS

3.1 Physical and biogeochemical characteristics

As a typical land-ocean transition zone, the Changjiang River estuary and its adjacent coastal waters showed great spatial heterogeneity in physical and biochemical properties (Figure 2 & 3). In summer, the well-mixed estuarine water displayed high temperature (mean: 28 °C), extremely low salinity (mean: 0.14 psu) and low DO (3.7 mg/L). On the continental shelf, the water column was stratified with the thermocline and halocline of less than 10 m depth, and the surface water was characterized by comparably higher temperature (> 28 °C), salinity (< 30 psu) and DO (> 6.2 mg/L) than the estuary (Figure 2b, 2c, 2f & 3b, 3c, 3f). Moreover, the doming of temperature, salinity and DO isolines was associated with elevated dissolved inorganic nitrogen (DIN, the sum of NO_3-N, NH_4-N and NO_2-N), phosphate (PO_4-P) and silicate (SiO_3-Si) (Figure 2g, 2h, 2i & 3g, 3h, 3i), which indicated the summer upwelling of the TWC bottom waters along the slope of submerged river valley beneath the surface frontal zone (Pei et al., 2009). The DIN and SiO_3-Si concentrations declined sharply in the frontal zone along the transect B-C-A1 and A2, whereas the PO_4-P concentrations peaked at the center of upwelling region, owing to the bottom supply of nutrients-rich waters, as well as the transport barrier effect of the fronts. High Chl *a* spots were found in the surface water of frontal/upwelling region (A1-1~A1-4) and nearby (A2-5) (Figure 2j & 3j). This could be attributed to the upwelling of rich nutrients to the surface layer that alleviates the potential PO_4-P limitation on one hand (Figure 2k & 3k), and on the other hand the rapid decrease of turbidity from the estuary (23-123 NTU) to the frontal/upwelling zone (almost 0 NTU, Figure 2d & 3d) that dramatically enhances the light penetration and photosynthetically active radiation (PAR,

Figure 2e & 3e). In addition to the light and nutrients availability, the physical convergence at the frontal zone may have also contributed to these high Chl *a* concentrations (Li et al., 2022).

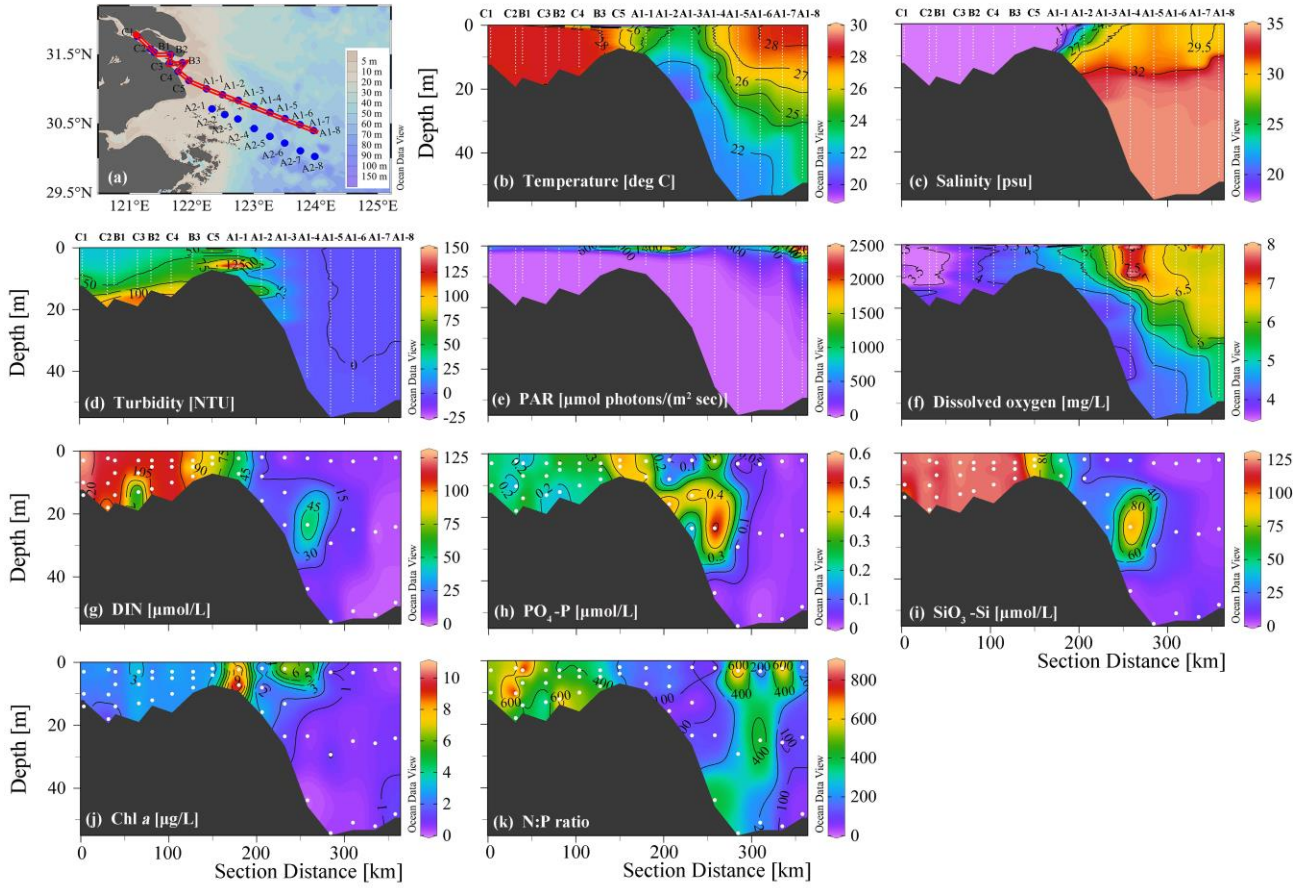

Figure 2. The vertical profiles of temperature (b), salinity (c), turbidity (d), PAR (e), dissolved oxygen (f), nutrients (g-i) and Chl *a* (j), N:P ratio (k) in section B-C-A1 (a). White dash lines at each station represent CTD sensor data, and white points represent the laboratory measurement data

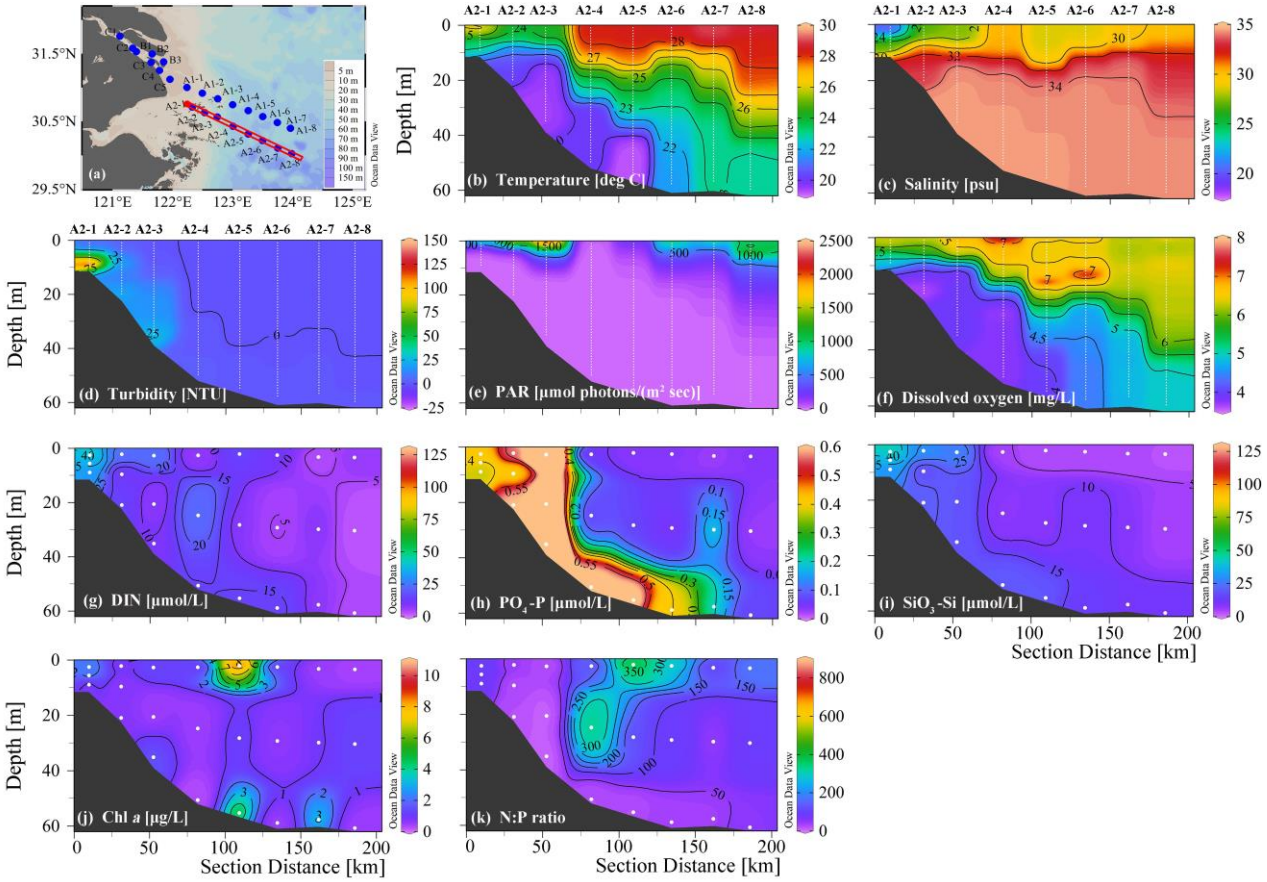

Figure 3. The vertical profiles of temperature (b), salinity (c), turbidity (d), PAR (e), dissolved oxygen (f), nutrients (g-i) and Chl *a* (j), N:P ratio (k) in section A2 (a). White dash lines at each station represent CTD sensor data, and white points represent the laboratory measured data

3.2 Occurrence and distribution of OPEs in seawater of Changjiang River estuary

The detection frequencies of twelve individual OPEs ranged from 25%-90% (Table S5). Except for EHDPP (25%), both Cl-OPEs (> 70%) and non-Cl-OPEs (> 60%) displayed high detection frequencies. The total OPE concentrations (dissolved + particulate, Σ_{12}OPEs) throughout the water column ranged from 0.73 to 1400 ng/L, with a mean and median of 350 ± 380 ng/L and 220 ng/L, respectively (Figure 4). Three Cl-OPEs dominated the composition profile with a mean contribution of 70 ± 28%, while

alkyl-OPEs and aryl-OPEs contributed 16 ± 25% and 14 ± 19% respectively. The major compounds were TCPPs (260 ± 290 ng/L) and TCEP (72 ± 79 ng/L), followed by TEP (24 ± 42 ng/L) and EHDPP (24 ± 49 ng/L). The dominance of Cl-OPEs, especially TCPPs, in seawater was consistent with the recent measurements in the Bohai Bay and Laizhou Bay (Chen et al., 2019; Lian et al., 2021), and of atmospheric OPEs (gaseous and aerosol phase) in coastal regions (Castro-Jiménez et al., 2014; Li et al., 2018; Ma et al., 2022), suggesting the importance of atmospheric sources. Detailed information of individual OPE concentrations is given in Tables S6-S8.

A large proportion (89 ± 12%) of Σ_{12}OPEs was in the dissolved phase (Figure S1), consistent with other studies in the aquatic environment (Pantelaki & Voutsa, 2021; Wang et al., 2018). Notably, despite the low concentrations of particulate OPEs, the detection frequencies of most individual OPE in particles exceeded 50%, except for EHDPP (15%). Two compounds, TCPPs (4.8 ± 6.4 ng/L) and TPhP (6.9 ± 4.5 ng/L), showed relatively higher abundance in the particulate phase (Table S5). The water-particle partitioning exhibited higher particulate fractions for TPhP and TEHP, with mean contributions of 93% and 50% respectively, followed by TDCP, TEP, TiPrP and TPeP with a mean of 33%-42%, while the average particulate fraction of TCPPs, TCEP, TPrP, TiBP and TnBP was only 6%-28% (Figure S2a). These results agreed with those observed in other coastal regions, such as northern Greece and San Francisco Bay (Pantelaki & Voutsa, 2021; Shimabuku et al., 2022).

The water-particle partitioning coefficient (K_P, L/kg) has been widely used to evaluate the partition behavior of OPEs in the aquatic environment (detailed calculation method in Text S5) (Pantelaki & Voutsa, 2021). The logarithm of K_P for individual OPEs

ranged from 0.06-5.0 in seawater, and a significantly positive correlation was observed between log K_P and log K_{OW} (Figure S2b), indicating the water-particle partitioning of OPEs was influenced by hydrophobic interactions. It is noteworthy that the observed K_P values were generally lower than the theoretical K_{OW}, since the field measurements not only included contaminants that were truly dissolved, but also colloidal and/or associated with particles less than 0.7 μm.

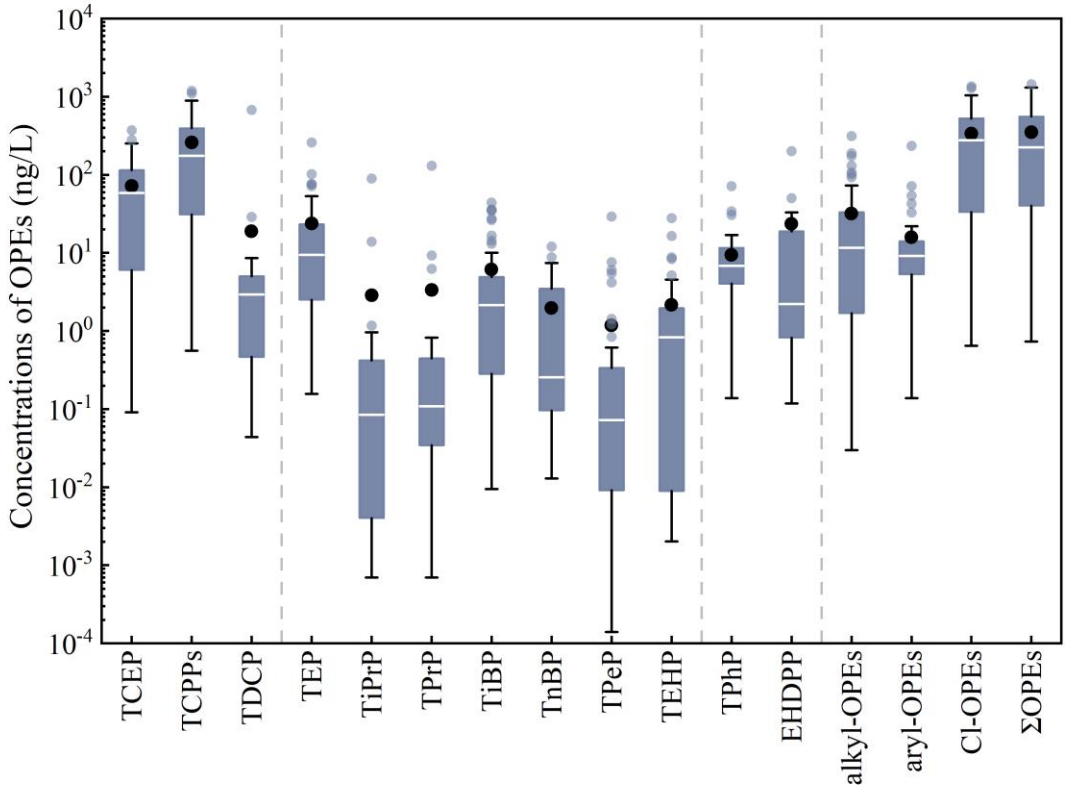

Figure 4. The statistical results of total (dissolved and particulate) OPE concentrations (ng/L) in (n = 61) of the Changjiang River estuary. The white horizontal line inside each box represents the median based on measured concentrations; the black solid circles represent the mean concentrations of OPEs; the small size circles represent outliners; the boxes represent the 25th and 75th percentiles of concentrations above MDL and the black vertical lines mark the 95% confidence interval; the gray vertical dashed lines are to distinguish the statistical results of Cl-, alkyl-, and aryl- individual OPE

317 Σ_{12}OPEs displayed great spatial variability in our study area (Figure S3, Figure 5).
318 Relatively higher OPE concentrations were found throughout the estuarine water column
319 (B-C transects), with some highest concentrations occurring in bottom waters. The high
320 OPE concentrations coincided exactly with regions of high turbidity. In contrast, the
321 OPEs generally showed a 'surface enrichment and depth depletion' pattern in both
322 transects of the continental shelf area (sites A1-5~A1-8 & A2-5~A2-8). It is noteworthy
323 that the inputs of OPEs from Changjiang River seemed to be interrupted in the
324 frontal/upwelling zone, with relatively lower OPE concentrations throughout the water
325 column between the estuary and the continental shelf (sites A1-1~A1-4 & A2-1~A2-4).
326 Due to the dominance of dissolved OPEs, they generally showed similar spatial
327 distribution with Σ_{12}OPEs (Figure S4). As for the particulate OPEs, their concentrations
328 gradually decreased in the water column from the estuary to the continental shelf (Figure
329 S5).

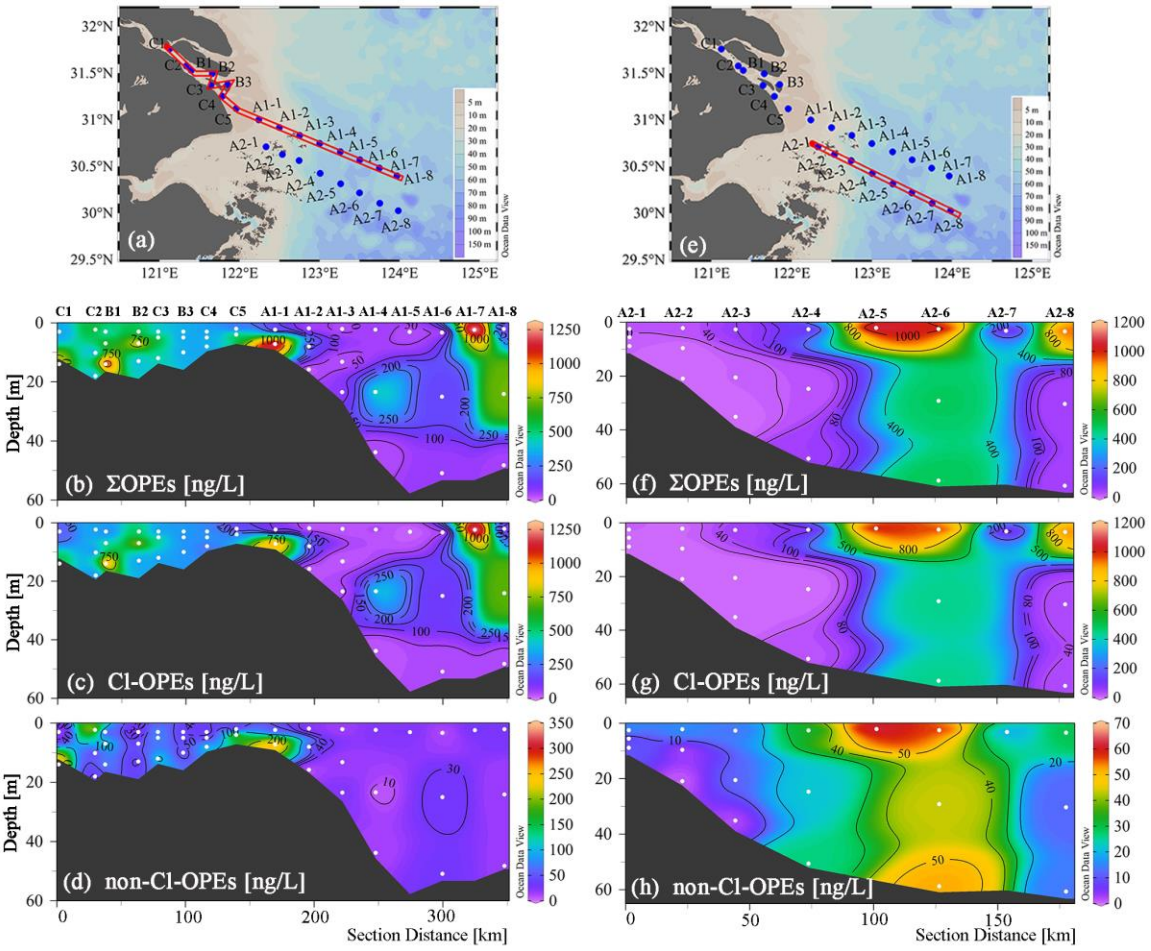

Figure 5. Vertical profiles of the total concentration of dissolved and particulate OPEs in water of the Changjiang River estuary. The concentration of Σ_{12}OPEs (b), Σ_3Cl-OPEs (c) and $\Sigma_9$non-Cl-OPEs (d) in transect B-C-A1 (a, n = 41); and the concentration of Σ_{12}OPEs (f), Σ_3Cl-OPEs (g) and $\Sigma_9$non-Cl-OPEs (h) in transect A2 (e, n = 20); white points represent the laboratory measurement data

3.3 Physical and biogeochemical drivers of OPE concentrations

For RDA, scaled explanatory variables were grouped according to likely regional drivers of contaminant accumulation: (i) sediment input to the estuary was represented by turbidity; (ii) salinity to distinguish seawater from freshwater and to indicate the riverine input; (iii) temperature and salinity indicated the summertime stratification and upwelling process; (iv) Chl *a* implied the potential effects of the biological pump. For all samples (n

342 = 61), RDA constraining variables explained a considerable amount of OPE variations in
343 our study area (27%, permutation test: p = 0.001; Figure 6), with the first axis of 24%
344 (permutation test: p = 0.002) and the second axis of only 3%. The OPE variations were
345 significantly/positively explained by environmental variables including temperature,
346 turbidity and Chl *a*, but negatively explained by salinity. Due to the complexity of the
347 topographic and hydrodynamic conditions of the Changjiang River estuary, the
348 predominant environmental variables differed greatly across the estuary,
349 frontal/upwelling zone, and continental shelf region. In the estuarine sites (n = 22), the
350 constraining variables only explained ~4% of the variation in OPE concentrations, and
351 the RDA model showed non-significance possibly due to the homogeneity in temperature,
352 salinity and Chl *a* at these estuarine sites. For the frontal/upwelling zone (n = 23), RDA
353 constraining variables explained 52% of the variance in OPE concentrations (permutation
354 test: p = 0.03; Figure S6a), with significant Chl *a*, turbidity and salinity contributions. Chl
355 *a* also had significant impact on the variance of OPEs in the continental shelf region, in
356 which 22% was explained by the RDA constraining variables (n = 16, permutation test: p
357 = 0.04; Figure S6b).

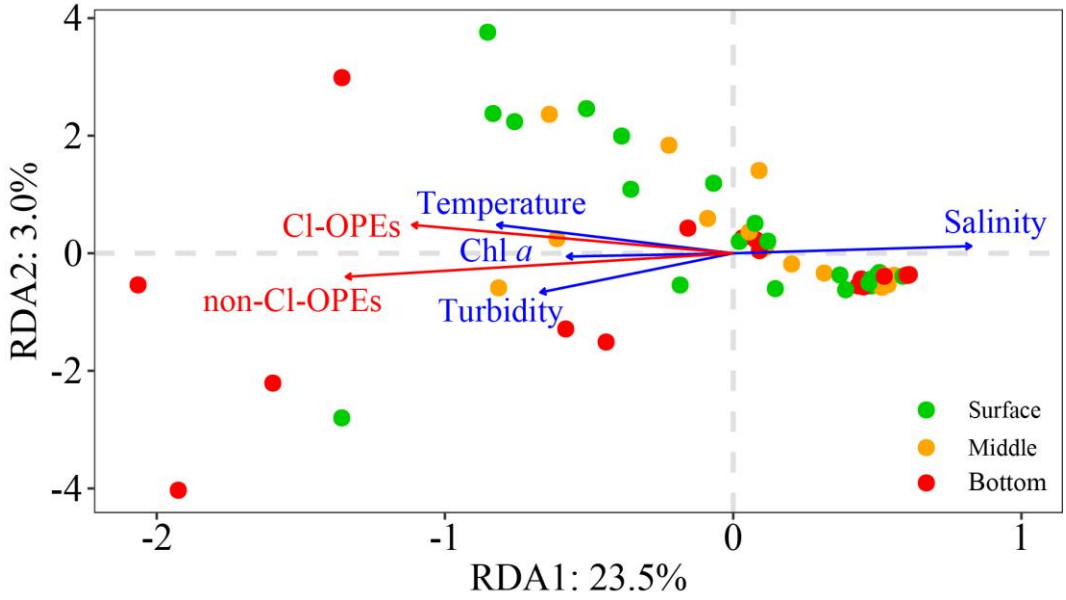

Figure 6. Transformation-based redundancy analysis (RDA) based on the concentrations of non-Cl-OPEs and Cl-OPEs (in red). Constraining variables: salinity, temperature, turbidity and Chl *a*, are shown in blue. Each point represents one individual sample, and color represents the sampling depth in each station (n = 61)

3.4 Source apportionments of OPEs

Three significant factors were identified from the PCA analysis, which explained 33%, 22% and 12% of the total variability of the original OPEs dataset, respectively (Table S9 and Table S10). PC1 was predominantly weighted by TCEP, TDCP, TPrP, TnBP, TEHP and TPhP (Figure 7a), which could be explained as industrial pollution, because these OPEs were widely used as sealants, coating products and lubricants (Van der Veen & de Boer, 2012). PC2 was mainly associated with some more hydrophilic compounds with relatively lower log K_{OW} values, including TCPPs, TiBP and TPeP. Thus, PC2 could be related to WWTPs discharge (Kim et al., 2017; Schreder & La Guardia, 2014). PC3 was predominantly composed of TEP and TiPrP, which were mainly used as

plasticizer additives and could originate from indoor environments (Blum et al., 2019). Therefore, PC3 could be regarded as consumer products' signature. Moreover, the following MLR results showed that the mean contributions were 59% for the WWTPs discharge, 21% for the industrial pollution and 20% for consumer products, respectively (Figure 7b).

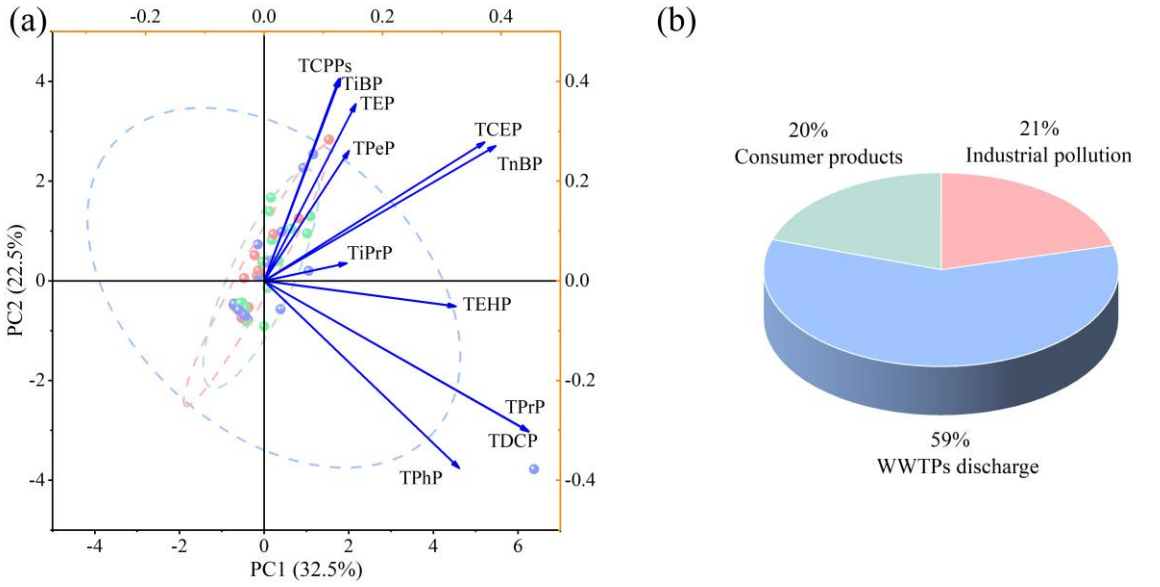

Figure 7. PCA results of OPEs in all water samples, and the dashed line represents the 95% confidence ellipse (a); Contributions of three potential sources obtained from MLR (b)

3.5 Riverine mass input to the ECS

The Changjiang River runoff was estimated as 117.8 billion cubic meters during July, 2021, and the corresponding daily mass input of dissolved OPEs ($\Sigma_{12}OPEs_{dis}$) from the estuary into the adjacent ECS was calculated to be 2.1 ± 0.79 t/d. TCPPs had the highest riverine mass inflow (1.4 ± 0.65 t/d), followed by TCEP (0.42 ± 0.16 t/d) and TEP (0.17 ± 0.15 t/d) respectively, probably due to the higher production and application of these compounds (Huang et al., 2022). Our results were lower than OPEs transported to the

South China Sea via eight tributaries of the Pearl River Estuary (Σ_9OPEs_{dis}, 16 t/d), probably due to several of the worlds' largest manufacturing centers located upstream of Pearl River Estuary (Wang et al., 2014). Yet the daily mass input of dissolved OPEs from Changjiang River observed in this study was significantly higher than the inflow of OPEs through forty rivers into the Bohai Sea in northern China ($\Sigma_{11}OPEs_{dis}$, 44 ± 8.8 kg/d) (Wang et al., 2015), as well as OPEs transported into the German North Sea via the Rhine-Meuse delta and Elbe estuary (Σ_8OPEs_{dis}, 140 kg/d) (Bollmann et al., 2012) and to the Gulf of Lion by the Rhône River (Σ_8OPEs_{dis}, 10-116 kg/d) (Schmidt et al., 2020). Notably, the massive sediment inputs also played a crucial role in carrying OPEs into the ECS. The mass inflow of particulate OPEs ($\Sigma_{12}OPEs_{par}$) was estimated as 72 ± 45 kg/d, comparable with those estimated in the Pearl River Estuary ($\Sigma_{10}OPEs_{par}$, 65 kg/d) (Lao et al., 2022). The dominant compounds for particulate inflow were TCPPs (38 ± 23 kg/d) and TPhP (14 ± 15 kg/d), respectively.

3.6 Ecological risk assessment of OPEs

As the primary producers of aquatic ecosystems, algae are most sensitive to anthropogenic OPEs. The dissolved OPEs posed high-moderate risk to algae at some estuarine sites, with $RQs > 1$ at sites C2 & C3, and $0.1 < RQs < 1.0$ at sites B1, B2, C1, C4, A1-1 to A1-3, while no significant or low risks were present at the other sites off the estuary ($RQs < 0.1$) (Figure 8a). Except for the C2 station, the OPEs posed low or no significant risk to crustaceans and fish (Figure 8b-8c). For individual OPE compounds, TPhP, TCPPs and EHDPP posed greater ecological threat to fish and crustaceans due to their elevated concentrations. In contrast, TEHP posed greater ecological risks to algae

413 than other individual OPEs, due to its relative lower PNEC value (Table S11).

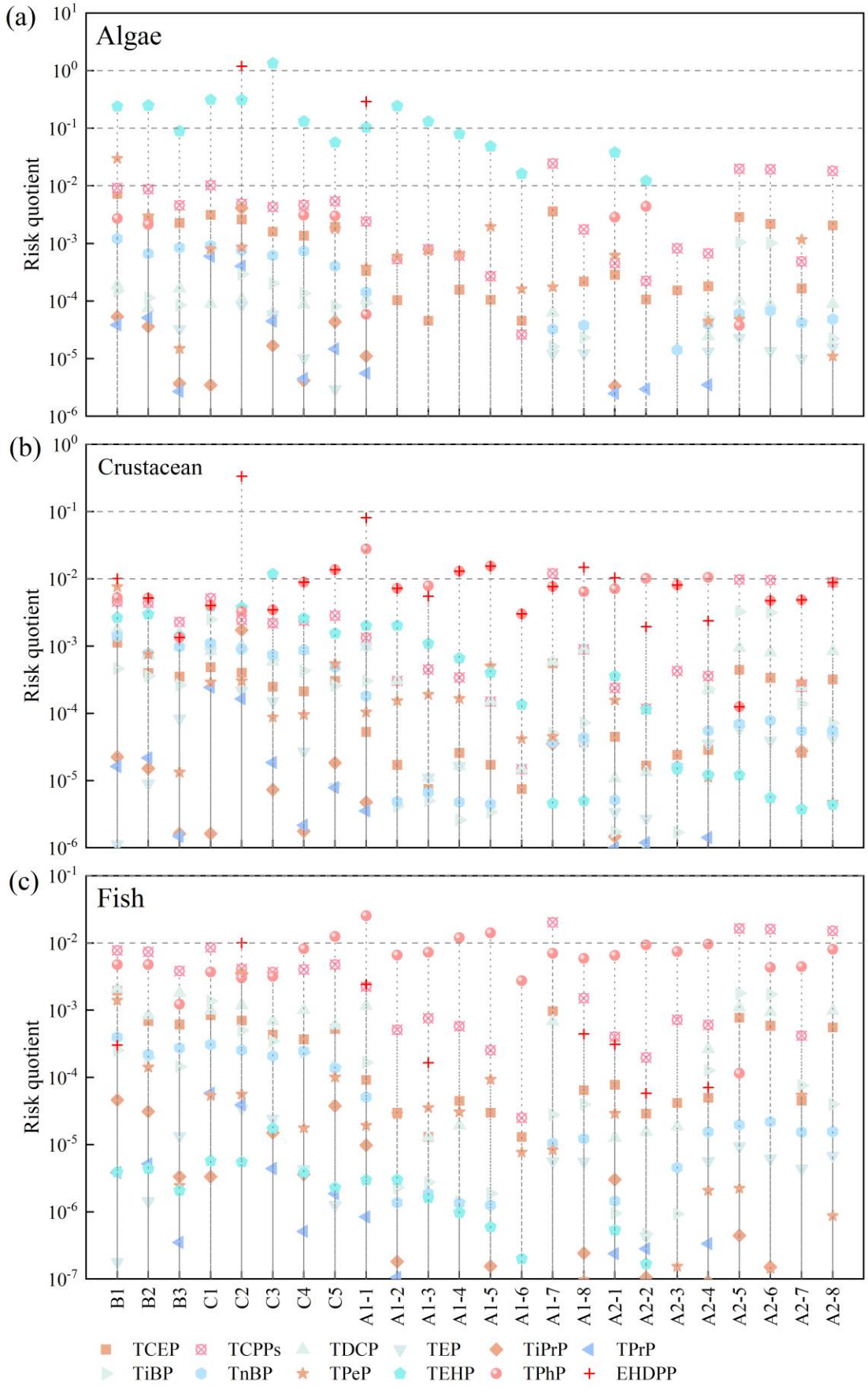
(a)
Algae
(b)
Crustacean
(c)
Fish
Risk quotient
B1
B2
B3
C1
C2
C3
C4
C5
A1-1
A1-2
A1-3
A1-4
A1-5
A1-6
A1-7
A1-8
A2-1
A2-2
A2-3
A2-4
A2-5
A2-6
A2-7
A2-8
TCEP
TCPPs
TDCP
TEP
TiPrP
TPrP
TiBP
TnBP
TPeP
TEHP
TPhP
EHDPP

Figure 8. Risk quotients of individual OPE on algae (a), crustaceans (b) and fish (c) in surface water from the Changjiang River estuary. The values of horizontal dashed line indicate the ecological risk thresholds: no significant impact ($RQ < 0.01$), low ($0.01 < RQ < 0.1$), medium ($0.1 < RQ < 1.0$) and high ($RQ > 1.0$)

4. DISCUSSION

4.1 Combined effects of fronts, upwelling and the biological pump

The physical and biogeochemical characteristics of the Changjiang River estuary and its adjacent coastal regions were highly variable in summer. The inputs of land runoff from the Changjiang River carried large amount of sediments and nutrients into the ECS, and formed the frontal area at the confluence of Changjiang diluted freshwater and seawater (Gao et al., 2015). Phytoplankton are known to preferentially accumulate in this region, benefitting from rich nutrients, sufficient light and suitable temperature (Ge et al., 2020). Additionally, the co-existed coastal upwellings also contributed to the supply of nutrients, and thus phytoplankton accumulation (Largier, 2020; Pei et al., 2009). In this study, the relatively higher OPE concentrations shown in the bottom water of the estuarine and frontal zones coincided exactly with the high turbidity regions. The RDA results also indicated the significant influence of turbidity in the study area (Figure 6). The bottom water with high turbidity could be due to either the massive inflow and accumulation of terrestrial sediments (B1 & C1), or the algal growth and subsequent sedimentation of biogenic particles (A1-1). The estuarine sediment is deemed a regional sink of terrestrial pollutants (Barletta et al., 2019), and the typically positive correlation between particulate OPEs and SPM (Pearson test, $r = 0.45$, $p = 0.03$) at estuarine sites (B1-B3 & C1-C5) further demonstrated the sedimentation capturing OPEs in this region.

In the frontal/upwelling and continental shelf area (A1-1 to A1-8 & A2-1 to A2-8), Chl *a* in seawater was significantly and positively correlated with SPM (Pearson test, r = 0.56, $p < 0.01$), indicating the contribution of planktonic particulate matter to SPM. The Σ_{12}OPEs in seawater was significantly and positively correlated with Chl *a* (Pearson test, r = 0.32, $p < 0.04$), but not with SPM. The RDA analysis also suggested the importance of Chl *a*, an indicator of the biological pump, in both frontal/upwelling and continental shelf regions. Therefore, some comparable higher OPE concentrations in the intermediate and bottom layers with high Chl *a* (A1-1, A1-4 and A2-6) could have resulted from the biological pump. Specifically, the OPEs attached to particulate organic matter produced by actively growing phytoplankton in the surface layer, and were gradually released during the settling process.

The enrichment of OPEs in the surface layer of the continental shelf (A1-7, A2-5, A2-6 and A2-8) region could be due to non-point sources - their continuous inputs from atmospheric deposition and riverine runoff/WWTPs discharge, as well as some point sources, such as microplastic releases (Sørensen et al., 2021). The strong seasonal thermocline and halocline/enhanced stratification that formed in summer further inhibited the vertical mixing of the contaminants, which resulted in relatively low concentrations of target contaminants in the intermediate and bottom layers of the continental shelf region. The vertical profile sampling in the continental shelf area was conducted at every other station, so no vertical profile observation was conducted at station A2-5, the peak position of Chl *a* (8.7 μg/L) of this transect. Notably, at the Chl *a* sub-peak position (A2-6, 1.1 μg/L) of this transect, the coupling between deposition of OPEs with the biological pump was obvious. The influence of the biological pump on the vertical transport of

462 hydrophobic organic contaminants, including polychlorinated biphenyls (PCBs), high
463 molecular weight polycyclic aromatic hydrocarbons (PAHs) and legacy organochlorine
464 pesticides (OCPs), has already been demonstrated in aquatic ecosystem (Galbán-Malagón
465 et al., 2013; González-Gaya et al., 2019; Nizzetto et al., 2012).
466

467 **4.2 Comparison analysis and other potential drivers**

468 Since most previous studies concentrated on dissolved OPEs, which also dominated
469 in this study, a specialized comparison was conducted for dissolved OPEs. The dissolved
470 OPE concentrations of this study (340 ± 380 ng/L) were comparable to the mean OPE
471 concentrations in worldwide coastal waters, such as the German Bight (400 ng/L) (Wang
472 et al., 2020) and the Amazon River mouth (460 ng/L) (Schmidt et al., 2019), but higher
473 than those observed in the open West Pacific Ocean (25 ng/L) (Xiao et al., 2021) and the
474 remote North Atlantic-Arctic Ocean (2.9 ng/L) (Li et al., 2017) (Table S12). However,
475 compared to previous studies on dissolved OPEs in the surface water of coastal China
476 Seas, our results were overall comparable but slightly lower than the mean OPE
477 concentrations detected in the Lianyungang (570 ng/L) (Hu et al., 2014), Pearl River
478 Estuary (630 ng/L), Yellow River Estuary (870 ng/L) (Lai et al., 2019) and Laizhou Bay
479 (1200 ng/L) (Lian et al., 2021).

480 The reduced level of OPEs detected in this study could be attributed to multiple
481 factors. First of all, the sampling period of this study, from July 12th to July 17th, is the
482 typical flood season. The summer runoff flux of the Changjiang River contributed ~70%
483 of its annual runoff (http://www.cjw.gov.cn/zwzc/bmgb/). As a result, the large amounts
484 of freshwater inputs diluted the pollutants in coastal regions. Secondly, the difference in

485 solubility of OPEs in freshwater and seawater, termed the ‘salting-out’ effect, can result
486 in enhanced volatilization (or settling) of dissolved OPE in the frontal zone. The ‘salting
487 out’/volatilization of dissolved Cl-OPEs in the frontal zone of freshwater and seawater
488 has already been observed at the mouth of the Nelson and Churchill Rivers of the
489 Canadian Arctic (Sühring et al., 2016). Additionally, the OPEs might be diluted by TWC
490 waters, which traversed a long distance from the Taiwan Strait and upwelled to the
491 surface/subsurface in the Changjiang River mouth (Wei et al., 2021). Although there is
492 currently no direct observation of summertime OPEs in TWC bottom waters, the strong
493 stratification in subtropical area during summer is very likely to cause low OPE
494 concentrations in bottom water as discussed above (Sanganyado et al., 2021). Moreover,
495 some OPEs in the study area might, at least partially, have already been microbially
496 hydrolyzed to inorganic phosphate (PO_4-P). The relatively low PO_4-P concentration and
497 high N/P ratio in the study area indicated that PO_4-P was the potentially limiting nutrient
498 in the Changjiang River estuary, especially during the sampling period of summer after
499 the conventional spring bloom (Figure 2 & 3). The alkaline phosphatase, mainly
500 produced by microorganism, can be induced under phosphorus-limited conditions. The
501 dissolved OPEs, components of dissolved organic phosphorus, can be microbially
502 hydrolyzed by alkaline phosphatase to inorganic PO_4-P (Xie et al., 2021), further
503 promoting the primary productivity in aquatic environment. Although OPEs inhibit the
504 activity of acetylcholine esterase (AChE), which play an important role in biological
505 nervous system, by covalently binding to its active site, OPEs do not adversely affect
506 bacteria, because bacteria do not possess AChE, and some microorganisms can even use
507 OPEs as an energy source (Singh & Walker, 2006). Both the laboratory and in-situ

incubation experiments demonstrated increasing alkaline phosphatase activity (APA) under phosphorus stress (Vila-Costa et al., 2019; Xie et al., 2021). Overall, the regions with reduced OPE levels could be attributed to the dilution of large amount of freshwater in summer, potential microbial degradation induced by phosphorus limitation, heaving of deepwater containing depleted OPEs, as well as the 'salting-out' effects, though further large-scale simultaneous air-water observations are still warranted.

As for the ecological risk, it appeared to be reduced due to these relatively lower OPE concentrations. However, the frontal and upwelling regions are regularly characterized by rich nutrients and high biological productivity, and good fishing grounds are commonly found in their vicinity (Largier, 2020). Therefore, the long-term ecotoxicity caused by the mixtures of OPEs cannot be ignored, considering the continuous high production, application and release of OPEs to the complex coastal environment (Vasseghian et al., 2022), as well as the bioaccumulation and biomagnification effects of some OPEs (such as EHDPP and TPhP) (Ding et al., 2020; Wang et al., 2019).

5. CONCLUSION

Dissolved and particulate OPEs were widely detected in the Changjiang River estuary. Concentrations were dominated by dissolved OPEs, and the water-particle partitioning of OPEs was strongly influenced by hydrophobic interactions. In contrast to non-Cl-OPEs, Cl-OPEs generally exhibited relatively higher detection frequencies and concentrations. Source apportionment suggested that the dominant OPE sources were WWTPs discharge, although there was also evidence of industrial emissions and release

from consumer products. In this study, we found that the OPEs generally posed a low ecological risk to aquatic life, but the long-term risks may not be insignificant as the exposure continues due to their constant high production and application.

Due to the complex hydrological and biogeochemical processes in the Changjiang River estuary, the vertical and horizontal occurrence and transport of OPEs displayed great spatial variability. OPE concentrations in the estuary were high, especially for the bottom waters, due to the massive terrestrial/sediment inputs; while the 'surface enrichment and depth depletion' of OPEs in the continental shelf was influenced by seasonal stratification. Overall, the water column in the frontal/upwelling zone had low OPE concentrations. However, the fronts/upwelling activity could induce phytoplankton blooms, and elevated OPEs were found just below the surface water where phytoplankton aggregated, indicating the combined impacts of frontal/upwelling and the biological pump. Considering the broad range in the physicochemical properties of OPEs, they can serve as tracers of competing biogeochemical and physical oceanographic processes. Some (mobile) OPEs basically trace water mass movement, while others are transported by sediments or move with plankton.

The Changjiang River estuary proved to be an ideal region to study the influence of coupled hydrological-biogeochemical processes on the OPE transport, because it is well characterized for its oceanographic processes, but is also strongly impacted by OPE emissions. The physical and biogeochemical processes discussed in this study, including riverine inputs, fronts and coastal upwellings, as well as the biological pump and biodegradation, are typical for global estuaries. Therefore, our methods, results and conclusions here could be generalized to assess the complicated environmental behavior

554 and fate of OPEs in other estuarine and coastal regions around the world.

555

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561

562 **Open Research**

563 **Data Availability Statement**

564 All data, including experiment details, instrument conditions, sampling information,
565 physicochemical properties of OPEs, QA/QC and detail OPE concentrations have been
566 deposited in ZENODO (https://doi.org/10.5281/zenodo.8418167). The above dataset is
567 also available in the supporting information.

568

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