


Article

Study of the Spatiotemporal Variations, Source Determination, and Potential Ecological Risk of Organophosphate Esters in Typical Coastal Tourist Resorts in China

Xuezhi Cao ¹, Bingbing Wang ², Xinxin Liu ², Jichun Cheng ¹ and Shiliang Wang ^{2,*} 

¹ School of History and Culture, Qufu Normal University, Qufu 273165, China; hjxyjz@126.com (X.C.); chengjcqf@163.cn (J.C.)

² School of Life Science, Qufu Normal University, Qufu 273165, China

* Correspondence: wangshiliang@tsinghua.org.cn

Abstract: Investigation of the environmental occurrence and behavior of organophosphate esters (OPEs) is very important and is becoming a hot topic in the academic community. In this study, 12 targeted OPEs in the water and sediment from 19 coastal tourist resorts in the Shandong Peninsula in China were analyzed to show their concentrations, spatial variations, and potential ecological risks. The results showed that the total concentrations of OPEs (Σ OPEs) were in the range of 18.52–3069.43 ng/L in the water and 3.20–568.76 ng/g in the sediment. The dominant OPEs in the water and sediment were tris (2-chloroisopropyl) phosphate (TCIPP), tris (2-chloroethyl) phosphate (TCEP), and triethyl phosphate (TEP). The OPE concentrations in the water were ranked as dry season > normal season > wet season. The sewage treatment plants near tourist resorts were important contributors to the level of OPEs in the water. Triphenyl phosphate (TPHP), tri-n-butyl phosphate (TNBP), and resorcinol-bis(diphenyl)phosphate (RDP) had a relatively higher ecological risk than other OPEs in the water samples. Industrial emissions might be the main source of OPEs in the coastal tourist resorts of Shandong Peninsula in China. The results of this study verified that OPEs occur in the water and sediment of coastal tourist resorts, and more attention should be given to the existence of OPEs and the safety of aquatic environments near coastal tourist resorts.

Keywords: organophosphate esters; spatial distribution; ecological risk assessment; coastal tourist resorts



Citation: Cao, X.; Wang, B.; Liu, X.; Cheng, J.; Wang, S. Study of the Spatiotemporal Variations, Source Determination, and Potential Ecological Risk of Organophosphate Esters in Typical Coastal Tourist Resorts in China. *Water* **2023**, *15*, 3976. <https://doi.org/10.3390/w15223976>

Academic Editors: Weiying Feng, Fang Yang and Jing Liu

Received: 4 October 2023

Revised: 9 November 2023

Accepted: 14 November 2023

Published: 16 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

There are many types of organophosphate esters (OPEs), such as chlorinated (Cl)-OPEs, alkyl-OPEs, aryl-OPEs, and brominated (Br)-OPEs [1,2]. They are used for a wide variety of consumer goods, including plastics, foams, textiles, electronics, and construction materials. Chlorinated OPEs are mostly utilized as flame retardants, whereas non-chlorinated OPEs are predominantly used as plasticizers [3,4]. OPEs were initially employed due to the restricted use of brominated flame retardants (BFRs), as they are more environmentally friendly and cost-effective [5]. Furthermore, OPEs have also been extensively utilized as additives [6]; they are often added to materials physically rather than combined with chemical substances and can be released into the environment by volatilization, leaching, and other similar methods [4]. OPEs are ubiquitous and widely distributed worldwide in various environmental matrices, including in the air, dust [3], water [7], sediment [8], soil [9], and biota [10]. In recent years, the focus of research has also shifted from investigating their levels in various environmental media to their effects on human health [11,12]. Numerous studies have indicated that exposure to OPEs may have negative effects on human health, such as reproductive inhibition, neurotoxicity, carcinogenicity, and endocrine disruption [13]. More thorough studies of their source and fate in the environment are required.

OPEs have been found in surface water all around the world. Additional research from the USA, Australia, and Europe, including Germany, Italy, and Spain, and Asia, including South Korea and Japan, revealed that the mean value of OPEs was in the range of 76–2230 ng/L, and Cl-OPEs were predominant [4]. OPEs have also been detected in Chinese waters, primarily in Taihu Lake and the Pearl River Delta [14,15]. The water in the Pearl River Delta contained in the range of 15–1790 ng/L, the water in Taihu Lake had concentrations in the range of 166–1530 ng/L, and the sediment in the lake had 2.8–47.5 ng/g [14,15]. Eight OPEs have been found in European river sediments, ranging from 2.5181 ng/g [16]. Fourteen OPEs were found in sediment from the North American Great Lakes, ranging from 0.44 to 47.8 ng/g [17].

The warm temperature and curved coastline of the Shandong Peninsula have proven ideal for the development of coastal tourism. Shandong Peninsula has the largest number of national and provincial coastal tourist resorts in China. However, many environmental issues have also arisen as a result of the rapid development of coastal tourist resorts. It is essential to protect the environmental quality of water bodies during the further development of coastal tourist resorts. Numerous man-made substances have been released into the Bohai Sea as a result of extensive anthropogenic activity along the shore, including urban and industrial refuse [18,19], which may have an immediate effect on human health. Thus, a more in-depth investigation of the contamination status and bioaccumulation of OPEs in the environment needs to be carried out.

The main purpose of this study was to (i) evaluate the presence and spatial distribution of 12 OPEs in the surface water and sediment of coastal tourist resorts, (ii) quantify the partitioning of OPEs between the water and sediment, (iii) analyze the seasonal correlations, the correlation of OPE levels in surface water and sediment, and the correlation between the physical and chemical characteristics of OPEs and their concentration, and (iv) identify potential sources of target OPEs in sampling sites; and (v) evaluate the ecological risk posed by OPEs around typical coastal tourist resorts in China.

2. Materials and Methods

2.1. Sample Collection

The water samples (S1–S19) were taken in August 2018 (wet season), December 2019 (dry season), and April 2019 (normal season) from coastal tourist resorts of the Shandong Peninsula. The sediment sampling locations were the same as the water sampling locations and were taken in December 2019. The sampling stations are shown in Figure 1 and summarized in Tables S1 and S2.

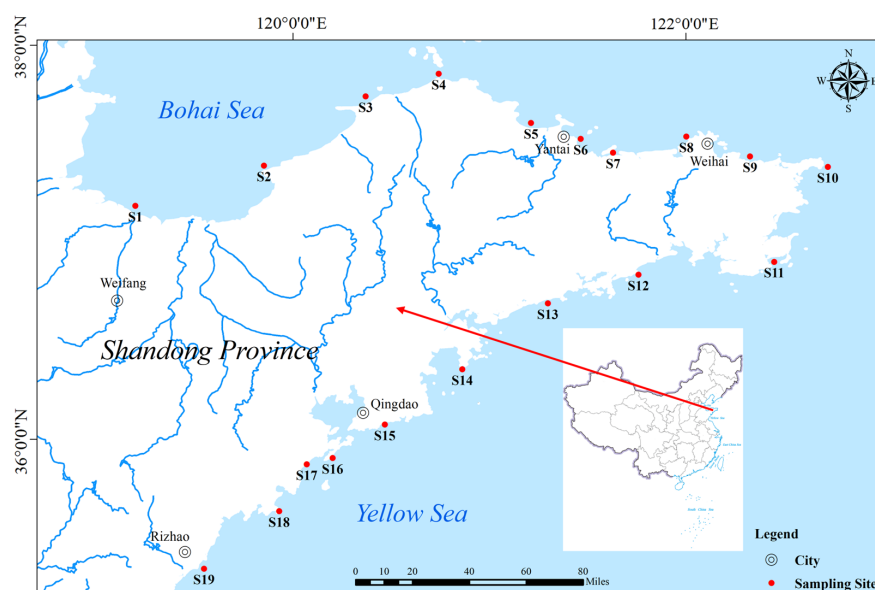


Figure 1. Sampling location map in the coastal tourist resorts of Shandong Peninsula.

A stainless-steel water sampler was used to simultaneously capture two 1 L water samples at each location. Before laboratory analysis, all samples were stored in brown glass jars that had been cleaned and then were refrigerated immediately after collection. To obtain more representative samples, at each monitoring site, surface water samples were taken five times and held in stainless-steel drums. Then, 1 L of the combined water sample was obtained, transferred into PP bottles, and kept frozen for no longer than 12 h. Milli-Q water in PP bottles was utilized as water sample blanks and was preserved identically to the samples. Stainless-steel grab samplers with a 0.2 m² surface area and 30 cm depth were used to gather sediment samples. Utilizing a previously cleaned stainless-steel scoop, sediment samples were collected and put into aluminum storage containers. All samples were kept at a temperature of −20 °C until further analysis.

2.2. Chemicals and Materials

Twelve OPEs were purchased from the Sigma-Aldrich (St. Louis, MO, USA), for which detailed information such as the CAS number, formula, molecular weight, Log K_{ow}, Log K_{oc}, Log P_{ow}, boiling point, water solubility, and application are listed in Tables S3 and S4. Before instrumental analysis, isotopically labeled internal standards were purchased from Toronto Research Chemicals Inc. in Canada and Sigma-Aldrich in the UK and were employed as stand-ins, as listed in Table S5. The target OPEs in this research were classified into three categories, tris (2-chloroethyl) phosphate (TCEP), and tris (2-chloroisopropyl) phosphate (TCIPP), tris (1,3-dichloro-2-propyl) phosphate (TDCIPP), and tetrakis (2-chloroethyl) dichloroisopentyl-diphosphate (V6) were classified as Cl-OPEs, bisphenol A diphenylphosphate (BDP), resorcinol-bis (diphenyl) phosphate (RDP), triphenyl phosphate (TPHP), and tris (methylphenyl) phosphate (TMPP) were classified as aryl-OPEs, and tris (2-chloroethyl) phosphate (TCEP), tripropyl phosphate (TPP), tris (2-butoxyethyl) phosphate (TBOPE), and tri-n-butyl phosphate (TNBP) were classified as alkyl-OPEs. The purity of the standard materials exceeded 98%.

The following chemicals were purchased from J.T. Baker (Darmstadt, Germany): HPLC-grade acetonitrile, methanol, n-hexane, dichloromethane, and ethyl acetate. Formic acid was purchased from CNW Technologies in Düsseldorf, Germany, with a purity of 99%. Oasis HLB cartridges were purchased (500 g, 6 mL) from Waters Company in the Milford, MA, USA and were used to perform solid phase extraction. Glass fiber filters were purchased (0.22 µm) from Whatman Company in the Maidstone, UK. Ultrapure water (18.2 MΩ cm) was generated by the Milli-Q Advantage A10 system from the Millipore Company in the Billerica, MA, USA.

2.3. Pretreatment and Analytical Procedure

The methods of water sample pretreatment were consistent with previous investigations [20–22]. The method was as follows: 1 L of water was first filtered through a 0.22 µm glass fiber filter, after which 20 ng of standard substitution was added to the filtered sample to remove solids such as particles. Next, using a vacuum pump, the sample was passed slowly, at a speed of 3 mL/min, through an Oasis HLB cartridge, which was pretreated with 6 mL of ultrapure water and 6 mL of methanol. Vacuum drying was carried out for 1 h after the extraction process to load the water sample completely. This was followed by three additions of 2 mL of dichloromethane and ethyl acetate (1:1, v/v). Subsequently, the eluate was concentrated to a dry state by passing through a gentle stream of nitrogen to a fixed volume of 1 mL with methanol/ultrapure water (1:3). Finally, the extract was transferred to a chromatography vial for instrumental analysis.

The technique outlined by [23] was used to extract OPEs from sediment. After being freeze-dried, sediment samples were run through a 60-mesh filter (0.25 mm) before 20 ng of the deuterated surrogate standard was added to 10 g of homogenous sediment and cultured overnight. The stainless-steel extractor was filled with the mixture, which had been prepared with 2 g of copper powder and 5 g of silica gel for purification. We used n-hexane: acetone (1:1, v/v) rapid solvent extraction to extract the samples. According

to [24], extraction conditions were as follows: the pressure extraction of 1500 psi, rinse volume of 60%, continuous nitrogen purge time of 60 s, temperature extraction of 100 °C, and two extraction cycles. The extracted substances were dried, and the remaining material was restructured with 1 mL of methanol/ultrapure water (1:3) during analysis.

2.4. Instrumental Analysis

The OPE concentrations of water and sediment were determined by an ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) system (an Agilent 1290 Infinity LC with an ABSCIEX QTRAP 5500 triple quadrupole mass spectrometry LC-MS/MS system) (Agilent Technologies, Inc., Santa Clara, CA, USA). Comprehensive information on the UPLC-MS/MS analytical parameters is given in Table S5. A Waters Xbridge BEH-C18 XP column (4.6 mm × 100 mm, 2.5 µm) from Waters Corporation (Milford, MA, USA) preserved by a Waters Xbridge BEH-C18 XP VanGuard pre-column (2.1 mm × 5 mm, 2.5 µm) from Waters Corporation (Milford, MA, USA) was used to analyze samples. Until they were injected into the instrument, the samples were kept at 10 °C. A partial loop was used to inject 10 µL of the sample once every 5 min at 45 °C. In this study, ultrapure water acidified with 0.1% formic acid was used as mobile phase A, and acetonitrile was used as mobile phase B for chromatographic separation. The flow rate was set at 0.2 mL/min. The gradient progressed as follows: 40% B for 0.5 min; 40–80% B for 3.5 min; 80% B for 2.0 min; 80–100% B for 2.0 min; 100% B for 4.5 min, back to 40% B for 1.0 min, and held for 2.5 min. A positive ion pattern electrospray ionization (ESI +/−) source in multiple reaction monitoring (MRM) patterns was employed for mass spectrometry analysis. In addition, the pH value and salinity of the water and total organic content (TOC) were also measured, and the results are shown in Table S6.

2.5. Quality Assurance and Control

Blanks of field and laboratory procedures were conducted for each batch of analyses. To reduce the probability of contamination, plastic and rubber materials were not used for sampling, sample storage, or sample transportation. The glass was cleaned in methanol and pure water before being baked for four hours at 450 °C. For the water samples, in addition to the samples themselves, field blanks and laboratory procedure blanks were calculated, and for the sediment samples, only laboratory procedure blanks were used.

Strict control measures were required during sample collection and analysis for quality assurance. For any batch of analysis, field blank and laboratory procedure blank were both required to be performed. All glassware used in the laboratory needs to be baked overnight at 450 °C again to reduce contamination during the experiment. Vessels were cleaned three times with ultrapure water, acetone, and ethyl acetate prior to the sample-collection procedure. The findings showed that there was background contamination. TEP, TNBP, TCIPP, TCEP, and TDCIPP were the primary OPEs with background concentrations in the field blanks for the water samples, as indicated in Table S7. Additionally, TBOPE, TEP, TDCIPP, and TCIPP were found in lab-related blanks. Background contamination of sediment samples was rare. A combination of internal and external standard methods was used in the analysis for quality control. The internal standards are given in Table S5 and were added before instrumental analysis. The Marking Line, encompassing 6 concentrations with correlation coefficients higher than 0.993, was obtained to quantify the target compounds. The concentrations corresponding to signal/noise ratios of 3 and 10, respectively, were designated as the limit of detection (LOD) and the limit of quantification (LOQ) [20]. The average blank plus the triple standard deviation of the procedure blanks was used to define the LOD of a chemical [25]. The LOQ was the analyte concentration that corresponded to the sample blank value plus 10 standard deviations [25]. The LODs of target OPEs in sediment and water were in the range of 0.01–0.32 ng/g and 0.01–0.35 ng/L, respectively. The LOQs of target OPEs in water and sediment were between 0.02–0.51 ng/L and 0.01–0.67 ng/g, respectively. To evaluate the extraction rates and procedures, known concentrations of the 12 OPEs standards and surrogate standards were generated con-

currently with the genuine samples and were introduced into the blank samples prior to extraction. Before conducting instrumental analysis using the recovery determination method, the inter-standard chemicals specified in Table S8 were added to the samples for quantization. For water and sediment, the recovery of the 12 OPEs was 70–112% and 61–112%, respectively.

2.6. Datum Analysis

The pollutant distribution between water and sediment, particularly through secondary releases of organic contaminants from sediments, was assumed to have a substantial effect on the quality of the aquatic environment [26,27]. Therefore, the distribution coefficient (K_d) of OPEs between water and sediment needed to be calculated. A significant factor that modifies the affinity of OPE molecules for sorbents is the amount of organic carbon in the substance [28,29]. Therefore, the normalized organic carbon/water partition coefficient (K_{oc}) of the OPEs needed to be calculated.

$$K_d = (C_s \times 1000) / C_w$$

$$K_{oc} = (K_d \times 100) / \text{TOC}$$

K_d was utilized to examine how OPEs transformed between the water and sediment in the tourist vacation districts of the Shandong Peninsula. K_{oc} was calculated from the values of K_d and TOC. TOC was the percentage of organic carbon in the sediment (%).

In the correlation analysis, SPSS 16.0 (SPSS Inc., Chicago, IL, USA) and Origin2021 (OriginLab Inc., Northampton, MA, USA) were used to perform the correlation analysis and principal component analysis (PCA). The correlation analysis included the correlation between the scientific properties of the 12 OPEs and their concentrations, the correlation between seasons, and the correlation of the OPE concentrations in surface water and sediment. In the PCA study, the eigenvalue had to be bigger than 1 to meet the PC extraction criteria.

2.7. Ecological Risk Assessment

According to some previous studies [7,24], the risk evaluation was based on the risk quotient (RQ), which was calculated by the measured environmental concentration (MEC). The MEC for individual OPE derived from the data of measurement was the average concentration. In the current investigation, the median effective concentration ($EC50$) and median lethal concentration ($LC50$) obtained from [30] were used to define the predicted no-effect concentration ($PNEC$). Three trophic levels (fish, algae, and aquatic invertebrates) were taken into consideration for the examination of the RQ values of the OPEs. The following equations were used to determine the RQ values of the OPEs [31]:

$$RQ = MEC / PNEC$$

$$PNEC = EC(L)50 / AF$$

where AF represents an assessment factor of 1000 when short-term toxicity data are used to derive $PNEC$ [30].

The OPEs represented no ecological risk when the RQ was less than 0.01. OPEs exhibited a low risk when $0.01 \leq RQ < 0.10$. OPEs exhibited a moderate risk when $0.10 \leq RQ < 1$. OPEs exhibited a high risk when $RQ \geq 1$ [32].

Since it was uncommon for a sample to contain a single pollutant, the ecotoxicological impact of OPE mixes was evaluated in accordance with the concentration-added effects [33]. The following equations were used to determine the RQ values of the mixtures:

$$RQ_{mix,algae} = \sum_{i=1}^n \frac{MEC_i}{EC(L)50_{i,algae}} \times AF$$

$$RQ_{mix,aquatic\ invertebrate} = \sum_{i=1}^n \frac{MEC_i}{EC(L)50_{i,aquatic\ invertebrate}} \times AF$$

$$RQ_{mix,fish} = \sum_{i=1}^n \frac{MEC_i}{EC(L)50_{i,fish}} \times AF$$

The RQ values of mixes in water samples for fish, algae, and aquatic invertebrates were represented by the $RQ_{mix,fish}$, $RQ_{mix,algae}$, and $RQ_{mix,aquatic\ invertebrates}$, respectively. The compound concentration in the mixed water samples was called the MEC. The median effective (deadly) concentrations of the ingredients in mixed samples of fish, algae, and aquatic invertebrates were $EC(L)50_{i,fish}$, $EC(L)50_{i,algae}$, and $EC(L)50_{i,aquatic\ invertebrates}$, respectively.

Additionally, based on sediment (marine water) PNEC and marine water PNEC from the previous study [30], an ecological risk assessment for the 12 OPEs was also carried out.

2.8. Data Analysis

Statistical analyses of this study were conducted with IBM SPSS Statistics v20. Students' *t*-test was used to assess the variance of the OPE concentrations and partition coefficients at different sampling stations. Principal component analysis (PCA) was used with the software SIMCA 13.0 to investigate possible sources of OPEs.

3. Results and Discussion

3.1. Concentration and Composition of OPEs in the Surface Water

The OPEs detected in surface water from coastal tourist resorts in the Shandong Peninsula are shown in Figure 2, and the concentration information is summarized in Table S9. All target OPEs were detected in surface water, demonstrating their prevalence in an aquatic environment. The aggregate concentrations of the 12 OPEs ranged from 18.52 to 3069.43 ng/L, with an average value of 561.39 ng/L. The majority of the OPEs had a high detection frequency (DF); their DFs were in the range of 26–100%. In all water samples, higher concentrations of Cl-OPEs and alkyl-OPEs were found in comparison to aryl-OPEs. However, the concentration of TPP was much lower. The Σ OPE concentrations in surface water were 3744.68 ng/L (the maximum value was 361.42 ng/L, the minimum value was 48.37 ng/L, and the average value was 197.09 ng/L), 2028.63 ng/L (the maximum value was 210.07 ng/L, the minimum value was 26.38 ng/L, and the average value was 106.77 ng/L), and 693.32 ng/L (the maximum value was 105.34 ng/L, the minimum value was 14.02 ng/L, and the average value was 50.70 ng/L) during the dry, normal, and wet season, respectively.

The concentration range of Cl-OPEs, alkyl-OPEs, and aryl-OPEs during the dry season was 0.94–204.53, 0.13–77.47, and 0.28–10.51 ng/L, respectively. The concentration range of Cl-OPEs, alkyl-OPEs, and aryl-OPEs during the normal season was 0.34–98.66, 0.33–98.66, and 0.10–4.66 ng/L, respectively. The concentration range of Cl-OPEs, alkyl-OPEs, and aryl-OPEs during the wet season was 0.11–66.24, 0.18–26.20, and 0.17–2.16 ng/L, respectively. These results revealed that the levels of all OPEs exhibited obvious seasonal variations, showing the highest level in the dry season and the lowest level in the wet season. Seasonal variations of OPEs in the present study were different from the results observed by a previous study that found organic contaminants in the wet season were generally higher than in other seasons because of rainfall erosion [34]. In this study, the high river flow and the heavy rainfall in the wet season might decrease the concentrations of OPEs in water [21]. The correlation analysis of OPE concentrations in the three seasons is shown in Figure S1. The different compositions and temporal fluctuations of the target OPEs can be seen. However, some compounds, such as TPP and all aryl-OPEs (TPHP, TMPP, BDP, and RDP), were not detectable in the wet season, which might be led by the water dilution or the solar irradiation degradation in the wet season [35].

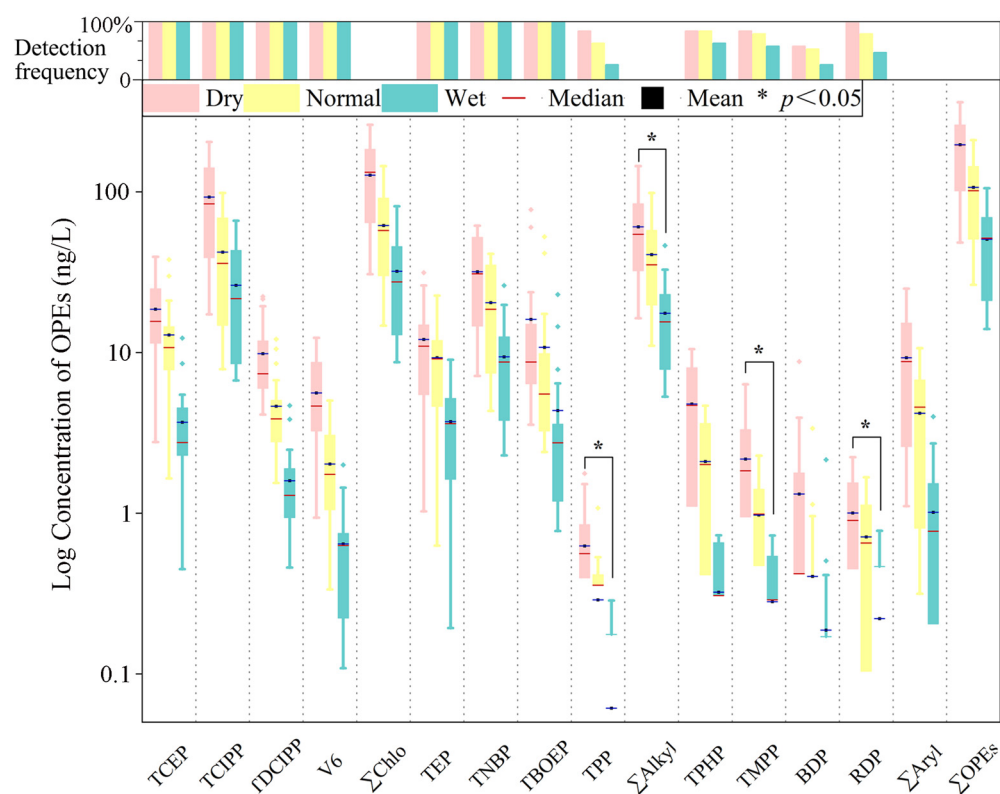


Figure 2. The concentrations of OPEs in surface water from coastal tourist resorts.

The percentage of OPEs varied from season to season. The percentage of target OPEs in surface water for each of the three seasons is shown in Figure 3. Cl-OPEs were the dominant compound in the water samples, while the content of alkyl-OPEs was lower, and the aryl-OPE occurred the least. Cl-OPEs accounted for 64.5%, 57.9%, and 63.4% of the total concentration during the dry, normal and wet seasons, respectively. Likewise, the alkyl-OPEs were accounting for 30.8%, 38.2%, and 34.6%, respectively. Aryl-OPE accounted for 4.7%, 3.9%, and 2.0%, respectively. Therefore, the percentages of the three types of OPEs were ranked as Cl-OPEs > alkyl-OPEs > aryl-OPEs across seasons. These results may have been related to the fact that Cl-OPEs are persistent, with a half-life of 8.6–21.3, with higher water solubility (C_{wsat}) and lower octanol-water partitioning coefficients (K_{ow}). In addition, in the surface water of the Shandong Peninsula, substantial amounts of TCIPP are typically found. This might be related to the fact that TCIPP is widely used in the production of polyurethane foam and polyvinyl chloride (PVC) plastic as an important additive. Moreover, the high water solubility of TCEP (7000 mg/L) and TCIPP (1600 mg/L) might facilitate their migration with runoff and diffusion into surface water.

The average levels of OPEs observed in this study were compared with other regions in the world, such as Asia, Europe, and North America. The OPE concentration in this study was often lower than at the coast near Dalian [36] and the Yellow Sea [37], especially the Northern Yellow Sea [38], and was below the value of the East China Sea [38], Northern South China Sea [38], Pearl River Estuary [39], Greater Bay area [40], Hong Kong [14], Tokyo Bay [14], Thermaikos Gulf [41], Marseille Bay [42], and San Francisco Bay [43]. These results implied that the water in the coastal tourist resorts of the Shandong Peninsula in China contained low levels of OPEs. However, high levels of OPEs or some of their homologs were observed in the water of some resorts. Because coastal tourism resorts have higher requirements for seawater quality, the quality monitoring of the water coming from the surrounding rivers should be strengthened.

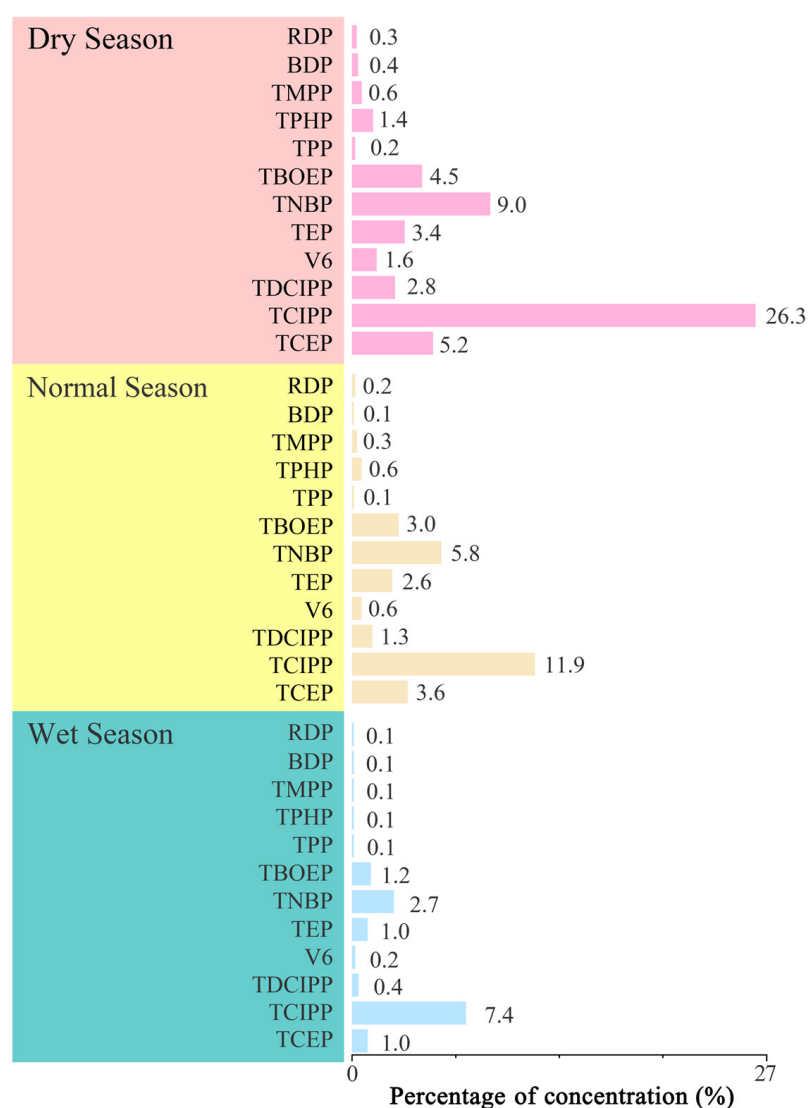


Figure 3. The percentage of OPE concentrations in the surface water during three seasons.

In conclusion, apparent temporal changes in OPEs were found in the seawater of coastal tourist resorts in the Shandong Peninsula. The average concentrations of OPEs were in the order of dry season > normal season > wet season. The average levels of the three types of OPEs were ordered as Cl-OPEs > alkyl-OPEs > aryl-OPEs. TCIPP had the highest level, and TPP exhibited the lowest level.

3.2. Concentrations and Composition of OPEs in Sediment

The concentration and DF of OPEs in sediment from coastal tourist resorts in the Shandong Peninsula are shown in Figure 4, and the concentration information is summarized in Table S10. All the target OPEs, with DF values ranging from 53% to 100%, were discovered in sediments. Individual OPEs for TCEP, TCIPP, TDCIPP, TEP, TNBP, TBOEP, TPP, and RDP had the highest DF (75–100%), followed by TPHP, TMPP, and BDP (60–75%). The DF of V6 was under 55%. In comparison to aryl-OPEs, Cl-OPEs, and alkyl-OPEs were generally found more often. Cl-OPEs accounted for the highest level of OPEs in sediment, at 62.7% of all OPEs, followed by alkyl-OPEs (31.7%) and aryl-OPEs (5.6%). The most prevalent substances in sediment were TCIPP and TEP; together, they accounted for nearly 71% of the Σ OPE concentrations. Compared to alkyl-OPEs and aryl-OPEs, Cl-OPEs were generally more commonly found due to increased usage or in relation to the TOC content and salinity in the sediments of the coastal areas. The Pearson correlation analysis revealed

that TCEP, TEP, TPHP, and TMPP were correlated with TOC ($p \leq 0.05$); V6, TNBP, and TPP were negatively correlated with TOC ($p \leq 0.05$); and the others were not correlated with TOC ($p \geq 0.05$). In addition, we found that TPHP, TMPP, and TDCIPP were significantly correlated with salinity ($p \leq 0.05$), BDP was correlated with salinity but not significantly ($p \leq 0.05$), TCIPP and RDP were negatively correlated with salinity, and the others were not correlated with salinity ($p \geq 0.05$). This suggested that the content of OPEs in the sediment was not significantly influenced by TOC and salinity but mainly by the emission source and their transport in water. The correlation of OPE concentrations in sediment with salinity and TOC is displayed in Figure S2.

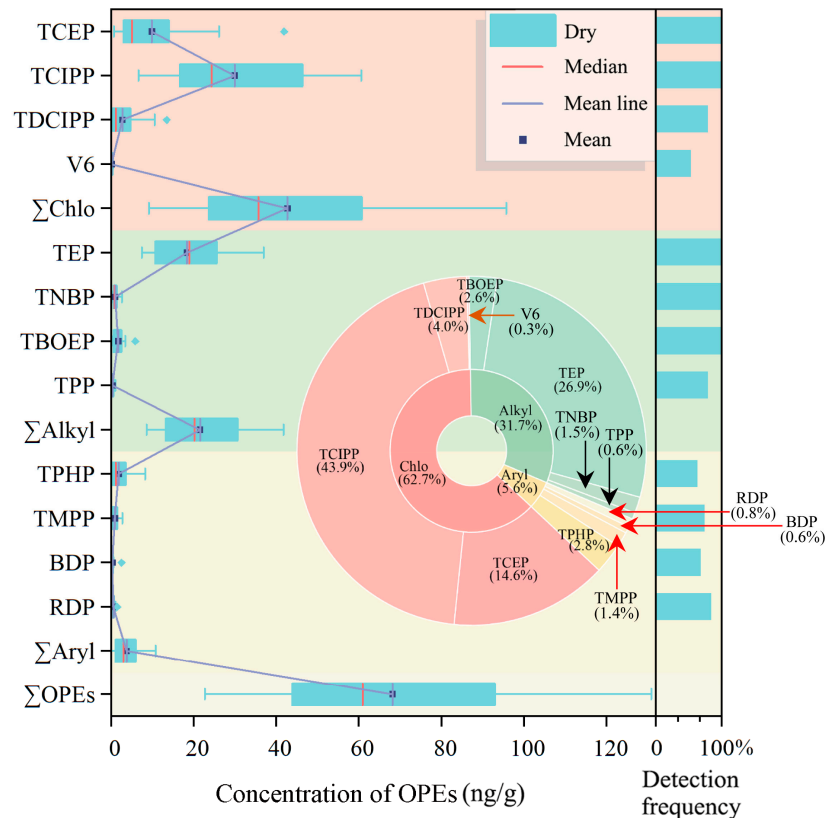


Figure 4. The concentrations of OPEs in sediment from the coastal tourist resorts.

During the dry season, the range of Σ OPE concentration values in sediments from the coastal tourist resorts of the Shandong Peninsula was 3.20–568.76 ng/g, with a median and average of 26.89 ng/g and 107.95 ng/g. TCIPP and TEP had higher average concentrations at 29.93 and 18.36 ng/g, respectively. Other OPEs had mean values less than 10 ng/g. Cl-OPEs levels were the highest among the three types of OPEs, with a mean of 42.78 ng/g. Alkyl-OPE and aryl-OPE were the next highest, with a mean of 21.6 and 3.8 ng/g, respectively. The content of OPEs in the sediment was significantly less than in the water.

Compared with other coastal sediments of Asia, the OPE content of the Shandong Peninsula was lower than that of the Liao River Estuary [44], Yellow River Estuary [45], Jiaozhou Bay [29], Pearl River Delta [46], and Korean coast [47]. The OPE content of this study was higher than the Yellow Sea, except for V6, which at 0.17 ng/g was lower than in the Yellow Sea [48]. On the contrary, the OPE content of this study was lower than the East China Sea, except for TCIPP at 29.93 ng/g [49]. Compared with the coastal sediments of Europe, the OPE content of this study was lower than the Gulf of Lion [50]. The OPE content of this study was lower than in Marseille Bay, except TCIPP at 29.93 ng/g [42]. Compared with the coastal sediments of North America, the OPE content of this study was lower than the Palos Verdes Shelf (PVS), US [51].

In conclusion, the order of the different types of OPE concentrations in the sediment of the Shandong Peninsula coastal tourist resorts from high to low was Cl-OPEs, alkyl-OPEs, and aryl-OPEs, which was the same as the OPE concentrations in surface water. TCIPP levels were the highest, and V6 levels were the lowest.

3.3. Spatial Distribution of OPEs in the Shandong Coastal Tourist Resorts

For OPEs in the water of various vacation resorts across the three seasons, apparent spatial differences were also noted, as shown in Figure 5. For instance, the OPE levels of sites S13, S16, and S17 ranged from more than 325 ng/L during the dry season to around 200 ng/L during the normal season and less than 106 ng/L during the wet season. The highest OPE concentration was recorded at the S16 site in Qingdao, at 361.42, 210.07, and 105.34 ng/L in the dry, normal, and wet seasons, respectively. The major OPE at site S16 was TCIPP, which had concentrations of 204.53, 98.66, and 66.24 ng/L in the dry, normal, and wet seasons, respectively. Site S16 and S17 were located at the entrance to Jiaozhou Bay, near the Yellow Sea. Qingdao, in Shandong Province, is a highly industrialized and urbanized city with a thriving metallurgical industry, shipbuilding industry, print industry, automotive, electroplate industry, battery, and machine manufacturing industry. Jiaozhou Bay is affected by pollution discharges from Qingdao and its surrounding areas, resulting in the high OPE concentrations at these two locations. Therefore, industrial emissions might be the main factor leading to the high level of OPEs at site S16. During the three seasons, Site S10 had the lowest concentration of OPEs. This location is surrounded by natural areas and has a healthy ecological setting. It is far from urban centers and rarely suffers direct damage from industrial pollutants. On the other hand, TCIPP was the predominant OPE at site S10, with concentrations of 17.30, 7.88, and 6.70 ng/L during the dry, normal, and wet seasons, respectively. The concentrations at this site were obviously lower than at other locations. In summary, the levels of OPEs in different water samples of tourism resorts were significantly different. Tourist resorts that were more affected by nearby industrial activities had higher concentrations of OPEs, while those that were farther away from industrial areas had lower concentrations of OPEs. Therefore, residential activities and industrial pollutant emissions from the cities surrounding tourist resorts were the key factors determining OPE concentrations and high pollution levels.

During the dry season, apparent spatial variations for OPEs were also seen in the sediment of several tourist resorts, as shown in Figure 5. For instance, the values of sites S1 and S14–S16 were higher than 100 ng/g during the dry season. Sites S5–S9, S12, and S17 were between 55 ng/g and 100 ng/g, and S2–S4, S10–S11, S13, and S18–S19 were below 55 ng/g. Laizhou Bay is an important bay in Bohai Bay, and its water has poor self-purification ability, resulting in the easy accumulation of OPEs in the coastal sediments. Therefore, the Σ OPE value was high in sediments at site S1. Sites S15 and S16 are in Qingdao, with concentrations of 120.29 and 130.96 ng/g, respectively. Sites S15 and S16 are located on both sides of the entrance to Jiaozhou Bay, which serves as a discharge area for pollutants from Qingdao. Therefore, the highly urbanized and industrialized setting in Qingdao was the major cause of the high values of Σ OPEs in the sediment of S15 and S16. The OPE levels of water at sites S15 and S16 were also higher than other sites. Therefore, the migration of OPEs from water to sediment may also be an important reason for the high concentration of OPEs in sediment. Site S10 is in Weihai, where the concentration was 22.76 ng/g, which was the only value below 30 ng/g. The site is surrounded by natural areas and is ecologically sound. It is removed from urban centers and is hardly ever directly affected by industrial pollutants. The data showed that the concentration in the sediment was basically the same as that in the water. This phenomenon might have been related to the high OPE content in the surface water of the tourist resorts, indicating that the OPE contents in the surface water have a direct impact on the sediment content. The correlation of the OPE concentration in the water and sediment during the dry season is shown in Figure S2.

In conclusion, the highest OPEs in surface water and sediment were detected at S16 in Qingdao. The high levels of OPEs in the coastal water and sediment of Qingdao were related to the degree of urbanization and industrialization. The OPE concentrations of the tourist resorts that were most affected by nearby industry were higher, while the OPE concentrations of the tourist resorts that were far away from the industrial areas were lower. Therefore, the emission of industrial and domestic pollutants from nearby cities was the main factor affecting the content of OPEs near tourist resorts. These findings showed that urban activities have a significant influence on OPE spatial distribution.

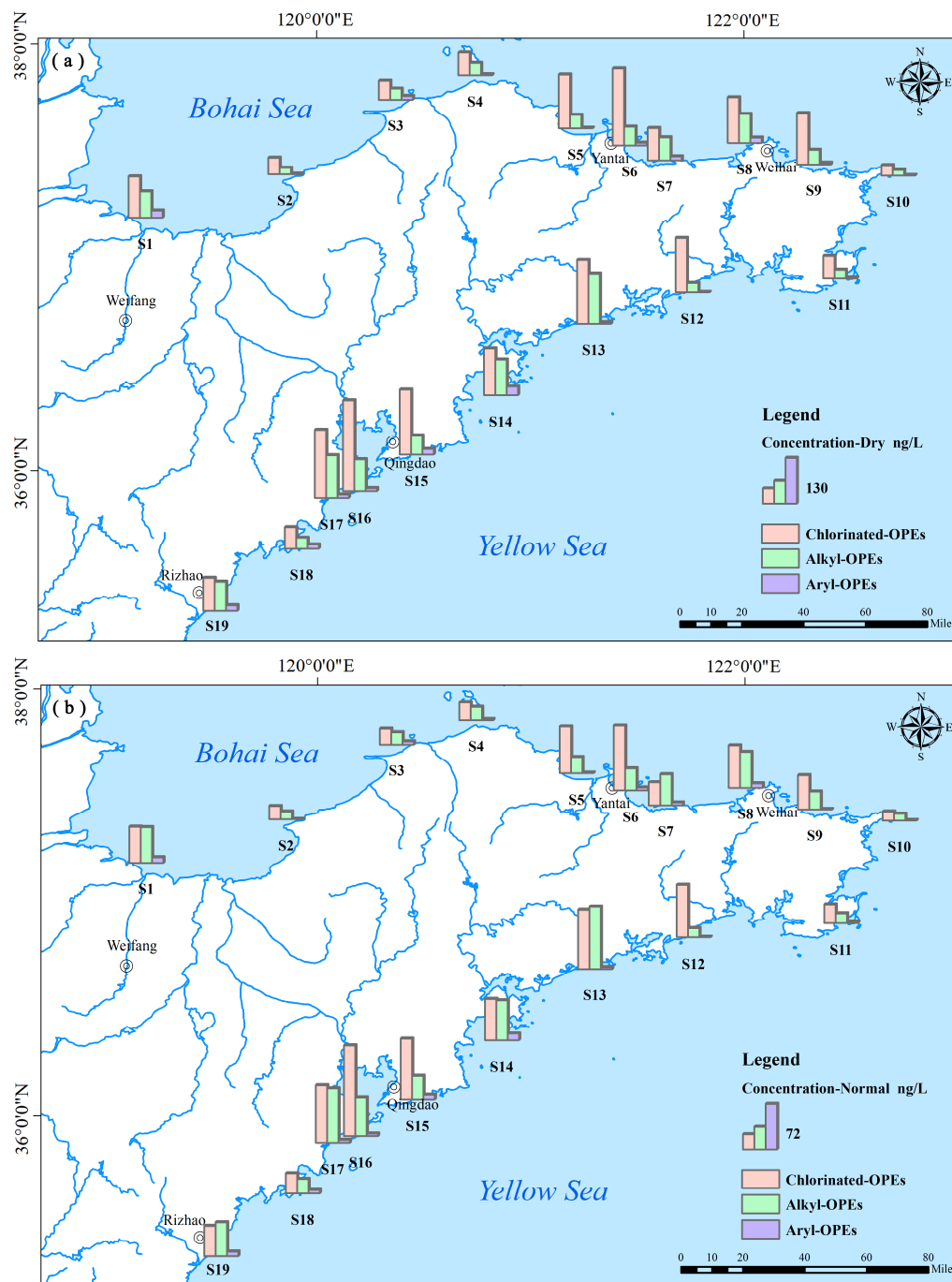


Figure 5. Cont.

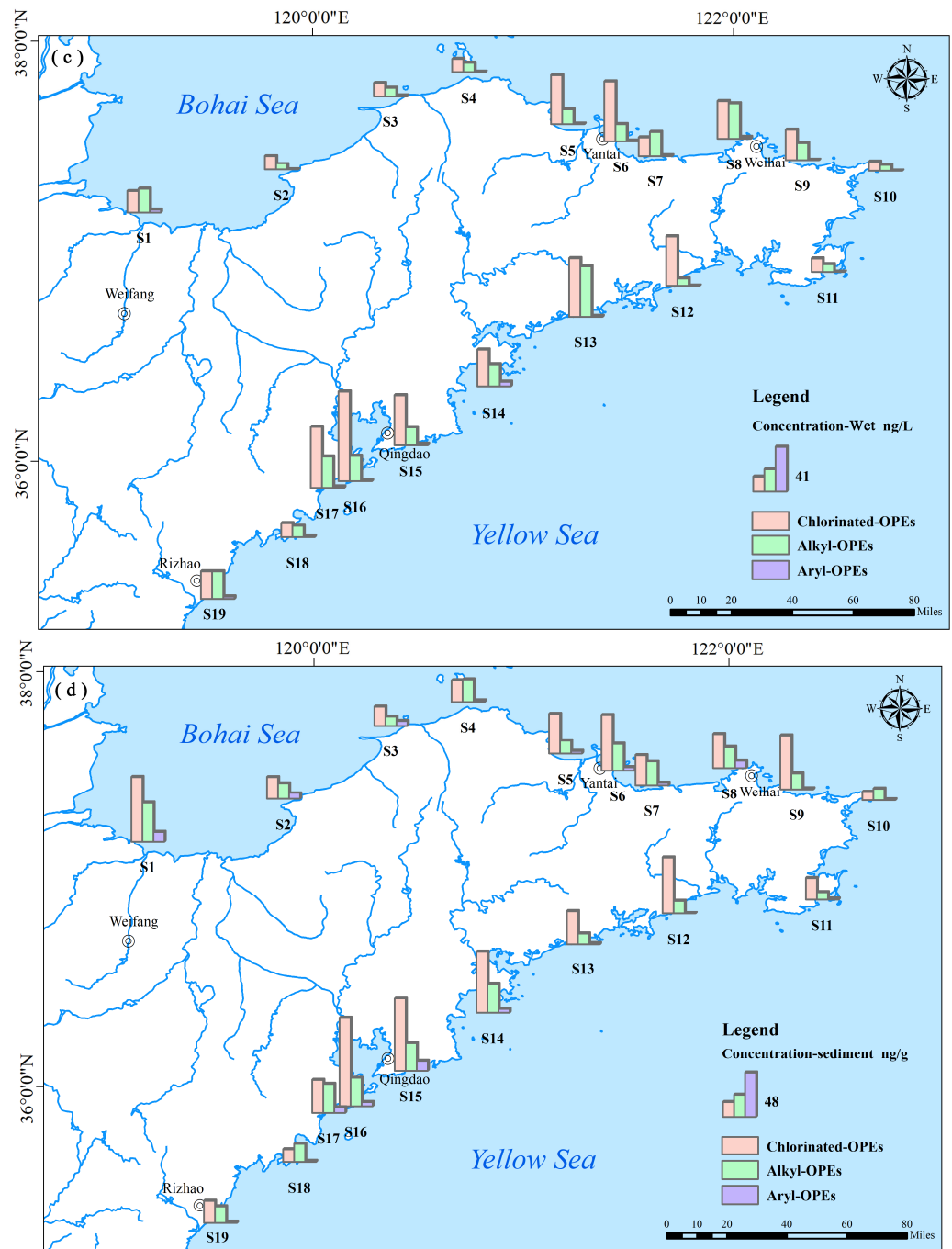


Figure 5. Spatial distribution of the three OPEs in the surface water during the dry season (a), normal season (b), wet season (c), and in the sediment (d).

TCIPP was the primary substance in the sediment of Shandong Peninsula coastal tourist resorts, accounting for 59.37%, 43.90%, and 49.97% of the total concentration of OPEs at sites S14–S16, respectively. TEP was the major substance in the sediment of site S1, accounting for up to 30.31%. The content of TCIPP in the sediments at many points was higher than TEP and was the highest content compound.

In addition, TCIPP and TNBP were predominant in water, accounting for 47.2% and 16.2% in the dry season, 39.6% and 29.8% in the normal season, and 51.7% and 18.6% in the wet season, respectively. There was a high TNBP content in the water samples. This may have been due to the impact of intensive mining activities in coastal cities. TNBP is widely used as an additive in hydraulic oils, lubricants for machinery and equipment, etc. [1].

TCIPP and TEP were predominant in sediment, accounting for 43.91% and 26.93%. TCIPP accounted for up to 59.37%, 43.90%, and 49.97% of the total concentration of OPEs at sites S14–S16, respectively. TEP accounted for up to 30.31% at site S1. A similar trend of regional variation in the water samples revealed that one of the major sources of sediment OPEs was OPE deposition in coastal water.

3.4. Water-Sediment Partitioning of OPEs

The $\text{Log } K_d$ was calculated to assess the behavior of OPEs in partitioning between water and sediment, and the $\text{Log } K_{oc}$ was calculated to evaluate the absorption of OPEs in sediment. The results are displayed in Figure 6. OPEs absorbed by sediments may be resuspended in coastal waters because of environmental disturbance. Therefore, in aquatic environments, OPEs can either be derived from or converge to the sediment. The K_d and K_{oc} of OPEs in the solid/liquid phase were important parameters in terms of their transformation and migration in the environment. In soils with various structures and levels of organic carbon [52], comparing the K_{oc} of various OPEs showed that the adsorption of OPEs can be affected by the amount of soil organic carbon. The correlation of other physical and chemical properties, such as soil organic carbon, with the concentration of OPEs, is shown in Figure S3.

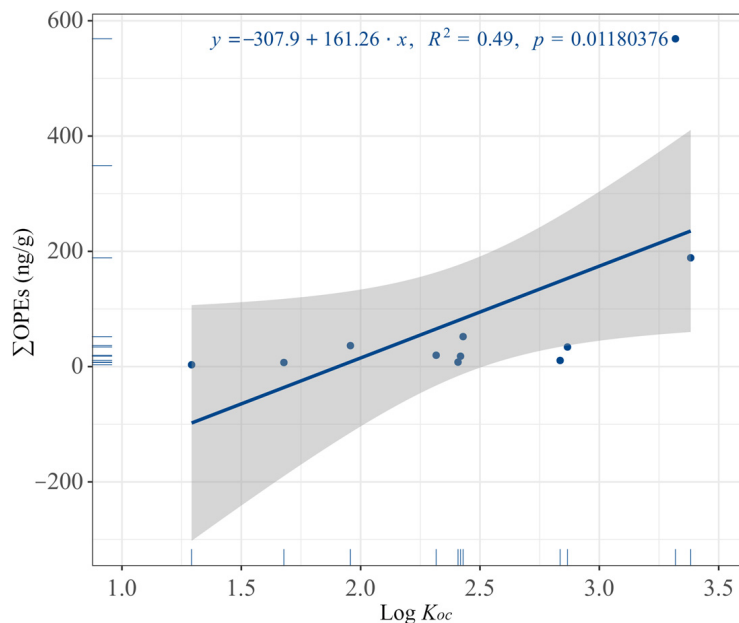


Figure 6. Correlations between ΣOPEs and $\text{Log } K_{oc}$ in the sediment.

The mean value of the $\text{Log } K_d$ of OPEs ranged from 1.53 to 3.25, and the OPE with the highest $\text{Log } K_d$ value was TEP. Except for V6 (1.67) and TBOEP (1.53), the $\text{Log } K_d$ values of the OPEs were all higher than 2.0, indicating that the sediment generally had a strong sorption capacity for these compounds. The strongest sorption capacity was for TEP, and the weakest sorption capacity was for V6 and TBOEP. TEP was absorbed on sediment more readily than other OPEs, and V6 and TBOEP were difficult to absorb on sediment. The mean value of the $\text{Log } K_{oc}$ of OPEs ranged from 1.29 to 4.04. The OPE with the highest $\text{Log } K_{oc}$ value was TEP, and the lowest $\text{Log } K_{oc}$ value was V6. K_{oc} was shown to be inversely correlated with the overall amount of soil organic carbon, indicating that high levels of organic carbon may specifically increase the mobility of certain OPEs in soil [27]. In other words, the K_{oc} value increased with a decreasing TOC value, and the $\text{Log } K_{oc}$ value decreased with an increasing K_{oc} value. For the same OPEs, there was a higher migration rate of sediment OPEs or a lower content in sediment and higher content in water. Thus, TEP was the only type of OPE that was more abundant in sediment than water.

3.5. Source Identification

The PCA of 12 OPEs was determined to indicate potential sources of OPEs in Shandong Peninsula coastal tourist resorts. Two principal components (PCs) were identified, accounting for 71.1% of the overall variance, as displayed in Figure 7a, with PC1 and PC2 obtaining respective weights of 53.8% and 17.3%. Except for TBOEP and TCIPP, all OPEs were close to the *x*-axis between the first and fourth quadrants, which indicated that TBOEP and TCIPP were not similar to the other OPE sources. Large loadings of V6, RDP, TEP, TDCIPP, TPP, TPHP, and BDP were seen in PC1. Previous research showed that TDCIPP and V6 in the environment typically come from discarded furniture and appliances, including building supplies, cotton drapes, and hardwood furniture [45]. Thermoplastics commonly contain TMPP, TPP, and TPHP [53], and electronic recycling factories are the main environmental sources [54]. Considering the above, waste recycling facilities were identified as OPE source 1.

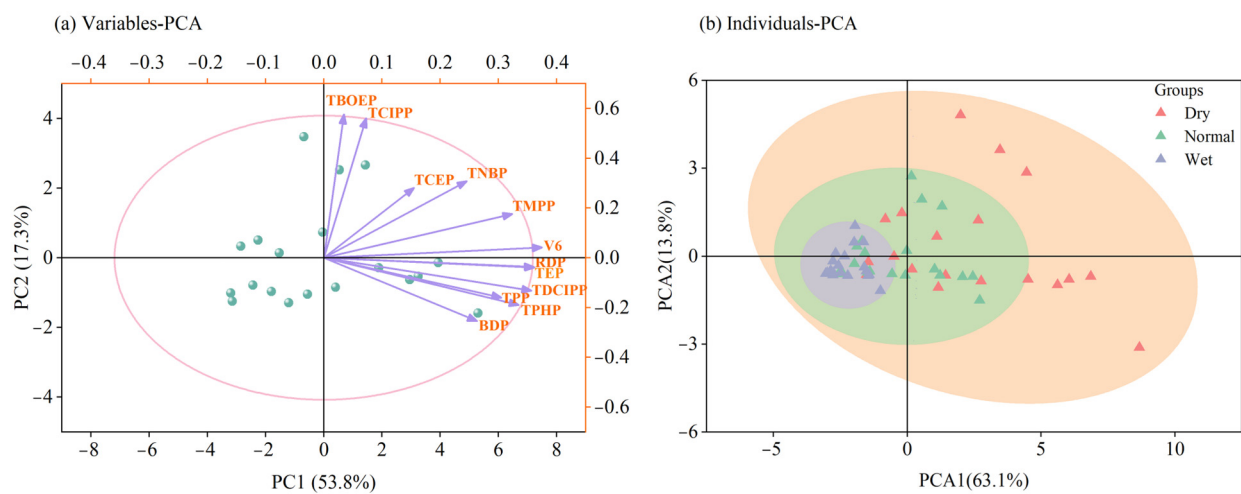


Figure 7. The variables-PCA and individuals-PCA of OPEs during three seasons.

For Cl-OPEs in the water of coastal tourist resorts, source 2 was heavily weighted. TCIPP and TBOEP were of similar origin, and the TCIPP concentration was the highest. The prime source of Cl-OPEs in the aquatic environment was wastewater discharge from sewage treatment plants (STP) due to the lower removal rate of Cl-OPEs [4,6,55]. TBOEP and TNBP, two non-Cl-OPEs, were frequently found in STP effluents [56,57]. Because of the sewage emissions and surface water corrosion, PC1 was identified as a municipal source.

RDP and TEP showed a high association, suggesting the same source. The high TEP levels in this sampling region were in heavy industrial cities like Qingdao. Therefore, it was important to note the release of OPEs from industry in Qingdao. TEP is a common industrial catalyst that contributes significantly to environmental pollution when released from chemical facilities [53]. Numerous coastal tourist resorts are in proximity to industrial cities heavily influenced by the chemical industry. Therefore, source 3 was the chemical industry, and PC2 served as a hub for extensive industries. OPEs in surface water could have originated from a variety of sources, including STP wastewater, waste recycling plants, large-scale chemical industries, textile manufacturing, and plastic processing, after taking all the aforementioned factors into consideration.

As seen in Figure 7b, PC1 and PC2 identified the locations of sampling that had adequate seasonal variation. Two major components were identified, accounting for 79.6% of the total variance, with 63.1% and 13.8% for PC1 and PC2, respectively. The PC1 and PC2 results for the samples gathered during the wet season scored negatively. Most samples collected in the dry and normal seasons scored positively on PC1.

3.6. Ecological Risk Assessment of OPEs

Three trophic-level creatures (fish, algae, and aquatic invertebrates) were chosen to investigate the RQ of mixed and individual OPEs. RQs for 12 OPEs were higher during the dry season than the normal and wet seasons, according to the cluster analysis. Throughout the three seasons, no OPEs presented a moderate or high risk ($RQ \geq 0.1$) to fish, algae, or aquatic invertebrates. The highest RQs for the three trophic levels for individual OPEs were often less than 0.01, demonstrating that there was no ecological risk for individual OPEs. However, compared to other OPEs, TPHP (dry and normal season), TNBP (dry and normal season), and RDP (dry season) posed a comparatively greater danger to these trophic levels, even though the RQs were typically greater than 0.01 and the ecological risk was low. The EC(L)50 values of TPP and RDP for the three trophic levels, TCEP and TNBP for fish and TPHP for algae, were not found, so we did not analyze these items specifically here. In general, the ecological risk of the OPEs tended to be low.

Figure 8 displays the RQ value of OPEs at 19 sites. During the dry season, sites S2 and S10 had no ecological risk, sites S8 and S14 were moderate risk, and the others were low risk. During the normal season, sites S2, S4, S5, S9, S10, and S12 had no ecological risk, and the others were low risk. In the wet season, sites S1, S8, and S14 were low risk, and the others were no risk.

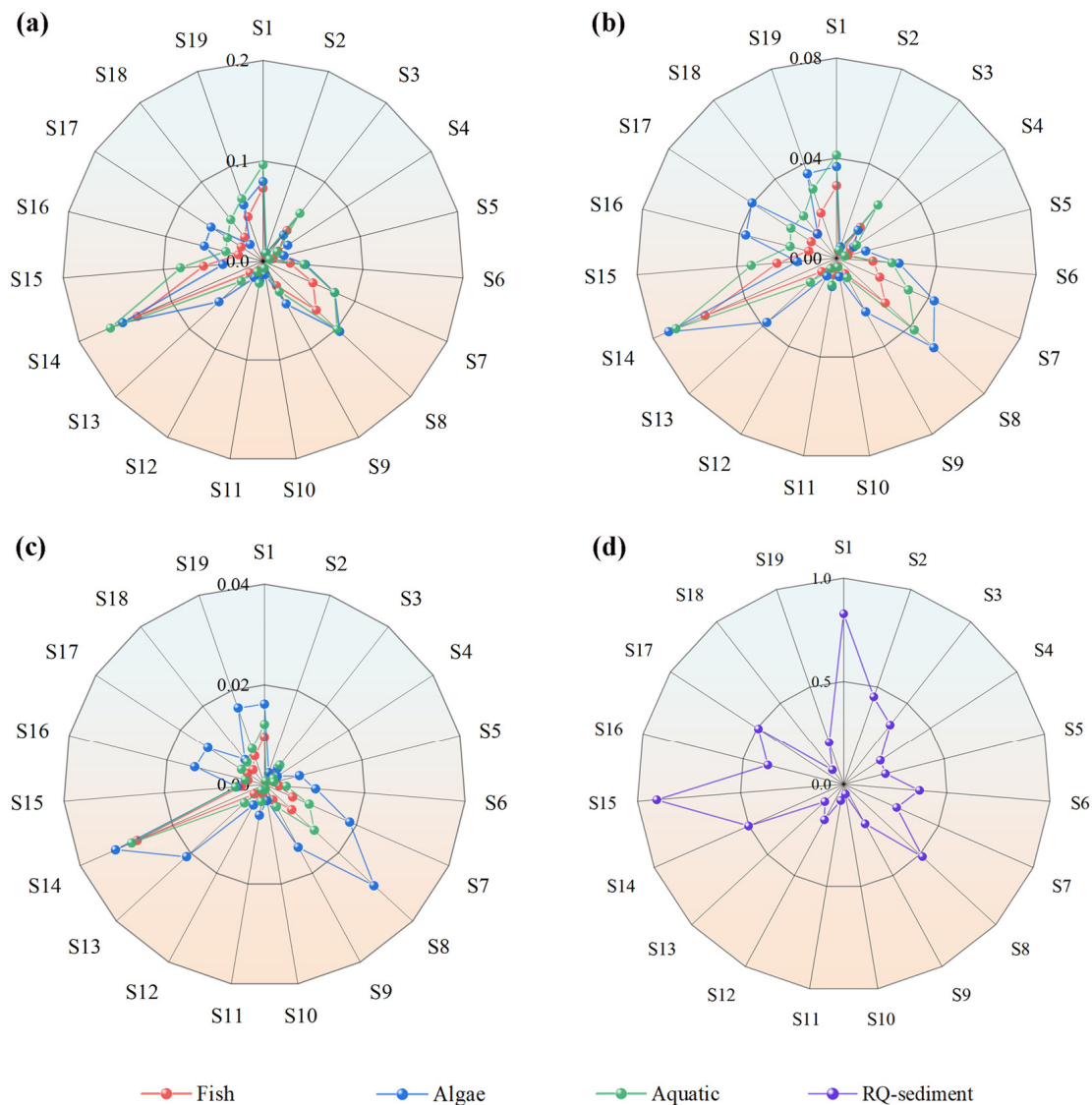


Figure 8. RQ value of OPEs in water at each sampling location during the dry season (a), normal season (b), wet season (c), and in sediment (d).

Another approach to ecological risk assessment was used in this study: direct calculation of RQ values based on the marine water PNEC [30]. The analysis revealed that all OPEs posed no ecological risk during the three seasons, except TDCIPP, TPHP, and BDP. TDCIPP had moderate ecological risk during the dry and normal seasons and low ecological risk during the wet season. TPHP had low ecological risk during the dry and normal seasons and no ecological risk during the wet season. BDP was a high ecological risk during the dry season and a medium risk during the normal and wet seasons. The values of marine water PNEC for TCEP, TPP, and RDP during the three seasons were not found, so we did not analyze these items here. In general, the target OPEs posed no ecological risk. The outcome of this analysis method was consistent with the aforementioned analytical results, based on EC(L)50 values for the three trophic levels (fish, algae, and aquatic invertebrates).

For sediment, TCIPP and TPHP showed moderate risk, and the rest of the substances were moderate or low risk. The NCEP of TCEP, TPP, and RDP were not found, so their ecological risk level in sediment was not analyzed here. In terms of sites, the RQ values were between 0.1 and 1, except for S10, S11, and S18, where the RQ values were between 0.01 and 0.1, indicating that only three sites were at low ecological risk, while the others were at moderate ecological risk.

4. Conclusions

This study is the first to investigate the spatiotemporal variations, partition characteristics, potential sources, and ecological risk of OPEs in the water and sediment of coastal tourist resorts in China. The results indicate that OPEs were widespread in the water and sediment of coastal tourist resorts. Cl-OPEs were the dominant type, and TCIPP was dominant in both the water and sediment. The water exhibited the highest concentrations of Σ OPEs during the dry season. Therefore, tourism activities in coastal tourist resorts should not be carried out during the dry season. Higher concentrations of Σ OPEs were observed in the study areas with denser populations and developed industry/agriculture, implying that human activities had influenced their spatial distribution. The LogK_{ow} of OPEs might have an important impact on the partition between water and sediment via the adsorption process. The PCA results verified that STP effluent may be an important source of OPEs in the water and sediment of coastal tourist resorts. The results show that OPEs presented a generally low degree of risk in the water of coastal tourist resorts of the Shandong Peninsula. Nevertheless, higher concentrations of OPEs in the water and sediment of some coastal tourist resorts were detected. Therefore, it is necessary to strengthen the environmental management of coastal tourist resorts in the future, as tourism demands high environmental quality. For example, a real-time monitoring system for water quality in tourist resorts should be established, and the water quality management of surrounding sewage plants and rivers entering the sea should be strengthened. Since the current sewage treatment technology of STPs pays little attention to the removal of organic pollutants, future studies should consider this.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15223976/s1>, Table S1. List of the coastal tourist resorts in Shandong Province; Table S2. Sampling coordinates about surface water during the dry, normal, and wet seasons from coastal tourist resorts of Shandong Peninsula; Table S3. The name, abbreviation and properties of the most common in the present study; Table S4. The application of organophosphate esters (OPEs); Table S5. Optimized MS/MS parameters for the targeted OPEs and their surrogate standards in the MRM mode; Table S6. Some characteristics of the water and sediment; Table S7. The recoveries and concentrations of targeted OPEs in blanks; Table S8. Coefficient of association, recovery, method limit of detections (LOD) and method limit of quantifications (LOQ) of the target OPEs; Table S9. Concentration range and the detection frequencies of each OPE in the water during the dry, normal and wet season (ng/L); Table S10. Concentration range and the detection frequencies of each OPE in the sediment during the dry season (ng/g); Figure S1. Correlation of OPEs concentration in surface water between three seasons; Figure S2. Correlation of OPEs concentration in water and sediment during dry season and correlation of OPEs concentration in sediment with salinity

and TOC; Figure S3. Correlation between the concentration of OPEs in water and sediment and their physical and chemical properties.

Author Contributions: X.C., conceptualization, methodology, software, and writing—original draft; B.W., methodology, software, and investigation; X.L., software and investigation; J.C., conceptualization, methodology, and investigation; S.W., methodology, writing—review and editing, and supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the Project of the Natural Science Foundation of Shandong Province, China (No. ZR2023DM032) and the China Postdoctoral Science Foundation (No. 2013M540103).

Data Availability Statement: All data will be made available on request.

Acknowledgments: We are very grateful to Qufu Normal University for providing us with the necessary experimental conditions and environment.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ye, L.J.; Li, J.H.; Gong, S.; Herczegh, S.M.; Zhang, Q.; Letcher, R.J.; Su, G.Y. Established and emerging organophosphate esters (OPEs) and the expansion of an environmental contamination issue: A review and future directions. *J. Hazard. Mater.* **2023**, *459*, 132095. [[CrossRef](#)] [[PubMed](#)]
2. Greaves, A.K.; Letcher, R.J. A Review of Organophosphate Esters in the Environment from Biological Effects to Distribution and Fate. *B Environ. Contam. Tox.* **2017**, *98*, 2–7. [[CrossRef](#)] [[PubMed](#)]
3. Hou, M.; Shi, Y.; Na, G.; Cai, Y. A review of organophosphate esters in indoor dust, air, hand wipes and silicone wristbands: Implications for human exposure. *Environ. Int.* **2021**, *146*, 106261. [[CrossRef](#)] [[PubMed](#)]
4. Wei, G.-L.; Li, D.-Q.; Zhuo, M.-N.; Liao, Y.-S.; Xie, Z.-Y.; Guo, T.-L.; Li, J.-J.; Zhang, S.-Y.; Liang, Z.-Q. Organophosphorus flame retardants and plasticizers: Sources, occurrence, toxicity and human exposure. *Environ. Pollut.* **2015**, *196*, 29–46. [[CrossRef](#)]
5. Li, J.; Xie, Z.; Mi, W.; Lai, S.; Tian, C.; Emeis, K.-C.; Ebinghaus, R. Organophosphate Esters in Air, Snow, and Seawater in the North Atlantic and the Arctic. *Environ. Sci. Technol.* **2017**, *51*, 6887–6896. [[CrossRef](#)]
6. Chen, M.-H.; Ma, W.-L. A review on the occurrence of organophosphate flame retardants in the aquatic environment in China and implications for risk assessment. *Sci. Total Environ.* **2021**, *783*, 147064. [[CrossRef](#)]
7. Qi, Y.; Yao, Z.; Ma, X.; Ding, X.; Shangguan, K.; Zhang, M.; Xu, N. Ecological risk assessment for organophosphate esters in the surface water from the Bohai Sea of China using multimodal species sensitivity distributions. *Sci. Total Environ.* **2022**, *820*, 153172. [[CrossRef](#)]
8. Liao, C.; Kim, U.-J.; Kannan, K. Occurrence and distribution of organophosphate esters in sediment from northern Chinese coastal waters. *Sci. Total Environ.* **2020**, *704*, 135328. [[CrossRef](#)]
9. Han, B.; Chen, L.; Li, Y.; Yu, L.; Zhang, J.; Tao, S.; Liu, W. Spatial distribution and risk assessment of 11 organophosphate flame retardants in soils from different regions of agricultural farmlands in mainland China. *Sci. Total Environ.* **2022**, *842*, 156806. [[CrossRef](#)]
10. Pantelaki, I.; Voutsas, D. Occurrence, analysis and risk assessment of organophosphate esters (OPEs) in biota: A review. *Mar. Pollut. Bull.* **2020**, *160*, 111547. [[CrossRef](#)]
11. Du, J.; Li, H.; Xu, S.; Zhou, Q.; Jin, M.; Tang, J. A review of organophosphorus flame retardants (OPFRs): Occurrence, bioaccumulation, toxicity, and organism exposure. *Environ. Sci. Pollut. Res.* **2019**, *26*, 22126–22136. [[CrossRef](#)] [[PubMed](#)]
12. Li, Z.; Zhu, Y.; Wang, D.; Zhang, X.; Jones, K.C.; Ma, J.; Wang, P.; Yang, R.; Li, Y.; Pei, Z.; et al. Modeling of Flame Retardants in Typical Urban Indoor Environments in China during 2010–2030: Influence of Policy and Decoration and Implications for Human Exposure. *Environ. Sci. Technol.* **2021**, *55*, 11745–11755. [[CrossRef](#)] [[PubMed](#)]
13. Yan, Z.F.; Feng, C.L.; Jin, X.W.; Qiao, Y.; Wang, J.D.; Huang, N.N.; Bai, Y.C. Unbalanced Pollution and Ecological Risk of Organophosphate Esters in Chinese Surface Water and Land Use Under Multiple Driving Factors. *Rev. Environ. Contam. T* **2023**, *261*, 18. [[CrossRef](#)]
14. Lai, N.L.S.; Kwok, K.Y.; Wang, X.; Yamashita, N.; Liu, G.; Leung, K.M.Y.; Lam, P.K.S.; Lam, J.C.W. Assessment of organophosphorus flame retardants and plasticizers in aquatic environments of China (Pearl River Delta, South China Sea, Yellow River Estuary) and Japan (Tokyo Bay). *J. Hazard. Mater.* **2019**, *371*, 288–294. [[CrossRef](#)] [[PubMed](#)]
15. Wang, X.; Zhu, L.; Zhong, W.; Yang, L. Partition and source identification of organophosphate esters in the water and sediment of Taihu Lake, China. *J. Hazard Mater.* **2018**, *360*, 43–50. [[CrossRef](#)] [[PubMed](#)]
16. Wolschke, H.; Sühling, R.; Massei, R.; Tang, J.R. Ebinghaus, Regional variations of organophosphorus flame retardants—Fingerprint of large river basin estuaries/deltas in Europe compared with China. *Environ. Pollut.* **2018**, *236*, 391–395. [[CrossRef](#)]
17. Cao, D.; Guo, J.; Wang, Y.; Li, Z.; Liang, K.; Corcoran, M.B.; Hosseini, S.; Bonina, S.M.C.; Rockne, K.J.; Sturchio, N.C.; et al. Organophosphate Esters in Sediment of the Great Lakes. *Environ. Sci. Technol.* **2017**, *51*, 1441–1449. [[CrossRef](#)]
18. Xing, R.G.; Zhang, P.; Zheng, N.; Ji, H.; Shi, B.; Ge, L.K.; Ma, H.R. Organophosphate esters in the seawater of the Bohai Sea: Environmental occurrence, sources and ecological risks. *Mar. Pollut. Bull.* **2023**, *191*, 114883. [[CrossRef](#)]

19. Shi, B.; Wang, T.; Yang, H.; Zhou, Y.; Yang, L.; Yoon, S.; Kim, T.; Khim, J. Perfluoroalkyl acids in rapidly developing coastal areas of China and South Korea: Spatiotemporal variation and source apportionment. *Sci. Total Environ.* **2021**, *761*, 143297. [CrossRef]
20. Li, W.; Yuan, Y.; Wang, S.; Liu, X. Occurrence, spatiotemporal variation, and ecological risks of organophosphate esters in the water and sediment of the middle and lower streams of the Yellow River and its important tributaries. *J. Hazard. Mater.* **2023**, *443*, 130153. [CrossRef]
21. Lian, M.; Lin, C.; Wu, T.; Xin, M.; Gu, X.; Lu, S.; Cao, Y.; Wang, B.; Ouyang, W.; Liu, X.; et al. Occurrence, spatiotemporal distribution, and ecological risks of organophosphate esters in the water of the Yellow River to the Laizhou Bay, Bohai Sea. *Sci. Total Environ.* **2021**, *787*, 147528. [CrossRef] [PubMed]
22. Qi, Y.; He, Z.; Yuan, J.; Ma, X.; Du, J.; Yao, Z.; Wang, W. Comprehensive evaluation of organophosphate ester contamination in surface water and sediment of the Bohai Sea, China. *Mar. Pollut. Bull.* **2021**, *163*, 112013. [CrossRef] [PubMed]
23. Luo, Q.; Wang, S.; Sun, L.; Wang, H. Simultaneous accelerated solvent extraction and purification for the determination of 13 organophosphate esters in soils by gas chromatography-tandem mass spectrometry. *Environ. Sci. Pollut. Res.* **2018**, *25*, 19546–19554. [CrossRef] [PubMed]
24. Luo, Q.; Gu, L.; Wu, Z.; Shan, Y.; Wang, H.; Sun, L. Distribution, source apportionment and ecological risks of organophosphate esters in surface sediments from the Liao River, Northeast China. *Chemosphere* **2020**, *250*, 126297. [CrossRef]
25. Shrivastava, A.; Gupta, V. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chron. Young Sci.* **2011**, *2*, 21. [CrossRef]
26. Zhao, Z.; Gong, X.; Zhang, L.; Jin, M.; Cai, Y.; Wang, X. Riverine transport and water-sediment exchange of polycyclic aromatic hydrocarbons (PAHs) along the middle-lower Yangtze River, China. *J. Hazard. Mater.* **2021**, *403*, 123973. [CrossRef]
27. Kim, S.; Carlson, K. Temporal and Spatial Trends in the Occurrence of Human and Veterinary Antibiotics in Aqueous and River Sediment Matrices. *Environ. Sci. Technol.* **2007**, *41*, 50–57. [CrossRef]
28. Chen, Z.; An, C.; Elektorowicz, M.; Tian, X. Sources, behaviors, transformations, and environmental risks of organophosphate esters in the coastal environment: A review. *Mar. Pollut. Bull.* **2022**, *180*, 113779. [CrossRef]
29. Wu, T.; Mao, L.; Liu, X.; Wang, B.; Lin, C.; Xin, M.; He, M.; Ouyang, W. Seasonal occurrence, allocation and ecological risk of organophosphate esters in a typical urbanized semi-closed bay. *Environ. Pollut.* **2021**, *290*, 118074. [CrossRef]
30. Homepage—ECHA. Available online: <https://echa.europa.eu> (accessed on 25 March 2023).
31. Liu, Y.; Song, N.; Guo, R.; Xu, H.; Zhang, Q.; Han, Z.; Feng, M.; Li, D.; Zhang, S.; Chen, J. Occurrence and partitioning behavior of organophosphate esters in surface water and sediment of a shallow Chinese freshwater lake (Taihu Lake): Implication for eco-toxicity risk. *Chemosphere* **2018**, *202*, 255–263. [CrossRef]
32. Wang, X.; Zhu, Q.; Yan, X.; Wang, Y.; Liao, C.; Jiang, G. A review of organophosphate flame retardants and plasticizers in the environment: Analysis, occurrence and risk assessment. *Sci. Total Environ.* **2020**, *731*, 139071. [CrossRef] [PubMed]
33. Backhaus, T.; Faust, M. Predictive Environmental Risk Assessment of Chemical Mixtures: A Conceptual Framework. *Environ. Sci. Technol.* **2012**, *46*, 2564–2573. [CrossRef] [PubMed]
34. Struger, J.; Grabuski, J.; Cagampan, S.; Sverko, E.; McGoldrick, D.; Marvinm, C.H. Factors influencing the occurrence and distribution of neonicotinoid insecticides in surface waters of southern Ontario, Canada. *Chemosphere* **2017**, *169*, 516–523. [CrossRef] [PubMed]
35. Xu, L.; Zhang, B.; Hu, Q.P.; Liu, Y.; Shang, T.; Zeng, X.Y.; Yu, Z.Q. Occurrence and spatio-seasonal distribution of organophosphate tri- and di-esters in surface water from Dongting Lake and their potential biological risk. *Environ. Pollut.* **2021**, *282*, 1170313. [CrossRef]
36. Zhang, L.; Wang, Y.; Tan, F.; Yang, Y.; Wu, X.; Wang, W.; Liu, D. Tidal variability of polycyclic aromatic hydrocarbons and organophosphate esters in the coastal seawater of Dalian, China. *Sci. Total Environ.* **2020**, *708*, 134441. [CrossRef]
37. Zhong, M.; Tang, J.; Guo, X.; Guo, C.; Li, F.; Wu, H. Occurrence and spatial distribution of organophosphorus flame retardants and plasticizers in the Bohai, Yellow and East China seas. *Sci. Total Environ.* **2020**, *741*, 140434. [CrossRef]
38. Zheng, H.; Cai, M.; Yang, C.; Gao, Y.; Chen, Z.; Liu, Y. Terrigenous export and ocean currents' diffusion of organophosphorus flame retardants along China's adjacent seas. *Environ. Pollut.* **2022**, *299*, 118873. [CrossRef]
39. Shi, Y.; Zhang, Y.; Du, Y.; Kong, D.; Wu, Q.; Hong, Y.; Wang, Y.; Tam, N.F.Y.; Leung, J.Y.S. Occurrence, composition and biological risk of organophosphate esters (OPEs) in water of the Pearl River Estuary, South China. *Environ. Sci. Pollut. Res.* **2020**, *27*, 14852–14862. [CrossRef]
40. Gao, X.; Lin, Y.; Li, J.; Xu, Y.; Qian, Z.; Lin, W. Spatial pattern analysis reveals multiple sources of organophosphorus flame retardants in coastal waters. *J. Hazard. Mater.* **2021**, *417*, 125882. [CrossRef]
41. Pantelaki, I.; Voutsas, D. Organophosphate esters in inland and coastal waters in northern Greece. *Sci. Total Environ.* **2021**, *800*, 149544. [CrossRef]
42. Schmidt, N.; Castro-Jiménez, J.; Oursel, B.; Sempéré, R. Phthalates and organophosphate esters in surface water, sediments and zooplankton of the NW Mediterranean Sea: Exploring links with microplastic abundance and accumulation in the marine food web. *Environ. Pollut.* **2021**, *272*, 115970. [CrossRef]
43. Shimabuku, I.; Chen, D.; Wu, Y.; Miller, E.; Sun, J.; Sutton, R. Occurrence and risk assessment of organophosphate esters and bisphenols in San Francisco Bay, California, USA. *Sci. Total Environ.* **2022**, *813*, 152287. [CrossRef]

44. Luo, Q.; Wu, Z.; Wang, C.; Gu, L.; Li, Y.; Wang, H. Seasonal variation, source identification, and risk assessment of organophosphate ester flame retardants and plasticizers in surficial sediments from Liao River estuary wetland, China. *Mar. Pollut. Bull.* **2021**, *173*, 112947. [[CrossRef](#)] [[PubMed](#)]
45. Wang, Y.; Wu, X.; Zhang, Q.; Hou, M.; Zhao, H.; Xie, Q.; Du, J.; Chen, J. Organophosphate esters in sediment cores from coastal Laizhou Bay of the Bohai Sea, China. *Sci. Total Environ.* **2017**, *607–608*, 103–108. [[CrossRef](#)]
46. Tan, X.-X.; Luo, X.-J.; Zheng, X.-B.; Li, Z.-R.; Sun, R.-X.; Mai, B.-X. Distribution of organophosphorus flame retardants in sediments from the Pearl River Delta in South China. *Sci. Total Environ.* **2016**, *544*, 77–84. [[CrossRef](#)] [[PubMed](#)]
47. Choi, W.; Lee, S.; Lee, H.-K.; Moon, H.-B. Organophosphate flame retardants and plasticizers in sediment and bivalves along the Korean coast: Occurrence, geographical distribution, and a potential for bioaccumulation. *Mar. Pollut. Bull.* **2020**, *156*, 111275. [[CrossRef](#)] [[PubMed](#)]
48. Zhong, M.; Wu, H.; Mi, W.; Li, F.; Ji, C.; Ebinghaus, R.; Tang, J.; Xie, Z. Occurrences and distribution characteristics of organophosphate ester flame retardants and plasticizers in the sediments of the Bohai and Yellow Seas, China. *Sci. Total Environ.* **2018**, *615*, 1305–1311. [[CrossRef](#)]
49. Fan, Q.; Zou, X.; Gao, J.; Cheng, Y.; Wang, C.; Feng, Z.; Ding, Y.; Zhang, C. Assessing ecological risk of organophosphate esters released from sediment with both of total content and desorbable content. *Sci. Total Environ.* **2021**, *772*, 144907. [[CrossRef](#)]
50. Alkan, N.; Alkan, A.; Castro-Jiménez, J.; Royer, F.; Papillon, L.; Ourgaud, M.; Sempéré, R. Environmental occurrence of phthalate and organophosphate esters in sediments across the Gulf of Lion (NW Mediterranean Sea). *Sci. Total Environ.* **2021**, *760*, 143412. [[CrossRef](#)]
51. Kim, U.-J.; Oh, J.K.; Kannan, K. Occurrence, Removal, and Environmental Emission of Organophosphate Flame Retardants/Plasticizers in a Wastewater Treatment Plant in New York State. *Environ. Sci. Technol.* **2017**, *51*, 7872–7880. [[CrossRef](#)]
52. Cristale, J.; Dantas, R.F.; De Luca, A.; Sans, C.; Esplugas, S.; Lacorte, S. Role of oxygen and DOM in sunlight induced photodegradation of organophosphorous flame retardants in river water. *J. Hazard. Mater.* **2017**, *323*, 242–249. [[CrossRef](#)] [[PubMed](#)]
53. Verbruggen, E.M.J.; Rila, J.P.; Traas, T.P.; Posthuma-Doodeman, C.J.A.M.; Posthumus, R. Environmental Risk Limits for Several Phosphate Esters, with Possible Application as Flame Retardant. Rijksinstituut voor Volksgezondheid en Milieu RIVM. 2006. Available online: <https://rivm.openrepository.com/handle/10029/255802> (accessed on 29 March 2023).
54. Matsukami, H.; Tue, N.M.; Suzuki, G.; Someya, M.; Tuyen, L.H.; Viet, P.H.; Takahashi, S.; Tanabe, S.; Takigami, H. Flame retardant emission from e-waste recycling operation in northern Vietnam: Environmental occurrence of emerging organophosphorus esters used as alternatives for PBDEs. *Sci. Total Environ.* **2015**, *514*, 492–499. [[CrossRef](#)] [[PubMed](#)]
55. Liang, K.; Liu, J. Understanding the distribution, degradation and fate of organophosphate esters in an advanced municipal sewage treatment plant based on mass flow and mass balance analysis. *Sci. Total Environ.* **2016**, *544*, 262–270. [[CrossRef](#)] [[PubMed](#)]
56. Cui, K.; Wen, J.; Zeng, F.; Li, S.; Zhou, X.; Zeng, Z. Occurrence and distribution of organophosphate esters in urban soils of the subtropical city, Guangzhou, China. *Chemosphere* **2017**, *175*, 514–520. [[CrossRef](#)]
57. Meyer, J.; Bester, K. Organophosphate flame retardants and plasticisers in wastewater treatment plants. *J. Environ. Monit.* **2004**, *6*, 599–605. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.