Determination and environmental risk assessment of organophosphorus flame retardants in sediments of the South China Sea

Xin Pan · Aifeng Liu · Minggang Zheng · Jianxin Liu · Ming Du · Ling Wang

Abstract
As ubiquitous contaminants in the environment, organophosphorus flame retardants (OPFRs) would eventually settle in marine sediment. In this study, concentrations, spatial distributions, and ecological risks of seven OPFRs in sediment samples of the South China Sea (SCS) were investigated for the first time. Total concentration of all OPFRs ranged from 2.5 to 32.3 ng/g dry weight (dw), in which the abundance of tri-cresyl phosphates (TCPs) was the highest. OPFRs in the SCS were at a medium level compared with those from other parts of the world. The nearshore ocean current, ship transportation, and riverine inputs might influence the spatial distributions of OPFRs. The total inventory of six OPFRs in sediment was estimated to be 202.8 tons (16.7×10⁴ km²). The hazard quotient (HQ) of OPFRs ranged from 0 to 3.2E−02, indicating the ignorable ecological risk of OPFRs in sediments of the SCS. This study provides insight into the occurrence of current-use OPFRs in the SCS which deserved long-term concern in the future due to their continuous terrigenous inputs.

Keywords Organic phosphate · Spatial distribution · Mass inventory · Coastal sea of China · Hazard quotient

Introduction
As substitutes for polybrominated diphenyl ethers (PBDEs), organophosphorus flame retardants (OPFRs) are used as artificial industrial additives in flame retardants and plasticizers (He et al. 2019; Mo et al. 2019). Global demand for OPFRs has an annual increasing rate of 4.6% over the past decade and these are used worldwide (Lee et al. 2018). The global output of OPFRs has increased from 1.98×10⁵ tons per year in 2007 to 2.92×10⁵ tons per year in 2011 (Liang and Liu 2016) and reached about 3.00×10⁶ tons per year in 2018 (Zeng et al. 2020). According to their functional groups, OPFRs are classified into halogenated OPFRs and non-halogenated OPFRs. The former are mainly used as flame retardants in textiles, furniture, and electronics (Regnery and Puttmann 2010; Yang et al. 2014), and the latter are used as additives for hydraulic oils, defoamers, and plasticizers (Bollmann et al. 2012; Marklund et al. 2003). Usually, OPFRs are directly mixed with other materials without chemical binding so that they are easily released from the product into the surrounding environment during manufacturing, use, and disposal (Shi et al. 2016; Wang et al. 2019). The World Health Organization (WHO) has proven many adverse health effects of OPFRs, such as neurotoxicity, cytotoxicity, genotoxicity, developmental toxicity, and reproductive toxicity (Hales and Robaire 2020; Hoffman et al. 2017). Tri-o-cresyl phosphate (o-TCP), isomer of tri-cresyl phosphates (TCPs), is a severe nerve agent responsible for neurodegenerative disease called organophosphorus-induced delayed neuropathy (OPIDN) (Ji et al. 2020). Triphenyl phosphate (TPP) causes contact allergic effects and infertility; tris(1,3-dichloro-2-propyl) phosphate

Responsible Editor: Roland Peter Kallenborn

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(TDCPP) is associated with changes in male hormone levels and decreasing of semen quality (Hales and Robaire 2020).

In recent years, sediments have become the main focus of studies assessing OPFRs concentration because they are generally considered to be sinks for OPFRs (Tan et al. 2016). In most of the studies, it was observed that nonchlorinated OPFRs were more abundant in sediments compared to the chlorinated OPFRs (Chokwe et al. 2020). In the sediments of the Bohai Sea and the northern East China Sea, the concentration of OPFRs was as high as 169 ng/g dw, with detection rate ranging from 1.1 to 94.5% (Liao et al. 2020). The sediment concentration of OPFRs (13–49 ng/g dw) in the northwest Mediterranean was slightly lower than that of the Bohai Sea and the northern East China Sea, but seawater concentration of OPFRs was as high as 1012 ng/L, and the detection rates in sediment and seawater were 67–100% and 28–100% for the specific individuals, respectively (Schmidt et al. 2021). The long-distance transport potential of OPFRs has been proven, as nine OPFRs were detected in the range of 0.01–7.4 ng/g dw in sediment samples collected at Ny-Alesund, the Arctic (Gao et al. 2020). OPFRs in the ocean could accumulate (Du et al. 2019) and be enriched in organisms (Ding et al. 2020). Due to bioaccumulation, the average concentration of total OPFRs in fish samples in coral reef fish from the South China Sea (SCS) was as high as 40.4±39.7 ng/g dw (Wang et al. 2022). The bioaccumulation and biomagnification properties of OPFRs could cause more serious toxic effects in higher organisms (Du et al. 2019); the OPFRs reserved in the sediment might pose direct exposure to marine organisms, especially the benthos (Bekele et al. 2019).

The SCS is a typical marginal sea of China, with the Pearl River being the largest river entering (Zeng et al. 2018b). The rapid economic development, industrialization, and urbanization along the Pearl River have led to the emission of a large number of OPFRs (Chen et al. 2020). Tributyl phosphate (TBP), TPP, tri-m-cresyl phosphate (m-TCP), and TDCPP are the commonly detected OPFRs in the Pearl River Delta (PRD), which are also chosen as targets in this paper. The concentration of OPFRs in the PRD was as high as 72.6 ng/g dw in sediments with a detection rate of 40–100% (Zeng et al. 2018b). Rivers carry a large amount of land-based water and sediments to the coastal ocean (Gong et al. 2019), constituting the main source of OPFRs in the ocean (Lai et al. 2015). For example, the total concentration of OPFRs homologues in the 40 main rivers entering the Bohai Sea (1549 ng/g dw) was 15 times that of the adjacent ocean (100 ng/g dw), indicating their terrigenous input source (Wang et al. 2015; Zhong et al. 2020). Pollutants entering the sea with the river can undergo sedimentation processes by absorbing onto particles and settling down into marine sediment with the ocean current (Zhong et al. 2018). Seawater OPFRs could be diluted after entering the sea, but the sediments could also act as a secondary source of OPFRs (Liu et al. 2018).

China’s marginal seas are densely populated, economically developed, and greatly affected by human activities. Until now, a large number of OPFRs have been reported in sediments of the East China Sea, the Yellow Sea, and the Bohai Sea (Li et al. 2014; Liao et al. 2020), but the concentration levels, sources, and fates of OPFRs in the SCS are not clear. The OPFRs in Pearl River and PRD were speculated to be direct sources of the SCS, especially for the coastal areas. The purposes of this study are to (1) investigate the concentration levels and distribution characteristics of OPFRs in sediments of the SCS, (2) analyze the source of OPFRs and examine the relationships between individual OPFR congeners, and (3) evaluate the mass inventory and risk levels of OPFRs in sediments of the SCS based on the concentration levels. As there is no report on the occurrence of OPFRs in the SCS at present, the results of this study will provide fundamental data for further understanding of the contamination burdens of OPFRs on the marine environment, their environmental fate, and ecological toxicity.

Material and methods

Chemicals and materials

Reference standards of TBP, TDCPP, TPP, tri (2-butoxyethyl) phosphate (TBEP), o-TCP, m-TCP, and tri-p-cresyl phosphate (p-TCP) were purchased from AccuStandard (New Haven, CT, USA). The basic physicochemical properties of the selected OPFRs are summarized in Table 1.

Dichloromethane, n-hexane (purity > 99%), ethyl acetate, acetone, and acetonitrile were obtained from Merck & Fisher Scientific Co (Germany). Anhydrous sodium sulfate (purity 99%) was backed at 500 °C for 6 h prior to use.

Sample collection

In this study, 15 surface sediment samples (0–5 cm) were collected using a box sampler from the SCS during the cruise from “Xiang Yang Hong 18” in August 2020 (Fig. 1). The maximum depth of the sampling site was 3980 m, and the average depth was 1571 m; two sampling sites were less than 100 m. The exact information about the latitude, longitude, and water depth of the sampling station was listed in Supplementary Table S1. All samples were immediately stored at −20 °C before analysis.

Sample preparation and instrumental analysis

The same pretreatment method for sediments is based on previous studies (Yadav et al. 2018) and well-evaluated...
In brief, sediment samples (5 g) were spiked with 20 ng of d27-TBP, mixed with 15 g anhydrous sodium sulfate, and extracted with 150 mL n-hexane/acetone (1:1; v/v) for 24 h at a flow rate of 5 mL/min using a Soxhlet extractor. After being treated with active copper granules to remove elemental sulfur, the extract was concentrated to 1 mL and solvent-changed to n-hexane for further purification using an ENVI-Florisil SPE column (6 mL, 1 g, Supelco, USA). The column was first washed with 6 mL n-hexane:dichloromethane (8:2; v/v) and then eluted with 20 mL ethyl acetate, which was further concentrated and solvent-changed to 1 mL n-hexane. Finally, 50 pg 13C12-PCB-204 (Wellington Laboratories, Canada) was added as the internal standard.

Target OPFRs were analyzed by an Agilent 7890/5975 GC–MS (Agilent Technologies, Santa Clara, CA, USA) in electron impact (EI) mode (Gustavsson et al. 2017). The injector was operated in the pulsed splitless mode, held at 280 °C. The initial oven temperature was set at 100 °C, held for 3 min, and then increased to 300 °C at 10 °C/min and kept for 3 min. An Agilent DB-5MS capillary column (0.25-mm inner diameter × 0.25-μm film thickness) was used for the analysis of OPFRs. OPFRs were analyzed under selective ion monitoring (SIM) mode, and the SIM ions for each analyte were previously investigated in the literature (Suo et al. 2018).

### Quality control and quality assurance

The blank samples were treated experimentally with each 5 samples, and the concentration of OPFRs in each blank sample was below the detection limit. All experimental results were corrected with surrogate standard (d27-TBP) recoveries. OPFRs standards were analyzed with a good linear range, and the correlation coefficients were larger than 0.999 (R^2 > 0.999). The limit of detection (LOD) and limit of quantification (LOQ) of OPFRs are determined by the signal-to-noise ratios of 3 and 10. LOD and LOQ in sediment samples were in the range of 0.1–0.7 ng/g dw and 0.3–2.1 ng/g dw, respectively. Recovery tests for the targets were in the range of 80.2–95.4%. The precision was intra-/inter-day RSDs: 3.1–5.4%/4.2–6.3%, and the matrix effects were between −8.1 and 12.3%.

### Statistical analysis

A map of the spatial distribution of concentration was drawn using ArcGIS 10.0 (ESRI, USA). The sampling
sites were generated by Ocean Data View (version: 5.3.0). Chemstation Data Analysis software was used to extract OPFRs concentration data, and Excel 2010 and SPSS 23.0 (IBM, USA) were used for further statistical analysis. Spearman correlation analysis was used to study the correlation between OPFRs concentration in sediments. In this study, $p$ values below 0.05 were considered statistically significant.

**Mass inventory**

The mass inventories of OPFRs, $\text{Inventory}_{\text{sediment}}$, in the present sampling area, were calculated by the following equation (Qi et al. 2021):

$$\text{Inventory}_{\text{sediment}} = C_{si} \times \rho_s \times d \times A \quad (1)$$

where $C_{si}$ (ng/g dw) is the average concentration of OPFR homologue $i$ in sediment, $\rho_s$ (1.5 g/cm$^3$) is the dry bulk density of sediment (Li et al. 2015), $d$ (5 cm) is the average sampling depth of sediment, and $A$ ($16.7 \times 10^4$ km$^2$) is the water area of the sampling region in the SCS.

**Risk assessment**

The European Commission’s Technical Guidance Document (TGD) recommended a hazard quotient (HQ) approach to characterize ecological risks (Li et al. 2019). The HQ of the contaminant in sediments is calculated using the following formula:

$$\text{HQ} = \frac{C_{\text{sediment}}}{\text{PNEC}_{\text{sediment}}} \quad (2)$$

where $C_{\text{sediment}}$ (ng/g dw) is the concentration of contaminant in sediment, and $\text{PNEC}_{\text{sediment}}$ (ng/g dw) indicates its predicted no-effect concentration in sediment, derived either from its toxicity data on sediment-dwelling organisms (Fan et al. 2021). The potential risks of OPFR exposure to aquatic organisms are classified into three levels based on the HQ values: low risk ($0.01 \leq \text{HQ} < 0.1$), medium risk ($0.1 \leq \text{HQ} < 1.0$), and high risk ($\text{HQ} \geq 1.0$) (Wang et al. 2020; Zeng et al. 2018a).
Results and discussion

Concentration of OPFRs in sediment and comparison to previous studies

Because of their long carbon chains and high values of log $K_{oc}$, OPFRs show a strong tendency to combine with carbon-rich suspended particles and accumulate in sediments (Net et al. 2015; van der Veen and de Boer 2012). Therefore, determining their concentration and distribution in sediments is essential for a better understanding of their potential impact on seafloor communities and global marine ecosystem function (Alkan et al. 2021). OPFR concentrations in the surface sediments of the SCS are shown in Fig. 2. Apart from TBEP, all six OPFRs were detected in sediment samples, and the total concentrations $\Sigma$OPFRs ranged from 2.5 to 32.3 ng/g dw. TBEP can be photodegraded in natural water or rapidly degraded by microorganisms, thus resulting in its low concentration in sediments (Regnery and Puttmann 2010; Wan et al. 2016). Among all the OPFRs, TDCPP was found at the highest detection rate (73%), followed by $m$-TCP (53%), TBP (53%), TPP (40%), $o$-TCP (27%), and $p$-TCP (20%). The high occurrence rate for most of the selected OPFRs in the samples indicated that they were widespread in the studied area. The concentration range of TDCPP was $<\text{LOD}$–5.6 ng/g dw, and the median concentration of TDCPP was 3 ng/g dw. Although with the highest detection rate, the concentrations of TDCPP were at similarly low levels. Trimethylphenyl phosphate has three isomers; $m$-TCP was $<\text{LOD}$–9.5 ng/g dw, $p$-TCP was $<\text{LOD}$–10.9 ng/g dw, and $o$-TCP was $<\text{LOD}$17.5 ng/g dw, respectively. Concentrations of TCPs were higher than other congeners, especially at SCS11 and SCS13 sites. The intensive fishery and commercial transportation activities could be the main factors causing TCPs point source pollution (Cai et al. 2018). The concentration ranges of TBP and TPP were $<\text{LOD}$–4.7 ng/g dw and $<\text{LOD}$–9.2 ng/g dw, and the median concentrations were 3.5 ng/g dw and 7.6 ng/g dw, respectively.

TBP, TDCPP, TPP, and $m$-TCP were also the commonly detectable OPFRs congeners in other marine sediments (Table 2). As the above OPFRs usually account for the majority of the total concentration, we compared the total concentration of organic pollutants in their sediments, unless otherwise stated. The results show that the average concentration of $\Sigma_4$OPFRs at all sites (11 ng/g dw) in sediments of the SCS was higher than that in sediments of the Bohai Sea and the northern part of the East China Sea (5 ng/g dw) (Liao et al. 2020). TDCPP was most frequently detected in this study, but it was detected only in one sediment sample from the Bohai Sea and the northern East China Sea (Liao et al. 2020). The average concentration of $\Sigma_4$OPFRs at all sites measured in this study was triple that reported at the Korean coast (3.1 ng/g dw), which was mainly due to the detection rate improvement of $m$-TCP (53%) compared with that of the Korean coast (20%) (Choi et al. 2020). As isomers of TCPs, a significant correlation between $m$-TCP and $p$-TCP ($r = 0.702$, $p < 0.01$) was observed. However, no obvious regular correlation was observed between other OPFRs detected in sediments.

![Fig. 2 Concentration and distribution of OPFRs in sediments of the SCS](image-url)
OPFRs are stable toxic compounds used in almost all plastic products (Bigley et al. 2019). It shows that in developed and densely populated areas, higher OPFR consumption is related to higher product demand for living, such as plastics, rubber, textiles, coating, and paper (He et al. 2021). The PRD includes the megacity of Guangzhou, the famous electrical/electronic manufacturing base in Dongguang, and the manufacturing area specializing in the production of plastics, textiles, and personal protective articles (Zeng et al. 2018b). A study shows that the average concentration of Σ_4OPFRs at all sites in the soil in Guangzhou of the PRD region was as high as 97.3 ng/g dw (Cui et al. 2017). The average concentrations of Σ_4OPFRs at all sites (22.8 ng/g dw) in sediments of the PRD were higher than those in this study (Tan et al. 2016). Contaminants from the PRD may also enter the SCS through surface runoff, creating long-term adverse effects on the coastal resources (Chen et al. 2006). Therefore, it is speculated that the OPFRs produced in the PRD are one of the sources of this study.

### Spatial distributions of OPFRs

The spatial distribution of OPFRs in the sampling area is shown in Fig. 3. The continental shelf of the SCS is mainly composed of the detrital fine-grained materials supplied by the Pearl River, and the nearshore ocean current is very important for the transportation of the detrital fine-grained materials (Liu et al. 2017). Terrigenous sediments of OPFRs have their provenance in rivers from Southwest Taiwan, explaining the high concentration of OPFRs at SCS11 (Kaiser et al. 2018; Liu et al. 2010). The coastal current flows southwestward in both summer and winter seasons (Liu et al. 2014). Accordingly, the Pearl River sediments are mainly transported southwestward by this coastal current and mostly deposited on the continental shelf of the SCS between the Pearl River mouth and Hainan (Liu et al. 2013, 2016); this may be a reason for the high concentration of OPFRs in the coastal sediments of the PRD.

OPFRs from industrial activities were directly released to Pearl River and then deposited in sediments, and OPFRs in both urban and rural the PRD regions (Tan et al. 2016) showed decreasing trend in water samples and sediments with the increase in the distance from rivers to inshore or offshore areas. Beijiang River flows through the largest electronic garbage area in the PRD, strongly affected by sediment transport in the coastal area, and this resulted in a high concentration of OPFRs at sites SCS2, SCS5, and SCS13. The most polluted sample SCS15 was obtained near the coastal area of Guiyu which indicated that e-waste is an important source of OPFRs (Zeng et al. 2018b). The average concentration of OPFRs in sediments of the Lian River in China is 87741 ng/g dw, which was one of the higher levels reported in the world (Li et al. 2019). A high

### Table 2 Comparison of OPFRs concentrations (ng/g dw, mean value) in sediments of this study and other areas in the world

| Sampling area                      | Sampling no | Sampling year | TBP  | TDCPP | TPP  | p-TCP | m-TCP | OTCP | ΣOPFRs | Reference                           |
|------------------------------------|-------------|---------------|------|-------|------|-------|-------|------|--------|------------------------------------|
| South China Sea, China             | 15          | 2020          | 3.6  | 0.35  | 12.8 | 6.4   | 7.5   | 0.09 | 8.6    | This study                         |
| Taiwan Strait, China               | 32          | 2016          | 7.92 | 0.55  | 0.55 | 3.5   | 0.55  | 0.09 | 4.5    | Zeng et al. (2020)                 |
| Pearl River Delta, China          | 48          | 2015          | 7.3  | 1.31  | 14.3 | 14.3  | 15.44 | 0.83 | 22.8   | Hu et al. (2017)                   |
| Pearl River Delta, China          | 15          | /             | 7.3  | 1.41  | 4.44 | 4.44  | 3.95  | 1.33 | 7.92   | Zeng et al. (2018b)                |
| The Bohai Sea and northern part of | 50          | 2011, 2012, 2016 | 4.21 | 1.78  | 1.78 | 1.78  | 3.94  | 1.33 | 4.41   | Liao et al. (2020)                 |
| Korean coast, Korea               | 50          | 2016          | 1.73 | 0.57  | 1.78 | 0.57  | 1.78  | 0.57 | 3.34   | Choi et al. (2020)                 |
| San Francisco Bay, USA            | 10          | 2014          | 1.83 | 0.96  | 1.83 | 0.96  | 1.83  | 0.96 | 3.69   | Shilton et al. (2019)              |
| Hainan Island, China              | 49          | 2015          | 1.9  | 0.39  | 1.9  | 0.39  | 1.9   | 0.39 | 4.41   | Mo et al. (2019)                   |

*only detectable in one sample
concentration of SCS15 might be attributed to the direct sewage disposal along the coast of the e-waste dismantling area in Guiyu.

The northern part of the SCS is an important international freight route connecting the Indian Ocean and the western Pacific Ocean. The correlation analysis between OPFR distributions and spatial pattern of the PRD socio-economic indicators indicated that ship transportation significantly correlated with the distributions of chlorinated OPFRs and alkyl-PFRs (Gao et al. 2021). The ship activities might also improve the level of OPFRs in the SCS (Peng et al. 2019). The waste discarded in the process of ship transportation is a possible source of OPFRs in the SCS (Cai et al. 2018), especially the plastic products such as derelict fishing gear (Kuczenski et al. 2021).

**Mass inventory and risk assessment**

Based on the available data, the inventories of OPFRs in surface sediment of the SCS were calculated and shown in Fig. 4. The total inventory of six OPFRs in sediment was estimated to be 202.8 tons (16.7×10⁶ km²). The mass inventory of OPFR per km² in the SCS was comparable to the mangrove sediments of the Pearl River Estuary (16.9×10⁻⁵ tons, 7.5 km²) (Hu et al. 2017), but about two magnitudes higher than that of the Taiwan Strait (13 tons, 189, 925 km²) (Zeng et al. 2020). TCPs (114.6 tons) exhibited the largest inventory, contributing to 56.5% of the total OPFRs burden in surface sediment of the SCS. Among them, o-TCP, m-TCP, and p-TCP accounted for 21.1%, 24.7%, and 10.7%.
of the total inventories, respectively. TPP (32.2 tons) and TDCPP (31.6 tons) were estimated to have similar inventories of and a proportion of 15.9% and 15.6%, respectively. TBP was the minimum contributor in the SCS, but it was the largest mass inventory contributor in the sediments of Taiwan Strait (69.4%) and mangrove sediments from Zhuhai (29.2%).

As shown in Supplementary Table S2, for the high and median exposure scenarios, the HQ values of all organic pollutants are far less than 0.1, indicating that the current level of OPFRs in sediments of the SCS will not pose a significant ecological risk to the aquatic biota. Compared with the other three OPFRs, the PNEC values of TCPs (710 ng/g dw) were at much lower levels, indicating their higher chronic toxicity. Although the detection rates of o-TCP and p-TCP in sediment were relatively low, in some sites, they were at relatively high levels; the continuous input may also induce possible risk in the future. Environmental exposure to TCPs and the possible formation of toxic metabolites such as cresol phosphate hydrochloride have neurotoxic effects on the human body (Hausherr et al. 2017). The inhibition of acetylcholinesterase (AChE) could be a potential mechanism of TCPs’ neurotoxicity (Hargreaves 2012). Although the detection rate of TBP in sediment samples was high, the HQ was low, indicating the low biological toxicity of TBP in the SCS.

Conclusions

Based on the analysis of 15 sediment samples, this study investigated the current situation, distribution, composition, and ecological risk of OPFRs in the SCS. OPFRs were frequently detected, and compared with other countries, OPFR pollution in the SCS was at a medium level. TDCPP showed the highest detection rate but a lower level. As for the concentration and mass inventory, TCPs contributed to the main individual components. In addition, the concentration of OPFRs in sediments from the SCS was mainly concentrated on the southwest coast of Taiwan and the coast of the PRD, which indicated that nearshore ocean current, ship transportation, and riverine inputs were important sources of OPFRs. The risk assessment showed that the current level of OPFRs pollution has a little toxic impact on aquatic organisms in the SCS. The data obtained in the present study shed light on the occurrence and risks of OPFRs in the SCS. Broader sediment monitoring activities are needed to collect information on a larger scale and to conduct long-term studies on the source identification, migration, and fate of OPFRs.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-022-20752-7.

Author contribution All authors contributed to the study’s conception and design. Material preparation, data collection, and analysis were performed by Xin Pan, Aifeng Liu, Minggang Zheng, Jianxin Liu, and Ling Wang. The first draft of the manuscript was written by Xin Pan. Ling Wang provided guidance for the experimental study, while the language was revised by Aifeng Liu and Ling Wang. Ming Du provided technical support. All authors read and approved the final manuscript.

Funding This research is funded by the National Natural Science Foundation of China (grant number: 22176105), and the NSFC Shiptime Sharing Project (grant number: 41949905).

Data availability Supplementary Tables S1 and S2 were shown in the Supplementary information.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Informed consent was obtained from all individual participants included in the study.

Competing interests The authors declare no competing interests.

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