Determination And Environmental Risk Assessment Of Organophosphorus Flame Retardants In Sediments Of The South China Sea

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Research Article

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Abstract

As ubiquitous contaminants in 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 was 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 ($16.7 \times 10^4 \text{ km}^2$). Hazard Quotient (HQ) of OPFRs ranged from 0 to 3.2×10^{-2} , indicating ignorable ecological risk of OPFRs in sediments of the SCS. This study provides insight for the occurrence of current-use OPFRs in the SCS which deserved long-term concern in future due to their continuous terrigenous inputs.

1. 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 with an annual increasing rate of 4.6% over the past decade and used widely worldwide (Lee et al. 2018). The global output of OPFRs has increased from 1.98×10^5 tons per year in 2007 to 2.92×10^5 tons per year in 2011 (Liang & Liu 2016) and reached about 3.00×10^6 tons per year in 2018 (Zeng et al. 2020). OPFRs are classified according to their functional groups into halogenated OPFRs and non-halogenated OPFRs, the former are mainly used as flame retardants in textiles, furniture, and electronics (Regnery & 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). World Health Organization (WHO) has proved many adverse health effects of OPFRs, such as neurotoxicity, cytotoxicity, genotoxicity, developmental toxicity, and reproductive toxicity (Hales & Robaire 2020, Hoffman et al. 2017). Tri-*o*-cresyl phosphate (*o*-TCP), isomer of tri-cresyl phosphates (TCPs), is a severe nerve agent resulting in a 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 (TDCPP) is associated with changes in male hormone levels and decreasing of semen quality (Hales & Robaire 2020).

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 $169 \text{ ng} \cdot \text{g}^{-1} \text{ dw}$, with detection rate ranging from 1.1% ~ 94.5%

(Liao et al. 2020). The sediment concentration of OPFRs ($13\text{--}49\text{ ng.g}^{-1}\text{ dw}$) in the northwest Mediterranean was slightly lower than that of 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 $67\% \sim 100\%$ and $28\% \sim 100\%$ for the specific individuals, respectively (Schmidt et al. 2021). Long-distance transport the potential of OPFRs have been indicated as nine OPFRs were detected in range of $0.01\text{--}7.4\text{ ng.g}^{-1}\text{ dw}$ in sediment samples collected at Ny-Ålesund, 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 concentrations of total OPFRs in fish samples in coral reef fish from the South China Sea (SCS) was as high as $40.4 \pm 39.7\text{ ng.g}^{-1}\text{ dw}$ (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 for the benthos (Bekele et al. 2019).

The SCS is a typical marginal sea of China, with Pearl River being the largest river entering (Zeng et al. 2018b). The rapid economic development, industrialization and urbanization along 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 $72.6\text{ ng.g}^{-1}\text{ dw}$ in sediments with the detection rate of $40\% \sim 100\%$ (Zeng et al. 2018b). Rivers carry a large amount of land-based water and sediments from the land 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 ($1549\text{ ng.g}^{-1}\text{ dw}$) was 15 times that of the adjacent ocean ($100\text{ ng.g}^{-1}\text{ dw}$), indicating their terrigenous input source (Wang et al. 2015, Zhong et al. 2020). Pollutants entering into the sea with 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 into 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. Till 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 Pear River and PRD were speculated to be direct sources of 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, 3) based on the concentration levels, evaluate the mass inventory and risk levels of OPFRs in sediments of the SCS.

2. Material And Methods

2.1. 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). Basic physicochemical properties of the selected OPFRs are summarized in Table 1.

Dichloromethane, n-Hexane (purity > 99%), ethyl acetate (EA), acetone and acetonitrile were obtained from Merck & Fisher Scientific Co (Germany). Neutral silica gel (0.1-0.2 mm) purchased from Macherey-Nagel (Düren, Germany). Anhydrous sodium sulfate (purity 99%) was backed at 500°C for 6 h prior to use.

2.2. Sample collection

In this study, 15 surface sediment samples (0–5cm) were collected using a box sampler from the SCS during the cruise from “XiangYangHong 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 meters. The exactly information about the latitude, longitude and water depth of the sampling station was listed in table 2. All samples were immediately stored at -20 °C before analysis.

2.3. Sample preparation and instrumental analysis

The pretreatment method of sediments is based on previous studies (Zhong et al. 2018). 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).

2.4. 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 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 0.03-0.27 ng.g⁻¹ dw and 0.10-0.92 ng.g⁻¹ dw, respectively. Recovery tests for the targets were in range of 80-95%. The precision was intra-/inter-day RSDs: 3–5%/ 4–6%; and the matrix effects were between –8.1% and 12.3%.

2.5. Statistical analysis

Map of 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.

2.6. 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):

$$\text{Inventory}_{\text{sediment}} = C_{si} \times \rho_s \times d \times A$$

1

where C_{si} (ng.g^{-1} dw) is the average concentration of OPFR homologue i in sediment, ρ_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 ($16.7 \times 10^4 \text{ km}^2$) is the water area of sampling region in the SCS.

2.7. 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:

$$\text{HQ} = C_{\text{sediment}} / \text{PNEC}_{\text{sediment}}$$

2

Where C_{sediment} (ng.g^{-1} dw) is the concentration of contaminant in sediment and $\text{PNEC}_{\text{sediment}}$ (ng.g^{-1} 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).

3. Results And Discussion

3.1. 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 & de Boer 2012). Therefore, determining their concentration and distribution in sediments is essential for better understanding of their potential impact on seafloor communities, and global marine ecosystem function (Alkan et al. 2021). OPFRs 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 Σ OPFRs ranged from 2.5 to 32.3 ng.g⁻¹ dw. TBEP can be photodegraded in natural water or rapidly degraded by microorganisms, thus resulting in its low concentration in sediments (Regnery & 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 study area. The concentration range of TDCPP was < LOD-5.6 ng.g⁻¹ dw, and the median concentration of TDCPP was 3 ng.g⁻¹ dw. Although with highest detection rate, the concentrations of TDCPP were at similar low levels. Trimethylphenyl phosphate has three isomers, *m*-TCP was < LOD-9.5 ng.g⁻¹ dw (median 7.3 ng.g⁻¹ dw). The other two isomers *p*-TCP and *o*-TCP were in range of < LOD-10.9 ng.g⁻¹ dw and < LOD-17.5 ng.g⁻¹ 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 < LOD-4.7 ng.g⁻¹ dw and < LOD-9.2 ng.g⁻¹ dw, and the median concentration were 3.5 ng.g⁻¹ dw and 7.6 ng.g⁻¹ dw, respectively.

TBP, TDCPP, TPP and *m*-TCP, were also the commonly detectable OPFRs congeners in other marine sediments (Table 3). 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 Σ_4 OPFRs at all sites (11 ng.g⁻¹ dw) in sediments of the SCS was higher than that in sediments of the Bohai Sea and northern part of the East China Sea (5ng.g⁻¹ dw) (Liao et al. 2020). TDCPP was the 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 Σ_4 OPFRs at all sites measured in our study was triple that reported at the Korean coast (3.1ng.g⁻¹ dw), which was mainly due to the detection rate improve 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.

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 products demand for living, such as plastics, rubber, textiles, coating, paper, etc. (He et al. 2021). The PRD includes the mega city 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_4 OPFRs at all sites in soil in Guangzhou of the PRD region was as high as 97.3 ng.g⁻¹ dw (Cui et al. 2017). The average concentration of Σ_4 OPFRs at all sites (22.8 ng.g⁻¹ 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 is one of the sources of this study.

3.2. 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 the 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, Liu et al. 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 the 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 resulted in a high concentration of OPFRs at site SCS2, SCS5 and SCS13. E-waste is an important source of OPFRs, and the most polluted sample SCS15 was obtained from the coastal area of Guiyu (Zeng et al. 2018b). The average concentration of OPFRs in sediments of the Lian River in China is $87741 \text{ ng.g}^{-1} \text{ dw}$, which was one of the higher levels reported in the world (Li et al. 2019). A high concentration of SCS15 might be attributed to the direct sewage disposal along the coast of 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 OPFRs 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).

3.3 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 ($16.7 \times 10^4 \text{ km}^2$). The mass inventory of OPFR per km^2 in SCS was comparable to the mangrove sediments of the Pearl River Estuary ($16.9 \times 10^{-3} \text{ tons}$, 7.5 km^2) (Hu et al., 2017), but about two magnitude higher than that of the Taiwan Strait (13 tons, $189,925 \text{ km}^2$) (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. As another dominant contributor to the total OPFRs in the sediment of the SCS, TPP was estimated to have an inventory of 32.2 tons and a proportion of 15.9%. TBP was the third contributor in the SCS, but its was the largest mass inventory contributor in the sediments of Taiwan Strait (69.4%) and mangrove sediments from Zhuhai (29.2%).

As shown in Table 4, 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 other three OPFRs, the PNEC values of TCPs ($710 \text{ ng.g}^{-1} \text{ dw}$) 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.

4. 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, OPFRs 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 were mainly concentrated in the southwest coast of Taiwan and the coast of the PRD, which indicated that the nearshore ocean current, ship transportation and riverine inputs were important source of OPFRs. The risk assessment showed that the current level of OPFRs pollution has 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.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent to publication

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

Competing interests

The authors declare that they have no conflict of interest.

Authors Contributions

All authors contributed to the study 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, Ling Wang. And Ming Du provided technical support. All authors read and approved the final manuscript.

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Availability of data and materials

All data and materials generated or analyzed during this study are included in this published article.

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Tables

Tables 1-4 is available in the Supplemental Files section.

Figures

Figure 1

Map of sampling sites in the SCS

Figure 2

Concentration and distribution of OPFRs in sediments of the SCS

Figure 3

Map of spatial distribution of the total OPFRs concentration in sediments of the SCS.

Figure 4

Calculated inventory ratios of OPFRs (ton) in the sediment of the SCS

Supplementary Files

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