



Legacy and emerging contaminants in coastal surface sediments around Hainan Island in South China



Ling Mo^a, Jing Zheng^{b,*}, Ting Wang^{c,d}, Yun-Gang Shi^e, Biao-Juan Chen^a, Bin Liu^a, Yan-Hua Ma^a, Min Li^b, Li Zhuo^e, She-Jun Chen^{c,**}

^a Water Quality Monitoring Section, Hainan Research Academy of Environmental Sciences and Hainan Provincial Environmental Monitoring Center, Haikou, 571126, China

^b State Environmental Protection Key Laboratory of Environmental Pollution Health Risk Assessment, South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou, 510655, China

^c State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

^d University of Chinese Academy of Sciences, Beijing, 100049, China

^e Chongqing Solid Waste Management Center, Chongqing, 401147, China

HIGHLIGHTS

- The emerging and legacy pollutants were present in the sediments except for PCBs.
- The HFRs in the sediments were dominated by deca-BDE and novel DBDPE.
- Terrestrial inputs are the primary source of PAHs, HFRs, and OCPs in the sediments.
- OPFRs had different emission sources or entry modes to the sediments from others.

ARTICLE INFO

Article history:

Received 1 September 2018

Received in revised form

2 October 2018

Accepted 4 October 2018

Available online 5 October 2018

Handling Editor: Myrto Petreas

Keywords:

Halogenated flame retardants (HFRs)

Organophosphorus flame retardants

(OPFRs)

Polycyclic aromatic hydrocarbons (PAHs)

Pesticides

Spatial distribution

ABSTRACT

Emerging and legacy hydrophobic pollutants, including halogenated flame retardants (HFRs), organophosphorus FRs (OPFRs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs), as well as polycyclic aromatic hydrocarbons (PAHs) were determined in coastal sediments of Hainan Island, southern China, where little information is known about their contamination. The HFRs were dominated by decabrominated diphenyl ethers (median = 1.32 ng/g) and novel decabromodiphenyl ethane (1.87 ng/g). HFR and PAH concentrations had similar spatial distributions, with higher levels in the river and near the estuary. The concentrations of \sum_{10} OPFRs ranged from 0.74 to 60.0 ng/g (median = 15.3 ng/g), displaying a different spatial distribution. \sum DDTs and β -HCH, with median concentrations of 1.41 and 3.44 ng/g respectively, were largely from historical inputs, but use of DDT still exists in Hainan. Principal component analysis revealed the associations between most of the pollutants (HFRs, OCPs, and PAHs) and perylene, indicating that terrestrial runoff plays a significant role in their presence in the coastal sediments. OPFRs had different emission sources or entry modes to the coastal ocean.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Humans and wildlife are exposed to a vast array of man-made organic chemicals released into the environment, such as

pesticides, industrial additives, and unintended by-products resulting from industrial processes or combustions (Walters et al., 2016). In particular, organic chemicals that are persistent and bio-accumulative have great potential for adverse effects and are of considerable concerns (Howard and Muir, 2010). Polybrominated diphenyl ethers (PBDEs) are chemicals that have been widely used in a variety of commercial and consumer products to enhance the product safety, and have become ubiquitous organic contaminants in the environment and in living organisms (Birnbaum and Staskal,

* Corresponding author.

** Corresponding author.

E-mail addresses: zhengjing@scies.org (J. Zheng), chenshejun@gig.ac.cn (S.-J. Chen).

2004). PBDEs have been included in the Stockholm Convention on Persistent Organic Pollutants.

With the phase-out or restriction of these chemicals, the market demand for alternative products is growing (van der Veen and de Boer, 2012). For instance, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE), have been used as replacements for commercial octa- and deca-BDE products (Kierkegaard et al., 2004; Hoh et al., 2005). Organophosphorus flame retardants (OPFRs) are also proposed as alternatives for PBDEs, and are often used in electronic equipment, plastics, textiles, furniture, and building materials (van der Veen and de Boer, 2012; Ma et al., 2017). In 2008, the US, Europe, and Asia (excluding Japan) consumed 72000, 83000, and 22000 metric tons of OPFRs, respectively (Ou and Lang, 2010). OPFR occurrence in various environmental compartments and humans has been increasingly reported (Kim et al., 2014; Venier et al., 2014; Suhring et al., 2016b; Kademoglou et al., 2017; Wang et al., 2018b; Wolschke et al., 2018). However, some of these chemicals are suspected to be carcinogenic, mutagenic, or neurotoxic as suggested in numerous studies (ATSDR, 2009; van der Veen and de Boer, 2012; Butt et al., 2014; Wei et al., 2015). Meeker and Stapleton (2010) found that house dust concentrations of OPFRs were correlated with hormone levels and semen quality parameters for men.

Sediment serves as an important sink and secondary source of these hydrophobic pollutants, which can be accumulated in aquatic organisms and subsequently exposed to humans through the food chain (Suhring et al., 2016a; Anim et al., 2017). Consequently, their sources, occurrence and risk in the aquatic environment have attracted considerable scientific research globally (Cao et al., 2017; Giulivo et al., 2017; Ma et al., 2017; Zhong et al., 2018). China is a large manufacturer and consumer of FRs because of the rapid economic development, with a total annual production volume of 200 000 tons (Zhang et al., 2011). High FR concentrations have been reported in sediments from industrialized regions and near electronic waste recycling sites in China (Chen et al., 2005, 2013; Zhu et al., 2014; Zhou et al., 2017). Hainan Island is the southernmost province and the largest Special Economic Zone of China. However, contamination of FRs and other hydrophobic pollutants in this region is lacking. Hainan Island has a tropical monsoon climate. Information on the environmental behaviors of hydrophobic pollutants in low-latitude regions is limited, especially for emerging pollutants.

The aim of this study was to determine the levels of a variety of emerging and legacy hydrophobic contaminants, including halogenated FR (HFRs), OPFRs, polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polycyclic aromatic hydrocarbons (PAHs), in coastal sediments of Hainan Island. Such a survey provides information regarding the environmental contamination status in sediments derived from industrial and agricultural activities in Hainan Island. We also aim to understand sources, transport, and fate of these contaminants in the aquatic environment.

2. Materials and methods

2.1. Sample collection

Hainan Island is located in a humid subtropical and tropical zone (Fig. 1), with prevailing strong NE wind during October–April and weak SE wind during other months (Fig. S1 in the Supplementary Material). Hainan Island has a generally lower population density, over nine million within an area of 33 900 km², relative to most regions in eastern China. There are four centers of urban life (red dotted circles in Fig. 1), and Haikou, the provincial capital, is the biggest city. Fishing is one of the leading industries of Hainan.

Surface sediment samples (top 0–5 cm) were obtained using a stainless steel grab sampler around the coast of Hainan Island between May and December 2015, specifically from the Qiongzhou Strait (i.e., the northern coast) ($n = 20$), near-shore area ($n = 14$), and off-shore area ($n = 9$) (Fig. 1). Sediments were also collected from the Nanduijiang River (Haikou section) ($n = 6$), which is the largest river in Hainan. The locations were selected to cover regions potentially affected by the four centers of urban life. All the samples were transported on ice to the laboratory, where they were stored at -20°C until analyzed.

2.2. Extraction and cleanup

Sediment samples were freeze-dried, ground, and homogenized by sieving through a stainless steel 80-mesh sieve (0.2 mm). Samples (15–30 g) were Soxhlet extracted with an acetone: hexane (1:1, V/V) mixture for 48 h for analyzing 22 HFRs, 12 OPFRs, HCHs, and DDTs (Table 1 and Table S1). Prior to the extraction, activated copper was added to remove elemental sulfur and surrogate standards (BDE77, BDE181, BDE205 for HFRs), (TPP-*d*₂₁, TCIPP-*d*₁₈ for OPFRs), (PCB30, PCB65, and PCB204 for OCPs and PCBs), (Nap-*d*₈, Acy-*d*₁₀, Phe-*d*₁₀, Chr-*d*₁₂, Per-*d*₁₂ for PAHs) were added to monitor the recoveries. The extracts were concentrated to 1–2 mL using a rotary evaporator and then purified through a silica/alumina column packed, from the bottom to top, with alumina (4.5 g), neutral silica (5.5 g, 3% deactivated), and anhydrous sodium sulfate (2.5 g). The column was eluted with 15 mL hexane (the effluents were not discarded) and subsequently 70 mL hexane:dichloromethane (7:3, V/V). The latter effluents were concentrated to near dryness under a gentle nitrogen stream and then dissolved in 300 μL of iso-octane. Quantitation internal standards (BDE118, BDE128, and ¹³C-BDE209 for HFRs, TCEP-*d*₁₂, TDCIPP-*d*₁₅ for OPFRs and PCB24, PCB82, PCB198 for PCBs and OCPs, and 2-fluorobiphenyl, p-terphenyl-*d*₁₄, and DahA-*d*₁₂ for PAHs) were added prior to instrumental analysis.

2.3. Instrumental analysis

HFRs were analyzed using a Shimadzu 2010 GC-MS operated in electron capture negative ionization mode (ECNI). Di through hepta-BDEs and DP isomers (*anti*- and *syn*-DPs) were separated with a DB-XLB (30 m \times 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific) capillary column; while for octa-BDEs through deca-BDEs DBDPE and BTBPE, a DB-5HT (15 m \times 0.25 mm i.d., 0.10 μm film thickness, J&W Scientific) column was used.

OPFRs, PAHs, PCBs and OCPs were analyzed using an Agilent 7890A/5975C GC-MS in electron ionization (EI) mode. Measurement of the OPFRs and PAHs was achieved using a DB-5MS (30 m \times 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific) capillary column and PCBs and OCPs were separated using a DB-5MS capillary column (60 m \times 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific). For all the targets, injection of 1 μL sample was performed with an automatic sampler in the splitless mode.

2.4. Quality control

A procedural blank was run with each batch of samples ($n = 11$). Only a few PAHs and OPFRs (TNBP, TCEP and TCIPP) were detected in the procedural blanks and they were corrected to the concentrations in the samples. The recoveries of surrogated standards (mean \pm standard deviation) were $112 \pm 15.7\%$ for BDE77, $90.0 \pm 7.3\%$ for BDE181, $85.9 \pm 9.3\%$ for BDE205, $84.8 \pm 11.5\%$ for TPP-*d*₂₁, $93.8 \pm 9.7\%$ for TCIPP-*d*₁₈, $95.5 \pm 13.1\%$ for PCB30, $83.8 \pm 5.8\%$ for PCB65, and $93.6 \pm 3.6\%$ for PCB204, $31.0 \pm 10.2\%$ for Nap-*d*₈, $71.4 \pm 11.9\%$ for Acy-*d*₁₀, $87.8 \pm 18.0\%$ for Phe-*d*₁₀, $113 \pm 13.0\%$ for Chr-*d*₁₂, $115 \pm 16.8\%$ for Per-*d*₁₂. The method

Download English Version:

<https://daneshyari.com/en/article/11010198>

Download Persian Version:

<https://daneshyari.com/article/11010198>

[Daneshyari.com](https://daneshyari.com)