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Conventional and emerging halogenated flame retardants (HFRs) in sediment of Yangtze River Delta (YRD) region, East China

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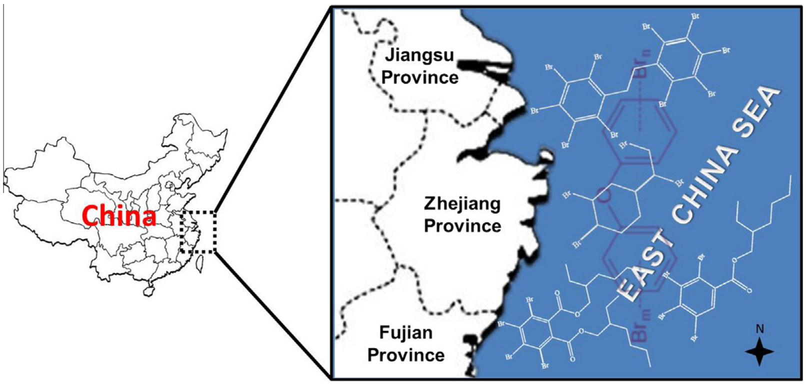
HIGHLIGHTS

- Eight out of twelve HFRs were detected in the sediment from YRD.
- TBECH and TBPH were first reported in the Chinese marine environment.
- PBDEs, DBDPE and TBECH were the three predominant HFRs in the sediment.
- Spatial patterns may indicate that HFRs originated from the eastern region of China.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence and distribution of polybrominated diphenyl ethers (PBDEs) and eleven non-PBDE halogenated flame retardants (HFRs) were investigated through the collection of marine and river sediment from Yangtze River Delta (YRD), East China. Among them, PBDEs, decabromodiphenyl ethane (DBDPE) and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) were the three predominant HFRs with the highest detection frequencies in the sediment. Significant correlation between PBDEs and DBDPE indicated that they may have the similar emission sources. The production and use of DBDPE is growing rapidly and comparable concentrations between PBDEs and DBDPE in YRD sediment may suggest that DBDPE will likely become one of the major HFRs emerging in the environment in China. Of the seven detected non-PBDE HFRs, this is the first time that TBECH was reported in the Chinese environment and its predominance and prevalence in the YRD may imply its extensive use in these areas.

1. Introduction

Halogenated flame retardants (HFRs) are a class of structurally diverse chemicals including chlorinated and brominated derivatives which have been widely applied in common household objects such as furniture, textiles, and electronics, and are therefore used in high volumes and prevalent in the environment (Covaci et al., 2011; Sverko et al., 2011). A well-known example of these is polybrominated diphenyl ethers (PBDEs) of which

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Penta- and Octa-BDE have been added to the Persistent Organic Pollutants (POPs) list of the Stockholm Convention due to their persistence, toxicity, bioaccumulation and long-range transport potential (http://chm.pops.int/Convention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx). Recently, Deca-BDE has also been exempted or phased out in the production of electronic applications in Europe and the United States (European Court of Justice, 2008; Wäger et al., 2012). Since the worldwide restriction on the production and use (Covaci et al., 2011), market demand for PBDEs is expected to decline, whereas that for its alternatives is projected to increase.

Over the past decades, some non-PBDE HFRs, e.g. 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), Dechlorane Plus (DP), hexabromobenzene (HBB), hexabromocyclododecane (HBCD), hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 2-ethylhexyl2,3,4,5-tetrabromobenzoate (TBB), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) and bis-(2-ethylhexyl)-tetrabromophthalate (TBPH) have been manufactured to replace some of the conventional HFRs such as PBDEs and these emerging non-PBDE HFRs have been recently investigated and reviewed to a certain extent, revealing their presence in a wide range of environmental compartments including biota (Covaci et al., 2011; Sverko et al., 2011). The presence of these non-PBDE HFRs in organisms indicates that they can be bioconcentrated and are bioavailable, and several studies have even reported some of these such as BTBPE, PBEB, PBT and TBECH in seabirds and marine mammals in the Arctic region (Tomy et al., 2008; de Wit et al., 2010), suggesting their capability of long range atmospheric transport (de Wit et al., 2010). In addition, many of these non-PBDE HFRs are showing similar environmental behavior as PBDEs, however, environmental data on these compounds are still very limited (Covaci et al., 2011).

Sources of contamination from riverine runoff, municipal and industrial discharges, and atmospheric deposition have contributed to numerous environmental pollutants such as POPs into the aquatic environment (Froescheis et al., 2000; Zhao et al., 2011). Due to their hydrophobic properties (Froescheis et al., 2000; Minh et al., 2007), POPs and some emerging HFRs are strongly particle-associated and tend to be accumulated in sediments (Mai et al., 2005; Shi et al., 2009). Accordingly, these emerging HFRs are expected to be prevalent in coastal sediment. In recent years, China has become one of the largest consumers of flame retardants (Flame retardants, 2011) with an expected annual growth rate of up to 7% of which brominated flame retardants (BFRs) accounted for the majority of consumption (Fink et al., 2008). With the large demand for HFRs in China, discharges from manufacturing processes, as well as, leaching from existing products that are in service or have been disposed of in landfills or e-waste sites could elevate the levels of both conventional and alternate HFRs in the environment (Han et al., 2009; Wu et al., 2010a,b; Zhao et al., 2009). Up till now, little is known about the presence of alternate HFRs in the Chinese environment, although some of these compounds have been reported in the Chinese coastal environment, for example, DP in coastal sediment of northern China (Wang et al., 2011), BTBPE and DBDPE in Pearl River Delta of south China (Shi et al., 2009; Zhang et al., 2009), and DBDPE in twelve lakes of China (Wu et al., 2012). For eastern China, however, there is still a lack of information on the recent status of these emerging compounds.

To this end, marine and riverine sediment samples were collected from the Yangtze River Delta (YRD), which is located on the east coast of China and is one of the most developed economic regions in China, for determination of the concentrations of PBDEs and eleven non-PBDE HFRs in order to elucidate their current contamination status. The objectives of this study were to determine whether PBDEs and these non-PBDE HFRs are present in the sediment of YRD and to determine their possible potential sources in this region. The results of this study would be useful for prioritizing these emerging HFRs for further environmental research.

2. Material and methods

2.1. Materials

Standards used in this study were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). All solvents used throughout the study were HPLC grade.

2.2. Sample collection

Surface sediment samples (upper 2–3 cm) were collected by stainless steel sampling device during a scientific expedition cruise in the East China Sea (Research Vessel KEXUE-3) conducted in summer 2011, and river surface sediment samples (upper 2–3 cm) were collected by stainless steel grab from three rivers located in Zhejiang Province, Lingjiang (LJ), Oujiang (OJ) and Qiantang River (QTJ) (Fig. 1). The GPS coordinates of the sampling locations and the water content of the sediment samples are shown in Table S1. All the samples were freeze-dried immediately after collection and stored at −20 °C until analysis.

2.3. Sample extraction and clean up

Pretreatment of HFRs analysis was accomplished by use of previously established methods (Lam et al., 2009; Ramu et al., 2010) with modifications. Duplicate samples were analyzed for the HFRs. Briefly, approximately 2 g of copper powder, used to remove elemental sulfur, was added to the bottom of a pre-cleaned accelerated solvent extractor (ASE200, Dionex) cell, followed by 2 g of dried sediment. The rest of the cell was filled up with anhydrous sodium sulfate (Na_2SO_4). Prior to extraction with hexane/DCM (1:9, v/v), 10 ng surrogate standard ($^{13}C_{12}$-labeled BDE28, BDE47, BDE99, BDE153, BDE154, BDE183, BDE197, BDE207, and BDE209; α-, β- and γ-$^{13}C_{12}$-labeled HBCD; $^{13}C_{12}$-labeled DBDPE, BTBPE and HBB) was added to each sample. The extract was purified using a multilayer silica/alumina column packed with activated silica gel (5 g), aluminum oxide (5 g), copper powder (2 g) and anhydrous sodium sulfide (1 g) (from the bottom to the top), then the target compounds was eluted with 150 mL hexane:DCM (1:2, v/v). $^{13}C_{12}$-labeled BDE139 and deuterized HBCDs (α-, β- and γ-HBCD-d_{18}) were added before concentrating to dryness under gentle nitrogen and finally reconstituted in 100μL of methanol.

2.4. Sample analysis

Instrumental analysis of twelve HFRs (Table 1) was performed based on the analytical method by Zhou et al. (2010) with modifications. Identification and quantification were performed using a liquid chromatography–tandem mass spectrometer system (LC–MS/MS) consisting of an Agilent 1290 Infinity LC (Agilent Technologies, Palo Alto, CA) coupled to AB SCIEX QTRAP® 5500 LC-MS/MS system with an atmospheric pressure chemical ionization (APCI) interface. A Zorbax SB-C18 column (2.1 mm × 100 mm, 1.8 μm; Agilent Technologies, Palo Alto, CA) was used for the chromatography separation. The mobile phase consisted of (A) methanol/water (85:15) and (B) methanol. LC separation was carried out at ambient temperature with a linear gradient elution at a flow rate of 200 μL min^{-1} from 100% A to 5% A with 95% B for the first 4 min, then increased to 100% B with 300 μL min^{-1} at 6 min before reverting to original conditions at 17 min. The injection volume was 2 μL.