



Brominated flame retardants in mangrove sediments of the Pearl River Estuary, South China: Spatial distribution, temporal trend and mass inventory



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HIGHLIGHTS

- PBDEs, DBDPE and BTBPE were determined in mangrove sediments of the PRE.
- The highest levels of BFRs were found in mangrove sediments from Shenzhen.
- BFRs in mangrove sediments were dominated by PBDEs, followed by DBDPE and BTBPE.
- Levels of BFRs in cores showed an increasing trend from the bottom to top layers.
- Mangrove sediments are important reservoirs for BFRs.

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ABSTRACT

Sediments were collected from three mangrove wetlands in the Pearl River Estuary (PRE) of South China to investigate spatial and temporal distributions of polybrominated diphenyl ethers (PBDEs), decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE). Concentrations of Σ PBDEs, DBDPE and BTBPE in mangrove sediments of the PRE ranged from 1.25–206, 0.364–34.9, and not detected–0.794 ng g⁻¹ dry weight, respectively. The highest concentrations of Σ PBDEs, DBDPE and BTBPE were found at the mangrove wetland from Shenzhen, followed by Zhuhai and Guangzhou, showing the dependence on the proximity to urban areas. PBDEs were the predominant brominated flame retardants (BFRs) in mangrove sediments. The concentrations of Σ PBDEs, DBDPE and BTBPE in sediment cores showed an increasing trend from the bottom to top layers, reflecting the increasing usage of these BFRs. The inventories of Σ PBDEs, DBDPE and BTBPE in mangrove sediments were 1962, 245, and 4.10 ng cm⁻², respectively. This is the first study to report the occurrence of DBDPE and BTBPE in mangrove ecosystems.

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1. Introduction

Brominated flame retardants (BFRs), as important additive/reactive flame retardants, have been widely used in electronics, paints, textiles, thermoplastics, polyurethane foams and building materials to reduce the flammability of many combustible products. Currently, at least 75 chemicals have been classified as BFRs

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(Alaee et al., 2003). Among them, polybrominated diphenyl ethers (PBDEs) have been widely used and are ubiquitous pollutants in the environment. There have been three major PBDE commercial formulations: Penta-BDE, Octa-BDE and Deca-BDE. Penta-BDE and Octa-BDE commercial products have been added to the list of emerging persistent organic pollutants (POPs) by the Stockholm Convention in May 2009 because of their persistence, bioaccumulation and toxicity, while Deca-BDE technical mixtures, banned in Europe and the United States of America, are still used in China (Besis and Samara, 2012). Due to restrictions and bans on the use

and production of PBDEs, decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) have been used as replacements for Deca-BDE and Octa-BDE technical mixtures in various products, respectively. Although information regarding the environmental behaviors of DBDPE and BTBPE is limited, the available data show that these alternative BFRs may also be persistent, bioaccumulative, toxic, and subject to long-range transport (Covaci et al., 2011).

Mangrove ecosystems, the intertidal wetlands along the tropical and subtropical coastlines, are rich in biodiversity and provide habitats for a wide variety of fauna and flora. Although their ecological and economic importance has received great attention, mangrove ecosystems, as one of the most threatened biogeocenoses, have been subjected to increasing pollution pressure from human activities due to rapid urbanization and industrialization in coastal regions (Lewis et al., 2011; Bayen, 2012). Mangrove sediments act as sinks for varieties of organic pollutants because of their unique properties such as abundant detritus, high organic carbon content, anoxic/reduced conditions, and rapid turnover and burial (Tam, 2006; Vane et al., 2009). Contamination of polychlorinated biphenyls, organochlorine pesticides and polycyclic aromatic hydrocarbons has been frequently reported in mangrove sediments (Vane et al., 2009; Bayen, 2012). Meanwhile, PBDEs have also been found in biotic and abiotic samples from mangrove wetlands (Bayen et al., 2005; Binelli et al., 2007; Qiu et al., 2010; Bodin et al., 2011; Zhu et al., 2014), but information on the occurrence of DBDPE and BTBPE is scarce. Therefore, monitoring data on DBDPE and BTBPE in mangrove ecosystems are essential to get better understanding of their environmental behaviors.

The Pearl River Estuary (PRE), located in the Pearl River Delta (PRD) region of South China, has become one of the most developed and urbanized regions in China. The PRE has acted as a major reservoir for man-made contaminants discharged from municipal sewage, industrial waste, and upstream runoff, which may pose adverse effects to mangrove ecosystems (Zhang et al., 2014). In addition, intensive electrical waste (e-waste) recycling activities emerged in the PRD region in the last decades, which have released large amounts of BFRs into the PRE environment. It has been estimated that 23 metric tons of PBDEs were discharged into the PRE during the last 20 years (Guan et al., 2007). Thus, the PRE is generally regarded as a hotspot for BFR contamination. More recently, relatively higher levels of PBDEs (1.71–114 ng g⁻¹ dry weight, dw) have been reported in mangrove sediments from Hong Kong, South China (Zhu et al., 2014). However, data on spatial distribution and temporal trend of BFRs (especially for DBDPE and BTBPE) in mangrove ecosystems of the PRE is limited.

In the present study, sediments from three mangrove wetlands in the PRE were collected and analyzed for the levels of PBDEs, DBDPE and BTBPE. The objectives of this study were to (1) explore the occurrence and spatial distribution of these BFRs in mangrove wetlands in the PRE, South China; (2) investigate temporal trend of BFRs in mangrove wetlands; (3) estimate the mass inventory of BFRs in mangrove wetlands. To the best of our knowledge, this is the first study to investigate the distribution and temporal trend of DBDPE and BTBPE in mangrove ecosystems.

2. Materials and methods

2.1. Sample collection

A total of 30 surface sediments and 3 sediment cores were collected between October and November 2012 from three main mangrove wetlands in the PRE, South China, namely Futian Mangrove Nature Reserve in Shenzhen, Qi'ao Island Mangrove Nature Reserve in Zhuhai, and Tantou Mangrove Nature Reserve in Guangzhou

(Fig. 1). The dominant mangrove species in Shenzhen, Zhuhai and Guangzhou mangrove wetlands are *Kandelia candel*, *Sonneratia apetala*, and *Aegiceras corniculatum*, respectively. The top 5 cm layer of surface sediments was collected with a stainless steel grab sampler. Five sub-samples were randomly collected to mix a composite sample at each sampling point with an area of 5 m × 5 m. The sediment cores were collected from the middle of the natural swamps of each mangrove nature reserve using a gravity corer and sectioned at 4 cm intervals. All the sediment samples were immediately transferred to the laboratory and stored at -20 °C prior to chemical analysis.

2.2. Sample extraction and cleanup

The extraction and cleanup procedures for BFRs in mangrove sediment samples were described by Chen et al. (2013). Briefly, sediment samples were freeze-dried, grounded, homogenized by passing through a stainless steel 80-mesh sieve (0.2 mm) and stored in dark glass containers at -20 °C prior to extraction. Approximately 10 g samples were spiked with surrogate standards (¹³C₁₂-BDE 209, BDE 77, 181, and 205) and then Soxhlet-extracted with acetone/hexane (*v/v* = 1:1) for 24 h. Activated copper granules were added to the extraction flasks to remove element sulfur. The extract solution was concentrated to 1 mL with a rotary evaporator and then purified by a multilayer column filled with 8 cm neutral silica, 8 cm acidified silica, and 2 cm anhydrous sodium sulfate from bottom to top. The column was eluted with 30 mL hexane/dichloromethane (*v/v* = 1:1). The eluate was concentrated to near dryness under a gentle nitrogen flow and reconstituted in 200 μL of iso-octane. Internal standards (BDE 118 and 128, 4-Fluoro-BDE 67, 3-Fluoro-BDE 153) were spiked before instrumental analysis.

2.3. Instrumental analysis

Tri- to hepta-BDE congeners (28, 47, 66, 100, 99, 154, 153 and 183) were quantified by an Agilent 6890 gas chromatography (GC) coupled with 5975 mass spectrometer (MS) with electron capture negative ionization (ECNI) in the selective ion-monitoring (SIM) mode and separated by a DB-XLB (30 m × 0.25 mm × 0.25 μm, J&W Scientific). The initial temperature was set at 110 °C (held for 1 min), and ramped at 8 °C min⁻¹ to 180 °C (held for 1 min), then 2 °C min⁻¹ to 240 °C (held for 5 min), subsequently 2 °C min⁻¹ to 280 °C (held for 15 min), finally 10 °C min⁻¹ to 310 °C (held for 10 min). Octa- to deca-BDE congeners (202, 197, 203, 196, 208, 207, 206, and 209), DBDPE and BTBPE were analyzed by a Shimadzu model 2010 GC coupled with a model QP2010 MS (Shimadzu, Japan) using ECNI in the SIM mode. A DB-5HT (15 m × 0.25 mm × 0.10 μm, J&W Scientific) was used for separation. The temperature of the DB-5HT was held at 110 °C for 1 min, then increased to 200 °C at a rate of 20 °C min⁻¹ (held for 5 min), finally raised to 310 °C at a rate of 10 °C min⁻¹ (held for 15 min). 1 μL of the sample was injected in the pulsed splitless mode. The monitored and quantitative ions were as follows: *m/z* 492.7 and 494.7 for ¹³C₁₂-BDE 209, *m/z* 486.7 and 488.7 for BDE 209, *m/z* 79 and 81 for other compounds.

An aliquot of the sediment sample was treated with 10% hydrochloric acid solution to remove inorganic carbon, washed with purified water to remove chlorine ion, and dried to constant weight at 60 °C before the determination of total organic carbon (TOC) by a CHN-O Rapid Elemental Analyzer (Heraeus, Germany). Acetanilide used as the external standard was analyzed with each batch of 20 samples to ensure the relative standard deviation less than 5%.

2.4. Quality assurance and quality control

One procedural blank was performed in each batch of the sample analysis. Trace amounts of BDE 153 were detected in the procedural

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