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Contamination of polybrominated diphenyl ethers (PBDEs) in urban mangroves of Southern China

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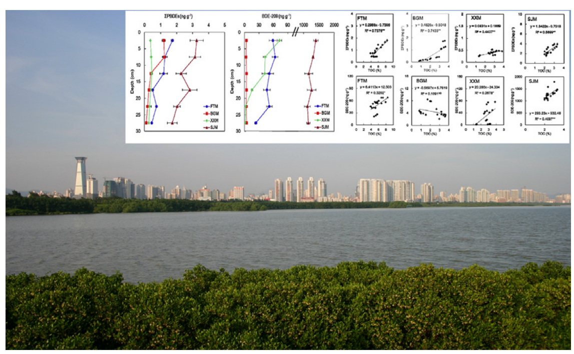
HIGHLIGHTS

- PBDEs in urban mangroves featured with different urban functional zonings were first reported.
- Concentration and risk of PBDEs were highest in SJM featured with industry district.
- TOC was influential in BDE-209 accumulations in SJM, XXM, and FTM.
- Transfer of BDE-209 from sediment to leaf was restricted in SJM featured with industry district.

GRAPHICAL ABSTRACT



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ABSTRACT

Mangroves are threatened due to urban development and human activities in coastal regions. Four urban mangroves in Shenzhen (rapidly developing city of China) were selected according to urban functional zoning, namely, Shajing mangrove (SJM) and Xixiang mangrove (XXM) featured with industry district, Futian mangrove (FTM) and Baguang mangrove (BGM) featured with central business district and ecological preserve. Eight BDE congeners (BDE-28, -47, -99, -100, -153, -154, -183, and -209) in mangrove sediments and leaves were determined. The highest level of BDE-209 in SJM was proximate to areas of point-source discharges of Dongbao River in Pearl River Estuary, China. Total organic carbon (TOC) was influential in BDE-209 accumulations in SJM, XXM, and FTM. Multiple variate analysis implied that PBDEs in SJM, XXM and FTM mainly composed of penta-, octa-, and deca-BDEs, with surface runoff to be the main contamination sources; while BGM was contaminated by penta- and octa-BDEs. Ecological risk of BDE-209 was high in SJM, with medium/negligible risk in the other urban mangroves. The transfers of BDE-209 from sediment to leaf were weak (BGM and FTM), improved (XXM), and restricted (SJM), respectively. This is the first reports of spatial distribution and bioaccumulation of PBDEs in urban mangroves featured with different urban functional zonings. More attention is required to reduce emission of PBDEs into the environment and manage PBDEs contamination in urban mangroves.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardant extensively used to reduce the flammability of many combustible products, including textiles, plastics, electronic components, and

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finishing materials (Kelly et al., 2008; Nelson et al., 2015). PBDEs are persistent, hydrophobic and bio-accumulated, and have attracted considerable concerns due to their impacts on environment and human health (Macías-Zamora et al., 2016). Currently, PBDEs released into the environment mainly focused on distribution (Mackintosh et al., 2015), exposure (Bramwell et al., 2016), toxicity (Yu et al., 2015), and temporal trends (Miller et al., 2015), with more concern on their environmental characteristics in marine system, especially of the mangrove ecosystem (Bodin et al., 2011; Zanaroli et al., 2015; Chen et al., 2018).

In the intertidal zones of coastlines in tropical and subtropical areas, mangroves acted as natural sinks/receivers preventing various contaminations in runoff from reaching coastal environments, such as heavy metals (Kulkarni et al., 2018), PCBs (Alegria et al., 2016), PAH (Assunção et al., 2017) and PBDEs (Salvadó et al., 2012), etc. PBDEs were reported to be low in mangrove water (<80 pg L^{-1})/sediment (<1 ng g^{-1}) in Singapore (Bayen et al., 2005), mangrove sediments (<4.6 ng g^{-1}) in Senegal (Bodin et al., 2011), and mangrove leaves/stems (not detectable) in Shantou, China (Liu et al., 2017). Compared with mangrove far away from the urban area, urban mangrove has received more attention due to its direct association with contamination from sewage, industry and runoff (Ranjan et al., 2018). In Pearl River Delta (PRD) of China, high levels of PBDEs have been reported to be accumulated in urban mangroves in Hong Kong, Guangzhou, and Zhuha (Zhu et al., 2014a; Wu et al., 2016, 2017). Nowadays, the contamination sources in urban mangroves have been empirically considered to be affected by surrounding human activities, and how to classify such impacts was one gap in evaluating urban mangrove ecology (Branoff, 2017, 2018). In the past three decades, Shenzhen in PRD of China has experienced rapid development (Wu et al., 2016), and Shenzhen mangroves mainly distributed in western, southern and eastern littoral featured with different urban functional zonings (Li et al., 2014; Tu et al., 2018; Yang et al., 2018). Furthermore, Shenzhen population aggregation and constructive land sprawl coexisted with massive release of man-made pollutants, including PBDEs (Ni et al., 2012; Sun et al., 2013). On the other hand, urban functional zonings have been proved to be effective in exploring contamination characteristics in urban area (Li et al., 2017; Llop et al., 2017). Knowledge on the occurrences of PBDEs in urban mangroves in view of different urban functional zonings is scarce.

In this study, we explored PBDEs contamination in urban mangroves in Shenzhen, including Shajing mangrove (SJM), Xixiang mangrove (XXM), Futian mangrove (FTM) and Baguang mangrove (BGM). Transfers of PBDEs from sediment to mangrove plant were also elucidated. Regarding urban functional zoning, urban mangroves were featured with industry district (SJM and XXM), central business district (CBD) (FTM), and ecological preserve (BGM) (Sanders, 1986; Tu et al., 2018; Yang et al., 2018). This study aims to characterize the spatial distribution of PBDEs and their bioaccumulation in urban mangroves to better understand these chemicals' fate in view of different urban functional zonings. It is hypothesized that PBDEs contamination in urban mangroves featured with different functional zonings could show a high spatial heterogeneity. In Shenzhen with 230 kilometer-long coastline, SJM and XXM are located on the western littoral (industry district) with many factories built in 1980s–1990s, and are affected by industry development of Fuyong-Shajing high-tech area, Guangming-Shiyan high-tech area, and Gongming-Songgang tradition industry area (Wu et al., 2016). FTM located in Futian region (CBD), and had the function of research and development, head offices, and creative studies. Despite FTM is a restricted area since establish of Futian Natural Reserve in 1980s, the high population density and busy traffic in adjacent areas would cause negative impacts on the environment inevitably. BGM is located in eastern littoral with relatively low population density (ecological preserve), and the adjacent environment is relatively clean (Li et al., 2014).

2. Material and method

2.1. Study area and sample collection

In August 2016, twelve surface sediments and four sediment cores were collected from urban mangroves in Shenzhen, China, namely SJM, XXM, FTM, and BGM (Fig. 1). The mangrove species in sampling points of four urban mangroves were *S. caseolaris* (SJM and XXM) and *Avicennia marina* (FTM and BGM), with mean height of 2.5–3.0 m. Mature leaves (the 3rd pair of full expanded leaves from the top of the branch) were collected at the same time and sampling point as the sediment sample. In each urban mangrove, three sampling points were chosen along the coastal line, with a distance of about 100 m between two consecutive sampling points. The sediments and leaves were selected due to their indicator in polluted environment (Pittarello et al., 2017). At each sampling point, four sub-samples (0–5 cm) were collected to mix a composite sample from an area of 5 m × 5 m using pre-cleaned stainless steel spades. One sediment core (0–30 cm) was collected from the middle of the four sub-samples. Each sediment core was evenly sliced into 5 cm increments and divided into two parts: one was immediately freeze-dried to a constant weight (seven days) for PBDEs determination; the other was air-dried for the analysis of sediment properties. Mangrove leaves were freeze-dried (seven days) for PBDEs determination.

2.2. Physicochemical properties of sediment

The air-dried sample was ground into powder and passed through a 0.5 mm sieve before the analysis of pH, salinity and total organic carbon (TOC). Sediment pH and salinity in the sediment slurry (sediment: water = 1:2.5 w/v) were determined using pH meter (Sartorius PB-10, Germany) and conductivity meter (LABORATORY BENCHTOP Meters, China). TOC was determined using Total Organic Carbon Analyzer (multi N/C 3100, Germany). The physicochemical properties of sediments were shown in Table S1.

2.3. Determination of PBDEs in sediment and plant

The extraction, purification and analysis of PBDEs in sediments and leaves were conducted according to Zhu et al. (2014a) and Pan et al. (2018). The sample extraction was performed with an accelerated solvent extraction system (ASE200) purchased from Dionex (USA), an EPA approved technique under Method 3545A. Sample analysis was performed with a 6890 N gas chromatograph (Agilent Technologies, Avondale, PA, USA) equipped with an Agilent 5975 mass spectrometer (GC/MS) using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. An HP-5 fused silica capillary column (15 m × 0.25 mm i.d., 0.25 μm film thickness) was used for the detection of BDE congeners. The oven temperature was initiated at 100 °C (hold for 2 min) and increased to 320 °C at 6 °C min^{-1} (hold for 5 min). Methane was used as the chemical ionization moderating gas and helium as the carrier gas at a flow rate of 2 ml min^{-1}. The ion source and interface temperature were set to 150 °C and 250 °C, respectively. PBDEs were quantified by monitoring ion fragments (m/z) 79 and 81 (Br^-) for all BDE congeners, and m/z 79, 81, 487 and 489 for BDE-209. For the surrogate standard, PCB-209, m/z 464, 498, and 500 were monitored. Peaks were quantified only if the ratio of the signal/noise was ≥3. The limits of detection, defined as a signal of three times the noise level, ranged from 0.01 to 0.05 ng g^{-1}. For quality control and the recovery of the method, a matrix-spike recovery test was used. The mean recoveries (n = 3) of BDE-28, -47, -99, -100, -153, -154, -183, and -209 were 83.44%, 91.97%, 84.64%, 88.45%, 108.23%, 113.61%, 109.87, and 96.38%, respectively. For the eight congeners, the recovery percentages (83.45%–113.61%) were comparable to the published values, which varied from 70% to 120% (Dodder et al., 2002), 50% to 120% (Oros et al.,