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Bioaccumulation and cycling of polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DP) in three natural mangrove ecosystems of South China

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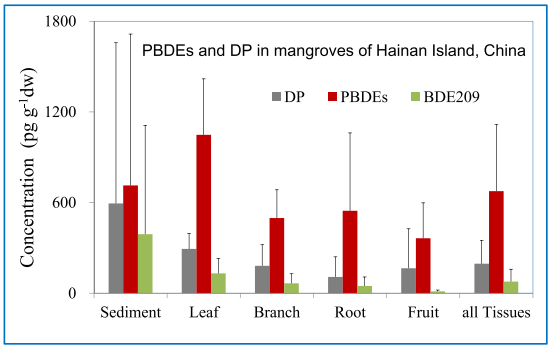
HIGHLIGHTS

- Concentrations of PBDEs and DP in natural mangrove plants are first reported.
- The elevated PBDEs and DP levels in mangrove leaves may be caused by atmospheric deposition.
- BSAFs of PBDEs in mangrove branches are positively correlated with log K_{OW}.
- Mangroves are playing an important role in retaining PBDEs and DP.

GRAPHICAL ABSTRACT



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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DP) in mangrove sediments and tissues of nine species from three Mangrove Reserves of Hainan Island were studied. The average concentrations of PBDEs and DP in mangrove leaves, branches, roots and fruits were 1048, 498, 546 and 364 pg g^{-1} dw, and 294, 181, 108 and 165 pg g^{-1} dw, respectively. The elevated PBDEs and DP concentrations in mangrove leaves may be caused by atmospheric sedimentation. The predominant PBDE congeners in sediments were BDE-209 and those in mangrove tissues were BDE-28. The average f_{anti} (ratio of [*anti*-DP]/[DP]) of DP in sediments and tissues were 0.47 and 0.32, respectively. *Sonneratia hainanensis*, a fast growing mangrove plant, has a relatively high tolerance and absorptive capacity to PBDEs and DP in sediments, suggesting that it could be used as an effective plant for phytoremediation. The biota sediment accumulation factors (BSAFs) of PBDEs in mangrove branches were positively correlated with log K_{OW} ($R^2 = 0.43$, $p < 0.05$). The standing accumulation, annual absorption, annual net retention, annual return, and turnover period of PBDEs and DP in mangrove tissues of the ecosystems were estimated, and the results indicated that mangroves are playing an important role in retaining PBDEs and DP.

1. Introduction

Mangrove ecosystems are important inter-tidal estuarine wetlands with high primary productivity, abundant detritus and rich organic

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carbon (Donato et al., 2011). Mangrove wetlands are preferential sites for uptake and preservation of persistent organic pollutants (POPs) (Bayen, 2012). Mangrove plants can potentially alter the distribution of pollutants by changing habitat characteristics and/or sediment properties. The interaction between pollutants and mangroves is a potentially important component of the POPs global cycle (Qiu et al., 2011). Polybrominated diphenyl ethers (PBDEs) are the brominated flame retardants which have been widely used in plastics, foam, and textiles in a variety of consumer products for many years to slow the spread of fire and the combustion of these products (de Wit, 2002); while dechlorane plus (DP) is a highly chlorinated flame retardant which has been primarily used in electrical wires and cables, computer connectors, and plastic roofing materials as a replacement for dechlorane (Sverko et al., 2011). Both PBDEs and DP have attracted increasing attention due to their persistence, toxicity and bioaccumulation, and they have been frequently detected in mangrove ecosystems (Lewis et al., 2011; Bayen, 2012; Zhang et al., 2014).

POPs in mangrove ecosystems are of particular concern because of their negative effects on mangrove fauna and flora. Organic pollutants at high concentrations can cause growth impairment of halophytic plants which in turn may limit buffering of storm event and stabilization of coastal sediment (Vane et al., 2009). There were some investigations on POPs in mangrove ecosystems, most of them focusing on POPs in mangrove sediments (e.g., Binelli et al., 2007; Vane et al., 2009; Zhu et al., 2014b; Zhang et al., 2015; Kaiser et al., 2016) and in mangrove biota (Páez-Osuna et al., 2002; Bodin et al., 2011; Wang and Kelly, 2017). However, concentrations of PBDEs and DP in natural mangroves have not been reported. There were only one investigation on polycyclic aromatic hydrocarbons (PAHs) levels in mangrove plants from the natural mangrove ecosystem of Shenzhen, China (Li et al., 2014), and a few studies on PAHs and PBDEs in mangrove seedlings from microcosm experiments (Wang et al., 2014; Zhu et al., 2014a; Li et al., 2015; Farzana et al., 2017). Over the past few decades, mangrove wetlands have been widely used for treating municipal, livestock and industrial wastewaters and even mine drainage, but how much pollutants have been intercepted by mangrove wetlands is unclear. Globally, mangroves assimilate 0.08–0.48 pg CO_2 per year—as much as around 10% of the total global emissions, even though mangroves account for only about 0.7% of the world's tropical forest areas (Donato et al., 2011; Murdiyarso et al., 2015), but how much POPs have been absorbed by mangrove plants is still unknown. To our knowledge, this is the first study on PBDEs and DP in mangrove plants from natural mangrove ecosystems.

The present study was conducted (1) to investigate the occurrence and fate of PBDEs and DP in three Mangrove Reserves of Hainan Island (Fig. 1); (2) to study characteristics of the biota sediment accumulation factor (BSAF) of PBDEs and DP in mangroves and relationships between BSAF of PBDEs and log K_{OW}; and (3) to estimate PBDEs and DP cycles (including the standing accumulation, annual absorption, annual net retention, annual return, and turnover period).

2. Materials and methods

2.1. Sample collection

There were 26 mangrove plant species distributing in Hainan Island while 27 species in China (Lin, 2001), with mangrove areas of 47.72 km^2, accounting for one-third of the total mangrove forest areas of China (Qiu et al., 2011). Mangrove tissues (leaf, branch, root and fruit) of nine species and sediment samples from Dongzhai Harbor, Saya Bay and Yalong Bay of Hainan Island were collected in August 2014 (Fig. 1 and Table S1). For each species, mangrove tissues samples were mixed by pooling together equivalent amounts of sample from three trees, and sediment samples were collected using the triangle sampling method. For more details on sample collection and processing, please refer to Supplementary material.

2.2. Sample pretreatment

Measurements of PBDEs and DP basically followed the procedures described previously (Qiu et al., 2010; Zheng et al., 2015). In brief, ~10 g mangrove tissues and sediment samples were spiked with PCB-209 as surrogate recovery standards and extracted using dichloromethane (DCM) for 36 h. For sediment samples, activated copper granules were added to the collection flask to remove elemental sulfur. Each sample extract was concentrated by a rotary evaporator and solvent-exchanged into hexane. Extracts were cleaned-up through an 8 mm i.d. alumina/silica column packed as follows (from top to bottom): anhydrous sodium sulfate (1 cm), 50% sulfuric acid silica (3 cm), neutral silica gel (3 cm, 3% deactivated) and neutral alumina (1 cm, 3% deactivated). PBDEs and DP were eluted with 20 mL of a mixture of dichloromethane: hexane (1:1, V/V), and concentrated to 0.5 mL under a gentle stream of nitrogen. A GPC column was used for the final cleanup step. 6.5 g of Bio-Beads S-X3 were used in a 15 cm glass column (id = 2 cm). The concentrated samples were loaded and eluted with 55 mL of a mixture hexane: dichloromethane (1:1, V/V). The first fraction (15 mL) was discarded, the following fraction (40 mL) containing the FR and the recovery standard was collected. 30 μL of dodecane containing 10 ng ^{13}C-PCB-141 (internal standard) were added as "keeper". Samples were concentrated to the final volume of 30 μL under a gentle nitrogen stream and then stored at −20 °C until injection.

2.3. Instrument analysis

GC-ECNI-MS (Agilent GC7890 coupled with 5975C MSD) with a DB5-MS capillary column (15 m × 0.25 mm i.d. × 0.25 μm film thickness) was used for the determination of ten PBDE congeners (BDE-28, 35, 47, 77, 99, 100, 153, 154,183 and 209) and DP (*anti*-isomer and *syn*-isomer). 1 μL of sample was injected in splitless mode (Zheng et al., 2015). Helium was used as carrier gas at the flow rate of 1 mL min^{-1}. Methane was used as chemical ionization moderating gas. The temperature of transfer line and ion source was maintained at 280 °C and 230 °C, respectively. The GC oven temperature started at 110 °C for 1 min, increased to 200 °C at a rate of 20 °C min^{-1} (held for 1 min), then to 310 °C at a rate of 10 °C min^{-1} (held for 12 min).

Total organic carbon (TOC) and total organic nitrogen (TON) in sediment was determined using a CHN Elemental Analyzer (Carlo-Erba model 1108) after removal of carbonates with HCl, and sediment grain size was analyzed with granulometry (SKC-2000, Japan) as described somewhere else (Qiu et al., 2011).

2.4. Quality assurance/control

Field blanks and procedural blanks were simultaneously analyzed with samples for monitoring the potential contamination during the processing and analysis. The method detection limit (MDL) of the targeted chemicals except BDE-209 (MDL: 28.6 pg g^{-1}) ranged from 1.3 to 7.6 pg g^{-1}, and the average (±SD) surrogate recovery of PCB-209 was 80 ± 9%. Reported PBDEs and DP concentrations in the present study are expressed on a dry weight basis (pg g^{-1} dw) and corrected according to the recoveries of the surrogate standards.

2.5. Statistical analysis

Statistical analyses were performed using SPSS for Windows Release 18.0, with a $p < 0.05$ taken to indicate statistical significance. Analyses of variance (ANOVA) were conducted to check if there was significant difference in the concentrations of the target contaminants between data groups.