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Organophosphorus flame retardants in mangrove sediments from the Pearl River Estuary, South China

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HIGHLIGHTS

- OPFRs and microbial community structure were determined in mangrove sediments.
- OPFRs were linked to the industrialization and urbanization.
- Distinct distribution patterns of OPFRs were found in the three mangrove wetlands.
- Eleven OPFRs in the sediments were significantly correlated with the PLFA profiles.

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ABSTRACT

Forty-eight surface sediments were collected from three mangrove wetlands in the Pearl River Estuary (PRE) of South China to investigate the distribution of organophosphorus flame retardants (OPFRs) and the relationship between OPFRs and microbial community structure determined by phospholipid fatty acid. Concentrations of ΣOPFRs in mangrove sediments of the PRE ranged from 13.2 to 377.1 ng g^{-1} dry weight. Levels of ΣOPFRs in mangrove sediments from Shenzhen and Guangzhou were significantly higher than those from Zhuhai, indicating that OPFRs were linked to industrialization and urbanization. Tris(chloropropyl)phosphate was the predominant profile of OPFRs in mangrove sediments from Shenzhen (38.9%) and Guangzhou (35.0%), while the composition profile of OPFRs in mangrove sediments from Zhuhai was dominated by tris(2-chloroethyl) phosphate (25.5%). The mass inventories of OPFRs in the mangrove sediments of Guangzhou, Zhuhai and Shenzhen were 439.5, 133.5 and 662.3 ng cm^{-2}, respectively. Redundancy analysis revealed that OPFRs induced a shift in the structure of mangrove sediment microbial community and the variations were significantly correlated with tris(1,3-dichloro-2-propyl)phosphate and tris(2-butoxyethyl) phosphate.

1. Introduction

Organophosphorus flame retardants (OPFRs), a class of flame retardants, have been widely used in televisions, computers, curtain, furniture, electronic equipment and household textiles, in order to delay the spread of fire after ignition and provide fire protection (Bergman et al., 2012; van der Veen and de Boer, 2012; Wei et al., 2015). With the phase-out or restriction of brominated flame retardants (BFRs), the market demand for alternative flame retardants, such as OPFRs, increase dramatically. It has been estimated that the global consumption of OPFRs is 150,000 metric tons (Ou, 2011). As OPFRs are usually mixed into the materials, rather than chemically bonded, they can be easily released into the environment from the OPFRs-containing products during production, use and disposal. More recently, OPFRs have been detected in various biotic and abiotic matrices (Wei et al., 2015; Iqbal et al.,

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2017). Meanwhile, the adverse effects of OPFRs on human and biota have also been reported. For example, OPFRs can inhibit specific liver carboxylesterases and cause altered hepatic lipid metabolism and serum hypertriglyceridemia in mice (Morris et al., 2014).

Mangrove wetlands are unique transitional coastal ecosystems between marine and terrestrial environments and have important socioeconomic value and ecological services. Although functions of mangrove wetlands have been receiving great attention, they have been often subjected to chemical pollution from anthropogenic activities due to rapid industrialization and urbanization in coastal areas (Vane et al., 2009; Lewis et al., 2011; Bayen, 2012). Mangrove sediments have been reported to act as important sinks for varieties of BFRs (Binelli et al., 2007; Bodin et al., 2011; Zhu et al., 2014; Zhang et al., 2015; Wu et al., 2016a) due to their unique properties, including high organic carbon content and abundant detritus. However, information on the distribution of OPFRs, the substitute of BFRs, in mangrove wetlands is rather scarce.

Mangrove wetlands have a diverse microbial community. The shift of microbial community structure in mangrove wetlands may occur after being exposed to organic contaminants. It has been reported that microbial community structure changed in constructed mangrove microcosms after artificial exposure to polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs) (Yen et al., 2009; Wang et al., 2014). Microorganisms in mangrove wetlands may also act as the potential bioindicators to degrade the organic pollutants. Characterization of the shift in microbial community structure may ignore the microbial members who were responsible for the degradation of the target organic pollutants (Ringelberg et al., 2001). Up to now, responses of microbial community to organic pollutants in actual environments are still poorly studied, Therefore, a field study is needed to better understand the relationships between microbial community structure and organic pollutants.

In the present study, sediments from three mangrove wetlands in the Pearl River Estuary (PRE) of South China were collected and analyzed for the OPFRs and microbial community structure determined by phospholipid fatty acid (PLFA). The objectives of this study were to (1) investigate the occurrence and spatial distribution of OPFRs in mangrove wetlands from the PRE; (2) estimate the mass inventory of OPFRs in mangrove wetlands; and (3) explore the relationships between microbial community structure and OPFRs in mangrove sediments.

2. Materials and methods

2.1. Sample collection

A total of 48 surface sediments were collected from three mangrove wetlands in the PRE of South China in November 2015, namely Tantou Mangrove Nature Reserve in Guangzhou, Qi'ao Island Mangrove Nature Reserve in Zhuhai, and Futian Mangrove Nature Reserve in Shenzhen (Fig. 1). The dominant mangrove species in Guangzhou, Zhuhai and Shenzhen mangrove wetlands are *Aegiceras corniculatum*, *Sonneratia apetala*, and *Kandelia candel*, respectively. The top 5 cm layer of surface sediments was taken with a stainless steel grab sampler. The sediment samples were divided into two parts and were immediately transferred to the laboratory. One part of samples was stored at −20 °C for OPFRs analysis and another part of samples was kept at −20 °C for microbial community analysis.

2.2. OPFRs analysis

The extraction and cleanup procedures for OPFRs in sediment samples were described by Tan et al. (2016). Briefly, sediment samples were freeze-dried, ground and homogenized by passing through a stainless steel 80 mesh sieve and stored in dark glass containers at −20 °C before extraction. Approximately 4 g samples were spiked with surrogate standard (TnBP-d_{27}) 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 by a rotary evaporator and then purified and fractionated by solid-phase extraction on an Oasis HLB cartridge (200 mg, 6 mL, Waters Corporation, Massachusetts, USA). The cartridge was pre-cleaned with 4 mL ethyl acetate, 4 mL methanol and 4 mL ultrapure water, and then eluted with 2 × 4 mL ethyl acetate. The effluents of ethyl acetate containing OPFRs were then evaporated to near dryness by a gentle nitrogen stream and redissolved in 100 μL isooctane. Known amounts of TPhP-d_{15} were spiked before instrumental analysis.

Eleven OPFRs, including triethyl phosphate (TEP), tri-isopropyl phosphate (TiPP), tri-*n*-propyl phosphate (TnPP), tri-*n*-butyl phosphate (TnBP), tris(2-chloroethyl) phosphate (TCEP), tris(-chloropropyl)phosphate (TCPP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), tris(2-butoxyethyl) phosphate (TBOEP), triphenyl phosphate (TPhP), ethylhexyl diphenyl phosphate (EHDPP) and tri-(2-ethylhexyl) phosphate (TEHP), were analyzed by a Shimadzu model 2010 gas chromatography coupled with a model QP2010 mass spectrometer (Shimadzu, Japan) using electron capture negative ionization in the selective ion-monitoring mode and separated by a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm, J&W Scientific). The temperature of the DB-5MS was held at 70 °C for 2 min, and then increased to 300 °C at a rate of 15 °C min^{-1} (held for 10 min). The ion source and interface temperatures were set at 200 °C and 290 °C, respectively. One μL of the sample was injected in the pulsed splitless mode. The monitored and quantitative ions were set as follows: m/z 155 and 127 for TEP, m/z 125 and 183 for TiPP, m/z 183 and 123 for TnPP, m/z 103 and 231 for TnBP-d_{27}, m/z 211 and 155 for TnBP, m/z 249 and 251 for TCEP, m/z 277 and 279 for TCPP, m/z 339 and 341 for TPhP-d_{15}, m/z 381 and 379 for TDCPP, m/z 299 and 199 for TBOEP, m/z 326 and 325 for TPhP, m/z 251 and 362 for EHDPP, m/z 99 and 113 for TEHP.

2.3. Total organic carbon (TOC) analysis

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

2.4. Microbial community analysis

The microbial community in mangrove sediments was determined by analysis of phospholipid fatty acids (PLFA). The lipid extraction procedure was described by Bossio and Scow (1998). Briefly, approximately 5 g freeze-dried sediment samples were extracted with 23 mL chloroform/methanol/phosphate buffer ($v/v/v$ = 5:10:4). The extract solution was moved into a separatory funnel after centrifugation to separate overnight. The chloroform layer was collected and dried under N_2 at 32 °C. Phospholipids were purified on a silica gel solid-phase extraction column (Supelco, Inc., Pennsylvania, USA). Neutral, glycol and polar lipids were eluted with 5 mL chloroform, 10 mL acetone and 5 mL methanol, respectively. Samples were then subjected to a mild alkaline methanolysis to become fatty-acid methyl esters, which were dissolved in 200 μL hexane. Internal standard (nonadecanoic acid methyl ester, 19:0)