Distributions and compositions of old and emerging flame retardants in the rhizosphere and non-rhizosphere soil in an e-waste contaminated area of South China

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ABSTRACT

We investigated rhizosphere effects on the distributions and compositions of polybrominated diphenyl ethers (PBDEs), novel brominated flame retardants (NBFRs), and dechlorane plus (DPs) in rhizosphere soils (RS) and non-rhizosphere soils (NRS) in an e-waste recycling area in South China. The concentrations of PBDEs, NBFRs, and DPs ranged from 13.9 to 351, 11.6 to 70.8, and 0.64 to 8.74 ng g^{-1} in RS and 7.56 to 127, 8.98 to 144, and 0.38 to 8.45 ng g^{-1} in NRS, respectively. BDE-209 and DBDPE were the dominant congeners of PBDEs and NBFRs, respectively. PBDEs, NBFRs, and DPs were more enriched in RS than NRS in most vegetables species. Further analysis suggested that the differentiation of the rhizosphere effect on halogenated flame retardants (HFRs) was not solely controlled by the octanol-water coefficients. This difference was also reflected by the correlations between total organic carbon (TOC) and PBDEs, NBFRs, or DPs, which indicated that organic carbon was a more pivotal controlling factor for PBDEs and DPs than for NBFRs in soil. We also found significant positive correlations between PBDEs and their replacement products, which indicated a similar emission pattern and environmental behaviour.

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1. Introduction

Halogenated flame retardants (HFRs) are used as additives to slow the spread of fire in numerous commercial and consumer products (Morf et al., 2005). As the historically brominated flame retardants (BFRs), commercial penta- and octa-polybrominated diphenyl ethers (PBDEs) have been added to the list of banned persistent organic pollutants (POPs) under the Stockholm Convention, as their environmental persistence has become apparent (Mohr et al., 2014). Restrictions on the use of PBDE congeners have paved the way for the use of "novel" BFRs (NBFRs), which commonly consist of decabromodiphenylethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (TBE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), hexabromobenzene (HBB), and pentabromoethylbenzene (PBEB) (Tian et al., 2012). In addition, dechlorane plus (DP), a widely used chlorinated flame retardant, is also of concern due to its bioaccumulative and potentially toxic effects.

Electronic waste (e-waste) recycling facilities have been highlighted as point sources of HFRs due to the unregulated waste-processing activities (Zhang et al., 2010; Huang et al., 2011; Leung et al., 2011; Wang et al., 2011b). The available information regarding the levels of HFRs in the areas around e-waste recycling sites is predominantly derived from studies of their distribution in environmental media, atmospheric transport and deposition, and soil-air-leaf exchange (Li et al., 2008; Leung et al., 2011; Chen et al., 2014). Data regarding the potential effects of the rhizosphere on the distribution and dissipation of HFRs in soil, especially for NBFRs, are notably lacking in the literature. However, soil is the principal receptor and an environmental reservoir for semivolatile organic contaminants (Wang et al., 2012). Thus, the fate of these contaminants in soil should be of concern, especially in rhizospheric soil, which might be associated with the pollutants being taken up by plants and subsequently resulting in an ecological risk.

The root-soil boundary represents one of the largest global biotic-abiotic mass—transfer interfaces and is a primary pollutant

entry point to the food chain (Limmer and Burken, 2014). Root rhizosphere can lead to different destinies of chemicals between rhizosphere soil and bulk soil, which could be linked to distinctive soil characteristics (White et al., 2002; Kaimi et al., 2006; Xu et al., 2010). For instance, degradation of organics to non-toxic or less-toxic compounds were more naturally occurred in rhizosphere soil than bulk soil, which can be attributed to the elevated microbial activity based on enhancement available carbon source derived from root exudations and other root depositions (Joner and Leyval, 2003; Gerhardt et al., 2009). In addition, enhancing the bioavailability of contaminants in soil solution, or the desorption of organic chemicals from soil organic matter (SOM) as a result of rhizosphere-mediated SOM decomposition, is a pivotal factor in determining the potential ecological risk (Welsh et al., 2009). Thus, the rhizosphere plays an important role in regulating the dissipation of chemicals in soil and soil-plant systems.

The importance of the rhizosphere community for the release or degradation of pollutants has been recognized; however, most previous studies have been conducted using pot experiments or artificial interference, in which chemicals tend to be bioavailable (Li et al., 2012; Becerra-Castro et al., 2013; Szoboszlay et al., 2015). Whether or not the results can be extrapolated to in situ contaminated sites is a significant concern and creates much uncertainty. There have been few investigations of the effects of the plant rhizosphere on the distribution, composition and bioaccumulation of established and emerging flame retardants around e-waste contaminated sites. Thus, we conducted this study on e-waste contaminated sites to: (1) identify the rhizosphere effect on the concentration of PBDEs, NBFRs, and DPs in soil; and (2) investigate the relationship among the distribution of PBDEs, NBFRs, and DP, and their possible influences from environmental variables.

2. Materials and methods

2.1. Study area

Our study area, the town of Guiyu, is located in eastern Guangdong Province [23° 3 N, 116° 03′E], South China. It is one of the most intensive e-waste recycling areas in China, where many home-based e-waste processing workshops have been established since the early 1980s. The agrotype in this area is red earth, and the average annual rainfall and temperature are 1721 mm and 21.5 °C, respectively (Yu et al., 2006).

The samples used in this study were in situ collected in the local vegetable gardens around the e-waste storage site in December 2012. In total, we collected 14 rhizosphere soils (RS) of different vegetable varieties and their corresponding non-rhizosphere soils (NRS). Plant was gently pulled from the soil, and the soil was mildly crushed and shaken to collect the soil located within 2 mm to the plant root surfaces which was defined as rhizosphere soil. Bulk soil located 10–20 cm away from the corresponding plant without significant root influence was collected as "non-rhizosphere" soil. (Wang et al., 2014). The 14 corresponding vegetables included cabbage lettuce (*Lactuca sativa L. var. capitata L*, P1), Chinese cabbage (*Brassica pekinensis*, P2), celery (*Apium graveolens*, P3), Chinese kale (*Brassica alboglabra L. H. Bailey*, P4), flowering cabbage (*Brassica campestris L. ssp.*, P5), shallot (*Allium fistulosum*, P6), cabbage (*Brassica oleracea var. capitata*, P7), radish (*Raphanus sativus L*, P8), taro roots (*Colocasia esculenta* (L.) *Schoot*, P9), crown daisy (*Chrysanthemum coronarium L.*, P10), pakchoi (*B. campestris L. ssp*, P11), snow peas (*Pisum sativum*, P12), sweet potato (*Ipomoea batatas* (L.) *Lam.*, P13), and lettuce (*var. ramosa Hort.*, P14) were also sampled randomly from the local vegetable gardens (Fig. 1), all of the vegetables were at least planted for 2 months. Each sample was composed of at least three subsamples taken from around the

Fig. 1. Sampling sites.

sampling site. All samples were wrapped with aluminium foil, placed in polythene zip-bags, and transported immediately to the laboratory. All of the samples were stored in −20 °C fridge until analysis.

2.2. Chemical analysis

2.2.1. Analysis of HFRs

Soil samples were freeze-dried and ground into fine powder. Subsequently, approximately 5 g of soil samples, spiked with relevant recovery standards (PCB 30, PCB 198, and PCB 209), were soxhlet extracted for 48 h with dichloromethane (DCM). The soil extracts were concentrated to ~0.5 mL after solvent-exchange to hexane. The extracts of soils were cleaned up using a multi-layer column that contained from the bottom to top: neutral alumina (3% deactivated), neutral silica gel (3% deactivated), 50% (w/w) sulphuric acid-silica gel, and anhydrous Na_2SO_4, with an eluent of 20 ml hexane/DCM (1:1, V/V). After being evaporated to approximately 50 μl, ^{13}C-PCB141 was added as the internal standard before instrumental analysis.

Gas chromatography-mass spectrometry using electron impact ionization and negative chemical ionization (GC-ENCI-MS: GC7890 coupled with 5975C (Mass Selective Detector (MSD), Agilent, Santa Clara, CA, USA) with a CP-Sil 13 CB column (15 m × 25 mm i.d. × 0.25 μm film thickness) was used to analyse BDE209. Other PBDEs (BDE28, 47, 99, 100, 153, 154, 183, and 209), dechlorane plus (DP), and NBFRs (TBB, TBPH, TBE, HBB, PBEB, and DBDPE) were analysed separately using a DB5-MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The analytical details have been described previously (Luo et al., 2015).

2.2.2. Total organic carbon (TOC) analysis

TOC in soil samples was determined using an elemental analyser (Vario EL-III, Elementar, Hanau, Germany) after the removal of carbonates with HCl. A detailed description of the method is reported elsewhere (Cheng et al., 2014).

2.3. QA/QC

A procedural blank, a spiked blank containing all the chemicals investigated and a duplicated sample were run with each batch of