



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 pentabromethylbenzene (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

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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; Szoboszlai 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, NBRFRs, and DPs in soil; and (2) investigate the relationship among the distribution of PBDEs, NBRFRs, 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 Na₂SO₄, with an eluent of 20 ml hexane/DCM (1:1, V/V). After being evaporated to approximately 50 µl, ¹³C-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 NBRFRs (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

10 samples to assess potential sample contamination and the repeatability of the analysis. With the exception of BDE-209 (mean 0.089 ng), none of the HFR congeners that we quantified were detected in the procedural blank. The surrogate recoveries for PCB 30, PCB 198 and PCB 209 in all samples were $59 \pm 19\%$, $82 \pm 14\%$ and $80 \pm 15\%$, respectively. The results of this study were corrected based on the surrogate recovery rates. The limit of quantitation for PBDEs, NBFrs and DPs is 22, 18, 29 pg/g respectively.

2.4. Data analysis

Statistical calculations, such as significant differences, correlations (Pearson), and principal component analysis, were performed using SPSS ver. 17.0. All of the data were normally distributed. The statistical significance of the differences and variance (p -value < 0.05) of the levels of HFR accumulation in soils were determined by paired sample t -test.

3. Results and discussion

3.1. Summary of PBDEs, NBFrs, and DPs concentrations in soil

The concentrations of PBDEs, NBFrs, and DPs in RS and NRS are plotted in Fig. 2. Overall, the concentrations of detected chemicals in RS were higher than in NRS. The concentration of PBDEs in RS ranged from 13.9 to 351 ng g⁻¹, while the corresponding concentrations in NRS ranged from 7.56 to 127 ng g⁻¹. The highest concentration of PBDEs was observed in the RS of cabbage lettuce, while the lowest concentration was recorded in the NRS of shallot. The geometric mean concentrations of the total PBDEs in RS and NRS samples were 50.6 and 35.4 ng g⁻¹, respectively. These values were similar to those reported for farmland soils in Qingyuan (2.9–207 ng g⁻¹) in South China (Luo et al., 2009) and for soils in the proximity of e-waste recycling areas (28.8–468 ng g⁻¹) (Cheng et al., 2014). However, they are much higher than in agricultural soils associated with e-waste dismantling activities in Hong Kong (0.60–8.07 ng g⁻¹) (Lopez et al., 2011). Such elevated values can be linked to the large usage of PBDEs as the flame retardants in China, which has experienced a sharp increase in recent years (Covaci et al., 2011).

The fluctuation in the levels of NBFrs among RS samples was not as strong as that of PBDEs, with the highest levels in RS and NRS

found in cabbage and snow peas, respectively. The concentration of NBFrs in RS and NRS ranged from 11.6 to 70.8 ng g⁻¹ and 8.98 to 144 ng g⁻¹, with geometric mean values of 23.90 and 24.68 ng g⁻¹, respectively. The concentrations reported here are higher than those reported for agricultural soils around the Pearl River Delta (28 ng g⁻¹) (Shi et al., 2009), but lower than those reported in agricultural soils around a BFR-manufacturing region in north China (111 ng g⁻¹) (Zhu et al., 2014).

Data regarding DP levels in soil are very limited. The concentrations of anti-isomer and syn-isomer were 0.64–8.74 ng g⁻¹ (geometric mean 3.47 ng g⁻¹) in RS and 0.38–8.45 ng g⁻¹ (geometric mean 2.80 ng g⁻¹) in NRS, respectively. These values were similar to those reported in industrial areas (0.03–4.65 ng g⁻¹), but much lower than those found at an e-waste recycling site in Qingyuan (3327 ng g⁻¹) (Yu et al., 2010).

As expected from previous studies, BDE-209 and DBDPE were the dominant congeners of PBDEs and NBFrs, respectively, accounting for more than 50% of Σ_8 PBDEs and Σ_6 NBFrs in both the RS and NRS at all sampling sites. Previous study has reported that DBDPE concentration was higher than BDE-209 in the background forest soil (Zheng et al., 2015). In contrast, we found no consistent relationships between DBDPE and BDE-209.

Variance analysis was performed to gain an insight of the accumulations of PBDEs, NBFrs, and DPs in RS and NRS of different vegetables species. As shown in Table S3 of SI, significance differences of PBDEs, NBFrs, and DPs accumulations in RS or NRS were observed among most of the vegetable species. On the whole, consistent significant differences were found for PBDEs, NBFrs, and DPs accumulations between RS and NRS of cabbage, as well as snow peas. The probably explanation would be linked to the differentiation of soil properties caused by the specific vegetable cultivation, and subsequently resulted in the discrepancy of chemicals distribution in RS and NRS.

3.2. Rhizosphere effect

Previous studies have reported a range of parameters affecting the dissipation of organics in the rhizosphere. For example, the concentration of PAHs has been shown to decrease logarithmically when moving toward the surface of a ryegrass root (Joner and Leyval, 2003). It also demonstrated that effects of degradation and dissipation leads to the concentration of PCBs in RS being lower than in bulk soils (Javorska et al., 2009). However, evidence of the rhizosphere effect on the release of adhered PBDEs in historically contaminated soil has also been reported previously (Wang et al., 2014). There is a publication indicating the enrichment of xenobiotic compounds in the rhizosphere, which is consistent with the results of this study. Similar results have also been reported for hydrophobic compounds, such as phenanthrene and pyrene, which can accumulate in the rhizosphere after their transport toward the roots is facilitated (Liste and Alexander, 2000). Such observations have created doubts regarding the dissipation effect of the rhizosphere on every xenobiotic compound. This discrepancy might be linked to several other factors including plant species, soil properties and chemical characteristics.

Our goal was to investigate the effect of the rhizosphere on the HFRs distribution in soil. We determined the C_{RS}/C_{NRS} ratio and plotted its relationship with the octanol-water coefficient (K_{ow}) of HFRs. The value of C_{RS}/C_{NRS} in most of the sampling sites was >1 , except for PBDEs in sweet potato ($C_{RS}/C_{NRS} = 0.37$), NBFrs in taro root ($C_{RS}/C_{NRS} = 0.11$), and DP in flowering cabbage ($C_{RS}/C_{NRS} = 0.52$). Root exudates are produced by the root fibrils of plants, and the release or desorption of POPs by root exudates has been demonstrated in previous studies (Luo et al., 2006). Thus, such anomalies might be attributed to the large volume of corms,

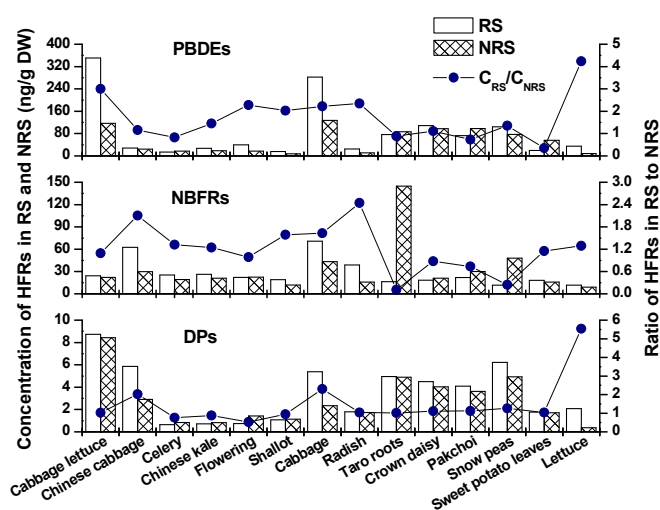


Fig. 2. Distribution of PBDE, NBFrs, and DPs in rhizosphere soil (RS) and non-rhizosphere soil (NRS).

relatively low root specific surface, and fewer root fibrils of these plant species, which would result in the reduced secretion of root exudates. Laboratory-derived C_{RS}/C_{NRS} measurements are often used to predict the rhizosphere effect on pollutants. For example, C_{RS}/C_{NRS} values of pyrene were reported to be 0.95, 0.92, and 0.93 at an initial pyrene concentration of 11, 52, and 106 mg kg⁻¹ (Ye et al., 2014). However, the soil-root boundary is complex and rarely at a steady state in the field. Degradation or adsorption may vary among plant species and varieties (Wiltse et al., 1998; Liste and Alexander, 2000), and different sampling procedures used to collect rhizosphere soil may also produce results that cannot be directly compared (Wang et al., 2014). Thus, the values of C_{RS}/C_{NRS} often vary more than laboratory-determined estimates.

Normally, K_{ow} is used to evaluate the potential sorption capacity of organic chemicals to SOM. Chemicals with a relatively high K_{ow} are likely to be strongly adsorbed to SOM and are difficult to desorb. The release or desorption of organic chemicals by root exudates, especially by organic acids, has been confirmed (Jones, 1998). Hence, the negative correlation of C_{RS}/C_{NRS} to the K_{ow} of PBDEs and NBFrs congeners may result from an increasing K_{ow} of the chemicals and a simultaneous desorption effect of PBDEs and NBFrs congeners from the rhizosphere. In agreement with this hypothesis, it has been shown that phenanthrene desorption in soils is promoted by the application of artificial root exudates to a greater degree than pyrene desorption, which can be attributed to the higher solubility of phenanthrene in water, and both its lower K_{ow} and molecular weight. Subsequently, the desorption of phenanthrene ($\log K_{ow} = 4.53$) is always greater than pyrene ($\log K_{ow} = 4.88$) at the same concentration of root exudates (Gao et al., 2010). In contrast to this hypothesis, we found no statistical relationship ($p = 0.075$ for PBDEs, $p = 0.157$ for NBFrs) between C_{RS}/C_{NRS} and K_{ow} , which indicated that the distribution of HFRs in RS and NRS was not solely influenced by the K_{ow} and rhizosphere effects (Fig. 3). The root-soil interface is complicated, and the fate of xenobiotic compounds in RS can be manipulated multifactorially. First, plant root exudates can activate the adhered compounds to pore water, and then enhance their transferability and bioavailability (Oleszczuk and Baran, 2007). Second, the degradation of xenobiotic compounds by indigenous microbes is improved, depending on the capacity of the contaminant degrader or plant promoting microbes to efficiently colonize growing roots (He et al., 2006; Gerhardt et al., 2009; Xia, 2012). Third, physicochemical

properties dominate the translocation of chemicals within plant tissue, which implies root uptake and transfer into shoot tissues occurs only for compounds falling within an intermediate hydrophobicity range ($0.8 < \log K_{ow} < 5.0$) (Dettenmaier et al., 2008). Thus, the plant species, biological characteristics of soil and chemical physicochemical properties are the major determinants of the fate of chemicals in rhizosphere colonization. In addition, chemotaxis towards specific root exudate compounds is also a key factor in efficient root colonization, and can be elicited by different compounds depending on the colonizing species (HarDOim et al., 2008). Although the “rhizosphere effect” occurs naturally, it can only do so given suitable plant-indigenous microbe pairs. Therefore, the differentiation of vegetable varieties may have had a large impact on the data presented here.

3.3. HFR profiles in soil

We plotted the homologue compositions of PBDEs and NBFrs to determine their profiles in soil (Fig. 4). Except the predominance of BDE-209 in PBDEs congeners, BDE-47 and penta-BDE (BDE-99 and BDE-100) were the major lower brominated PBDE homologue groups in RS and NRS, accounting for 5.69% and 6.96% of the PBDEs in RS, and 3.80% and 4.97% in NRS, respectively. As with previous studies, a clear predominance of BDE-47 among the lower brominated PBDEs congeners was confirmed once more here (Law et al., 2003).

With regard to NBFrs, DBDPE was the predominance congeners in NBFrs. We also found more abundant TBE in the RS than in the corresponding NRS in most samples. In addition, TBB plus TBPH are the major components of the commercial product Firemaster 550. Normally, the fraction of Firemaster 550 (represented by $C_{TBB}/C_{TBB+TBPH}$) is 0.77 ± 0.03 . However, the ratio of $C_{TBB}/C_{TBB+TBPH}$ here was 0.33 ± 0.15 ($N = 14$). This could be due to several factors. First, multidirectional sources of TBB or TBPH and multiple sources of individual compounds might lead to a different ratio than is typical for Firemaster 550. Second, the $\log K_{ow}$ coefficient of TBB ($\log K_{ow} = 8.75$) and TBPH ($\log K_{ow} = 10.1$) also indicated that TBPH tended to be more persistent and accumulative than TBB in the environment, which would in turn lower the $C_{TBB}/C_{TBB+TBPH}$. An analogous result was observed in another study that focused on the atmospheric levels in North America ($C_{TBB}/C_{TBB+TBPH} = 0.45 \pm 0.02$) (Ma et al., 2013). Generally, NBFr congeners, such as TBE, tended to be concentrated in RS, while the composition of lower brominated PBDEs didn't show the similar results. This might be an indication that NBFrs are influenced by the rhizosphere more profoundly than PBDEs. It has been reported that the desorption of phenanthrene and pyrene in soil is markedly influenced by the addition of artificial root exudates, and the desorption effects depend on the aging time and soil properties (Gao et al., 2010). Hence, it is likely that the residence time of PBDEs in soil is much longer than that of NBFrs in the study area, resulting in differences in their bioavailability.

The fraction of *anti*-DP and *syn*-DP within the total DP is generally used when discussing the environmental transportation and fate of the two structural isomers. We calculated f_{anti} as the concentration of *anti*-DP divided by the total concentration of *anti*- and *syn*-DP. The f_{anti} ranged from 0.48 to 0.58, with an average value of 0.54, which can be compared with the values in the commercial DP product ($f_{anti} = 0.75–0.8$). This suggests that the main source of DP in the study area might not be the raw commercial DP product, or due to the different environmental fates of *anti*-DP and *syn*-DP. *Anti*-DP is more environmentally persistent than *syn*-DP, which increase the value of f_{anti} . Previous investigations in areas adjacent to this study region in 2012 reported a f_{anti} of 0.74 (mean) in surface soil (Yu et al., 2010), which is very close to that of the commercial product. However, these somewhat

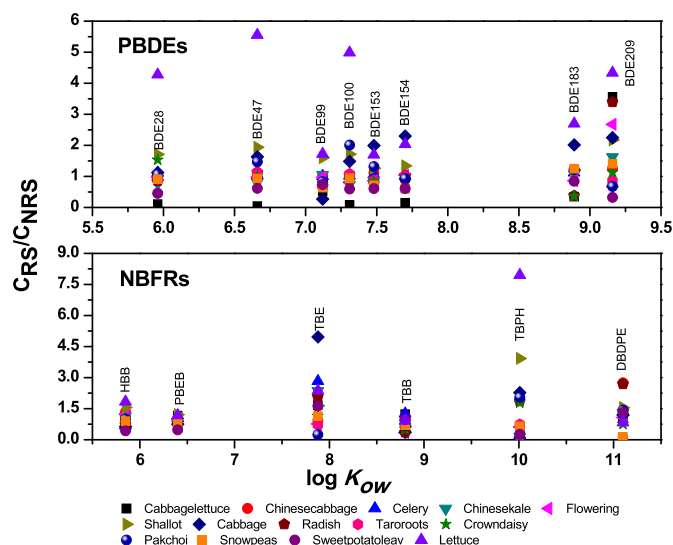


Fig. 3. Relationship between C_{RS}/C_{NRS} and $\log K_{ow}$ of PBDEs and NBFrs.

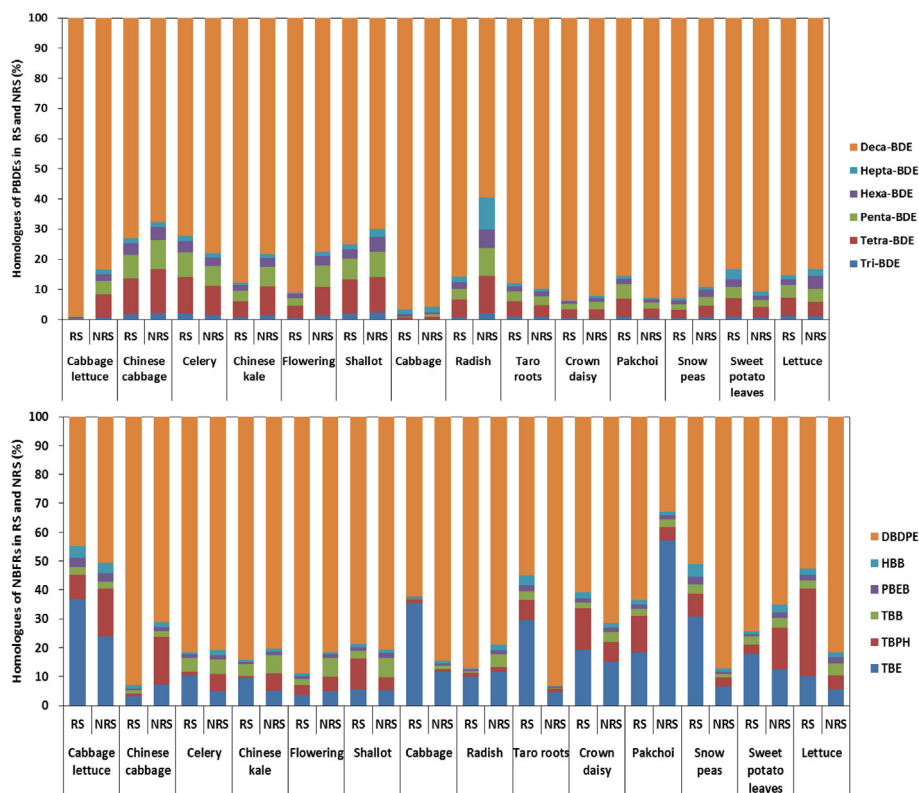


Fig. 4. Homologue patterns of PBDEs and NBFrs in RS and NRS.

lower f_{anti} values in the present study may indicate the preferential environmental degradation of the *anti*-isomer. Probably, the different biotransformation of DP congeners could explain the relatively low f_{anti} values reported here.

3.4. The co-linearity relation between HFRs in RS and NRS

Further analysis of the levels of HFR congeners in RS and NRS were performed to determine the rhizosphere effect on the distribution of HFRs (Table S1). Significant positive correlations in the levels between RS and NRS were found for BDE-153, BDE-183, and BDE-209, while no statistical relationships were found for lower brominated biphenyl (BDE-28 and BDE-47) between RS and NRS. These results seem to imply that the effects of the rhizosphere were more pronounced for the lower than for the higher brominated PBDEs. However, as mentioned in section 3.2, we did not expect $C_{\text{RS}}/C_{\text{NRS}}$ and K_{ow} to be negatively correlated. Such a relationship could be related to several factors, of which the source of HFRs and the potential biodegradation of specific congeners should be emphasized. On the one hand, BDE-47 is one of the most abundant PBDE congeners in most environmental media, which is consistent with our results (Fig. 4). On the other hand, indigenous functional microbes might be capable of degrading PBDEs after being acclimated for a long time. For example, the microbial degradation of BDE-47 was accelerated in RS due to the increased abundance of bacteria in the rhizosphere (Chen et al., 2015). In addition, the biotransformation of higher-brominated PBDE (e.g., BDE-209) congeners to lower-brominated PBDE congeners (e.g., BDE-47) occurs naturally in the environment (Gandhi et al., 2011). Thus, the impact of biological processes on chemicals, triggered by root and root secretions, should also be a focus of studies of the rhizosphere.

In contrast, significantly positive correlations in the levels between RS and NRS were found for PBEB ($r = 0.888$, $p = 0.001$) and

HBB ($r = 0.867$, $p = 0.006$) while no statistical relationship were found for other NBFrs congeners between RS and NRS. Rhizosphere effects were confirmed to be enhanced in heavily polluted areas compared to recently contaminated soils (Wang et al., 2014). Unlike PBDEs, NBFrs can be regarded as emerging xenobiotic compounds, which have not become tightly adhered to SOM over their relatively short history of use. This means that NBFrs in soils were, to some extent, more likely to be bioavailable than PBDEs and that the effect of roots on NBFrs was relatively profound, which was also shown by the relationship between TOC and HFRs in soil (see section 3.5). In addition, the levels of *anti*-DP and *syn*-DP in RS were both significantly correlated with the levels in NRS ($r = 0.838$, $p = 0.004$ for *anti*-DP; $r = 0.928$ for *syn*-DP, $p = 0.003$).

Another aim of our study was to investigate how market shifts may have influenced the environmental levels and distribution of HFRs in soils. As mentioned, DBDPE, TBE, and a mixture of TBPH and TBB have been used as replacements for deca-BDE, octa-BDE and penta-BDE. Thus, theoretically, negative correlations should be found between the concentrations of PBDEs and NBFrs in soil, which would be a result of the declining emissions or degradation of PBDEs and increasing emissions of NBFrs due to market shifts. However, total PBDEs in soils were positively correlated with total NBFrs in this study region ($r = 0.311$, $p = 0.04$). We also found a positive correlation between soil BDE-209 and soil DBDPEs ($r = 0.121$, $p = 0.03$), as well as penta-BDE and Firemaster 550 ($r = 0.685$, $p = 0.007$). These positive relationships indicated that they were from the similar sources. They also suggested that the replacements of deca-BDE by DBDPE and penta-BDE by Firemaster 550 were not yet evident in the e-waste handled at this site. These results were consistent with an earlier study of the distribution of NBFrs in background soil (Zheng et al., 2015).

Because of the similar properties of BDE-209 and DP, it is interesting to compare the environmental fates and behaviours of these two compounds. DP levels in this study were significantly

lower than those of BDE-209, which is consistent with a previous study, which reported that BDE-209 has a much higher worldwide use and production than DP (Yu et al., 2010). We also found significant correlations between the levels of BDE-209 and DP in RS and NRS respectively ($r = 0.755$, $p = 0.002$ for RS; $r = 0.693$, $p = 0.006$ for NRS), suggesting that BDE-209 and DP originated from similar sources. These results were consistent with the results of a previous study that indicated that DP and BDE-209 were significantly correlated in Dalian coastal sediments in China (Wang et al., 2011a).

3.5. Environmental factors

SOM was considered to be the key parameter controlling the distribution of POPs in soil (Sweetman et al., 2005). Normally, TOC is used to represent SOM; hence, we assessed correlations between TOC and soil HFRs to determine the potential influences of TOC on the environmental processes of HFRs (Table S2). The assessment showed that PBDEs and DP were significantly positively correlated with TOC ($r = 0.800$, $p = 0.001$ for total PBDEs; $r = 0.852$, $p = 0.004$ for PBDEs excluding BDE-209; $r = 0.924$, $p = 0.005$ for DP). There was no statistic relationship between NBRFs and TOC ($r = 0.193$, $p = 0.510$). Thus, we speculate that the influences of TOC on established and emerging HFRs in soil varied greatly, and that TOC was not the main factor controlling the distributions of emerging pollutants in soils.

To obtain better insight into the patterns of pollution among different contaminants, we conducted a principal component analysis (PCA). As shown in Fig. 5, the first two principal components (PCs) explained about 80.0% of the total variance. In the loading plot, component 1 accounted for 63.4% of the total variance and was strongly correlated with DP, HBB, PBEB, and hexa- and penta-BDE, indicating a similar source for these compounds in this region. Component 2 accounted for 16.6% of the total variance and had strong positive loadings on BDE-183, TBE, and BDE-209. Most of the PBDE congeners had a high loading in PC1, implying that these chemicals may have similar sources. TBB had a low loading in both factors, indicating that this compound might have some different sources from the other chemicals. This agrees well with the values of $C_{TBB}/C_{TBB+TBPH}$ reported in this study.

4. Conclusions

We investigated the in situ rhizosphere effects on the

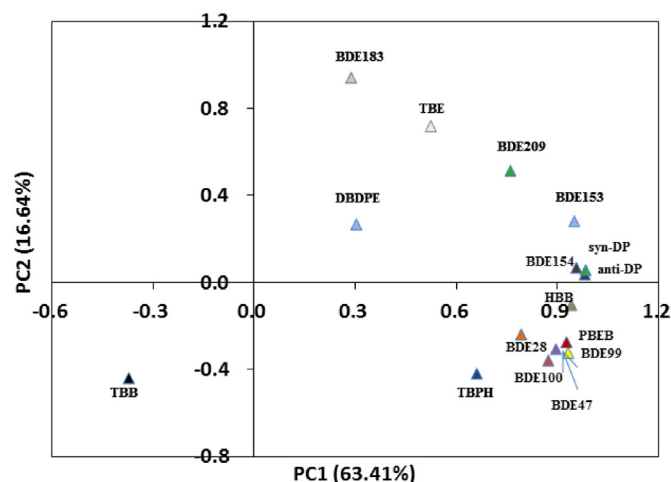


Fig. 5. Principal components analysis results based on the concentration of PBDEs, NBRFs, and DPs congeners.

distribution of old and emerging HFRs in soils around an e-waste contaminated site. Higher abundances of PBDEs, NBRFs, and DPs were observed in RS, suggesting that the enrichment of PBDEs, NBRFs, and DPs by plant roots occurred at the contaminated site. The relationship between C_{RS}/C_{NRS} and K_{ow} indicated that the fate of HFRs in the rhizosphere was not solely dependent on the K_{ow} . This rhizosphere effect was more prominent for the “emerging” NBRFs than the “established” PBDEs and DPs, which was also evidenced by the correlation between HFRs and TOC. This is an indication that the influence of environmental parameters and the rhizosphere effect might vary greatly between old and emerging flame retardants. In addition, significant positive correlations between BDE-209 and DBDPE, and penta-BDE and Firemaster 550 indicated that the replacements of BDE-209 by DBDPE and penta-BDE by Firemaster 550 are not yet evident. More attention should also be given to the translocation of HFRs from soil to roots and shoots, which might be associated with the safety of the ecosystem, as well as human health.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.10.038>.

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