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The influence of land use on the concentration and vertical distribution of PBDEs in soils of an e-waste recycling region of South China

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ABSTRACT

The vertical distribution of polybrominated diphenyl ethers (PBDEs) in soil at four sites within an e- waste recycling region of South China was investigated. PBDE concentrations in soil ranged from 1.38 to 765 ng/g. There was a trend of decreasing PBDE concentration with soil depth, especially in the paddy field. However, high concentrations of BDE-209 were found in deeper soils indicating a highly preferential migration. There was a stronger correlation between PBDEs and total organic carbon (TOC), compared to dissolved organic carbon (DOC), which suggests that the association between non-dissolved organic carbon (NDOC) and PBDEs is stronger than for DOC. Different land use types, in particular differences in farming activities, significantly influenced the vertical distribution of PBDEs in soils. PBDEs displayed a higher leaching tendency in moist paddy soil than in drier soils. The frequent flooding condition in paddy field may facilitate the vertical transfer of PBDEs to the deeper soils.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a group of halogenated chemicals (Zhang et al., 2010), that are ubiquitous in the environment (Hassanin et al., 2004; Miglioranza et al., 2013) and are considered persistent organic pollutants (POPs) due to their persistence, toxicity, bioaccumulation, and long-range atmospheric transport (Wang et al., 2014). PBDEs have been intensively used as brominated flame retardants in a wide array of materials over the past two decades, especially in electronic products (Wu et al., 2008). Commercial penta- and octa-BDE are PBDEs that were targeted for control and elimination by the Stockholm Convention in 2009;

however, commercial deca-BDE has not been restricted and remains in production. China uses about 20,000 to 40,000 tons of commercial deca-BDE per year (Li et al., 2014).

Soils, due to their strong sorption property and holding capacity, act as the major reservoir and sink for PBDEs. The sorption and desorption that occurs between PBDEs and organic matter are key processes that influence the mobilization and migration of PBDEs in soil (Hassanin et al., 2004; Mueller et al., 2006). PBDEs can adsorb to the surface of mineral particles or colloids in soil, particularly clay minerals (Weber et al., 1999; Harner and Shoeib, 2002). The strong tendency of PBDEs to bind to soil means that these chemicals can migrate with the transport of fine soil particles. The solubility and migration of PBDEs can also be enhanced by the presence of dissolved organic carbon in soil solution, despite the hydrophobic nature of PBDEs (Wessel-Bothe et al., 2000; de Jonge et al., 2008). Previous research has also found that the type of land use can affect the distribution and transfer of PBDEs in surface soils (Wang et al., 2010, 2011a), especially in areas that are cultivated with plants. Plants can either chemically or biologically enhance the degradation of organic pollutants (Baudoin et al., 2003; Rentz et al., 2005), as well as facilitate the transport of those compounds in soil by producing large quantities of dissolved organic carbon, such as sugars, amino acids, and fatty acids (Hodge et al., 1996; Bertin et al., 2003; Wang et al., 2014).

Currently, e-waste, which is generated from the disposal of electronic products, has become one of the fastest growing streams of waste due to the rapid emergence of new technologies. Unregulated e-waste recycling has resulted in the release of large quantities of PBDEs and other toxic chemicals into the environment, particularly in locations such as Qingyuan and Guiyu of South China (Wu et al., 2010; Luo et al., 2011). So far, most of the previous research on chemicals released from e-waste has focused on measuring the concentration in topsoil, sediment, air (Ma et al., 2009; Wang et al., 2011a), as well as quantifying human exposure (Bi et al., 2007; Yuan et al., 2008). However, there is little information available on the potential for PBDEs to migrate within and be transported from e-waste contaminated soils. This information is crucial to developing a comprehensive environmental risk assessment and effective site management program for e-waste pollution. The objectives of the present study were (1) to investigate the vertical distribution and migration potential of PBDEs in soil and (2) investigate the factors influencing the migration of PBDEs to deeper soils in the e-waste contaminated area of South China.

MATERIALS AND METHODS

Sampling collection

The sampling sites were located in the small village of Longtang Town [23° 34’ N, 113°1’ E], in Qingyuan City, Guangdong province, a copper-recycling region of South China (See Fig. 1). Land use activities in this area include a legacy of unregulated e- waste recycling, which involved open burning or acid processing of waste products to extract copper, which occurred for more than 30 years before it was banned several years ago, along with traditional agriculture such as rice and peanut farming. We collected soil cores from sites with four different land uses: an e-waste recycling site (ERS), a paddy field (PAF), a peanut field (PEF), and a reference site (RFS), which represent the most typical land use types in the e-waste recycling region. The reference site was a sparsely vegetated hilltop that experiences relatively less human disturbance, as it is >10 km away from the e-waste recycling facilities and was selected to represent relatively unpolluted soils by e-waste recycling activities. It is important to note that the paddy and peanut fields experience seasonal plowing, which affects the soil profile to a depth of about 20 - 30 cm.

Soil cores (0 - 80 cm) were collected in June 2011 using a stainless steel, hand- held auger (i.d.: 5 cm, length: 1 m). For each soil core, we gently excavated a pit at the site location and then collected soil profiles from the side of the pit. Soil depths were carefully measured using the scale marks on the auger, and any loose decaying litter was removed from the soil core. To reduce any cross contamination, the auger was carefully washed with water before collecting the next soil profile. Five soil cores were collected at each sampling site. After each soil core was collected they were immediately sliced into 10-cm sections on a polyethylene sheet, then corre- sponding 10-cm sections among the five core samples were mixed. All samples were wrapped with aluminum foil, put into polyethylene zip bags, transported to the laboratory, and stored at -20 ^{o} C.

Sample extraction and cleanup

All soil samples were freeze-dried, passed through a 2-mm sieve, and ground with an agate mortar. About 20 g soil was homogenized, spiked with surrogate standards (PCB-198 and PCB-209), and was extracted with dichloromethane (DCM) in a Soxhlet for 48 h with activated copper to remove any elemental sulfur. Following a solvent-exchange with hexane and concentrating to a volume of about 0.5 mL, the soil extract was purified by passing it through a multi-layer column filled with anhydrous Na_2SO_4, 50% (w/w) sulfuric acid-silica gel, neutral silica gel (3% deactivated), and neutral alumina (3% deactivated), from top to bottom, respectively, with an eluantof 20 mL hexane/DCM (1:1, v/v). The soil extract was then concentrated to approximately 20 mL using a gentle stream of N2, and was spiked with BDE-77 as the internal standard prior to analysis.

PBDE analysis

We quantified seven PBDE congeners (BDE-28, 47, 99, 100, 153, 154, and 183) using a GC-ECNI-MS (Agilent GC7890 coupled with 5975C MSD) with a DB5-MS capillary column (30 m x 0.25 mm i.d. x 0.25 µm) under SIM mode. BDE-209 was analyzed separately using a GC-ECNI-MS with a DB5-HT capillary column (15 m x 0.25 mm i.d. x 0.1 µm). The temperature program for the oven started at 110 ^{o} C (held for 5 min), increased at a rate of 15 ^{o} C/min to 200 ^{o} C (held for 3 min), then increased at a rate of 5 ^{o} C/min to 295 ^{o} C (held for 12 min). The injector temperature was kept constant at 290 ^{o} C, and the temperature for both the MSD source and quadrupole was kept at 150 ^{o} C.

QA/QC

A procedural blank, field blank, and spiked blank, consisting of all the chemicals used in the soil extraction process, were analyzed after every 12 samples to deter- mine if any contamination occurred during sample collection, extraction, or analysis. With the exception of BDE-209 (mean 0.096 ng), none of the seven PBDE congeners that we quantified were detected in laboratory blanks. The average recovery for the spiked blanks was 91.5 ± 9.5%. Instrumental detection limits

(IDLs) were 0.004 - 0.025 ng for the seven PBDEs (BDE-28, 47, 99, 100, 153, 154, and 183) and 0.080 ng for BDE-209. Concentrations below the IDLs were reported as not detected (N.D.). Method detection limits (MDLs) for the seven PBDEs in soil were 0.003 - 0.008 ng/g, and 0.020 ng/g for BDE-209. The surrogate recoveries for PCB-198 and PCB-209 were 84.1 ± 14.5% and 85.6 ± 13.1%, respectively. All reported concentrations of PBDEs were corrected by blanks, but not by the surrogate recoveries. All concentrations were normalized to dry soil weight.

Total organic carbon and dissolved organic carbon analysis

Briefly, about 1 g of dry soil was treated with 10% HCl to remove inorganic carbon, which was then washed with Milli-Q water until achieving a neutral pH (7 ± 0.2), and was dried overnight at 60 ^{o} C. Total organic carbon (TOC) in the soil sample was then quantified by flash combustion at 1030 ^{o} C followed by thermic conductivity detection with a Vario EL-III elemental analyzer. Acetanilide was used as an external standard. The MDL was 0.01%, and reproducibility of replicated standard is better than 0.001&. All values were normalized to the initial mass of the sample prior to any treatment.

Dissolved organic carbon (DOC) was quantified in water extracts with a carbon analyzer. Briefly, 2.5 g of fresh soil was added to 25 mL of Milli-Q water in a 50-mL centrifuge tube and shaken for 1 h. The suspension was centrifuged at 3000 rpm for 10 min, and then the supernatants were filtered through 0.45-µm polycarbonate filter membrane and acidified with 10 µL of 37% HCl (excessive amounts) to eliminate any inorganic carbon. The filtrate was analyzed for DOC using a TOC-VCPH analyzer (Shimadzu, Japan).

RESULTS AND DISCUSSION

PBDEs in surface soils

The concentration profiles of PBDEs in soil form the four land use types are presented in Fig. 2. The concentrations of the 7 PBDEs except BDE-209 (i.e. $PBDE_{sexc209}$) in the surface soils (0 - 20 cm) ranged from 0.12 ng/g (reference site, 10 - 20 cm) to 297 ng/g (e- waste site, 0 - 10 cm), while BDE-209 ranged from 28.8 ng/g (paddy field, 10 - 20 cm) to 468 ng/g (e-waste site, 0 - 10 cm). As expected, the highest concentrations of both $PBDE_{sexc209}$ and BDE-209 were found at a depth of 0 - 10 cm in soil at the e-waste site, indicating that the soil had been heavily contaminated by e-waste recycling activities. The lowest concentrations were measured at the reference site, which is >10 km distant from the e-waste recycling area and experiences less anthropogenic interference.

The paddy field was close to the peanut field, and both fields were <1 km distant from the e-waste site. Therefore, the amount of PBDEs that the paddy and peanut fields receive from atmospheric transport is likely similar to the amount of PBDEs generated at the e-waste site. Both the paddy and peanut field receive irrigation water from the same pond; however, the paddy field is irrigated more intensively than the peanut field. This suggests that PBDE concentrations in the paddy field would at least be similar to or even higher than that in the peanut field. The total concentration of the seven PBDE congeners in surface soil was approximately the same for the peanut and paddy fields, with the exception of BDE- 209 that was more than fourfold higher in the surface soils of the peanut field compared to the paddy field. Differences in the crop, tillage patterns, and/or irrigation frequency may have contributed to the difference in concentration and transfer of PBDEs in the paddy and peanut fields, despite their similar proximity to the e-waste recycling site. Rice is a semi-aquatic plant and requires ample water during the growing period. Therefore, the paddy fields need to be flooded regularly during the growth stage, which could lead to an increase in contaminant inputs via irrigation water. However, the concentrations of PBDEs in paddy field were low or comparable to those in the peanut field. Thus, the fate of PBDEs in the moist soil of paddy fields may be different than that for dry soil. During the flooding period, contaminants may experience three processes that could dramatically influence their fate in paddy field sediment. First, there may be some leaching of PBDEs with water alone or with fine particles in water, but more likely for leaching to occur with dissolved organic carbon. Second, PBDEs can be transported to nearby surface waters through mechanical and soil-solution runoff with surface soils. And finally, vaporization rates are greater in moist paddy soils due to the co-evaporation of more volatile PBDEs with water (Hippelein and McLachlan, 2000). Since the volatility of BDE-209 is very low, the low levels of BDE-209 in the topsoil of paddy fields can mostly be attributed to the adsorption to particles associated with leaching or runoff.

The total PBDE concentrations in paddy and peanut surface soils (31.7 - 143 ng/g) were comparable to those from other studies conducted near our study sites: 45.1 - 102 ng/g (Wong et al., 2007), 28.1 - 122 ng/g (Zou et al., 2007), and 9.7 - 51.7 ng/g (Wang et al., 2011b); however, they were much higher than reference areas in Tibet 0 - 0.027 ng/g (Wang et al., 2012) or Europe 0.065 - 12 ng/g (Hassanin et al., 2004). This suggests that even several years following the ban on unregulated recycling activities, soils in this e- waste recycling region remain heavily polluted. However, the relatively high concentration of BDE-209 in soil from the reference site may imply this site has been exposed to more PBDE contamination than expected.

Vertical distribution of PBDEs in soil cores

Fig. 2 also shows the vertical distribution of PBDEs in soil from the four different types of land use. The total concentrations of $\text{PBDE}_{\text{sexc209}}$ and BDE-209 in soil were highest at a depth of 0 - 10 cm or just below, and decreased thereafter with soil depth. PBDEs found in the deeper layers of soil (20 - 80 cm) were much lower in concentration than in the surface layers (0 - 20 cm), with a range of 1.37 - 203 ng/g and 0.01 - 17.9 ng/g for BDE-209 and $\text{PBDE}_{\text{sexc209}}$, respectively. In general, PBDE concentrations decreased exponentially with soil depth in all soil types, both in total or individual PBDE concentration (Figs. S1 - S4). Pearson analysis revealed significant negative correlations between soil depth and PBDEs ($p < 0.05$). These results are consistent with the vertical distributions reported for other POPs, such as PAHs, PCDD/Fs, PCBs, and PBDEs in agriculture or natural soils (Moeckel et al., 2008; Yang et al., 2010; Bergknut et al., 2011; Zhang et al., 2011).

Concentrations of PBDEs in the deep layers of soil at the e-waste site were much higher than other 3 sites, especially the reference site. The ratio (r) of PBDEs in deep soil layers (30 - 80 cm) to the total PBDE burden of soil core (0 - 80 cm) (i.e., $r = C_{30\text{-}80}/C_{0\text{-}80}$) was 49.7%, 67.5%, 44.4%, and 41.7% for BDE-209 and 17.4%, 59.5%, 27.5%, and 69.2% for $\text{PBDE}_{\text{sexc209}}$, at the e-waste site, paddy field, peanut field, and reference site, respectively. High C30e80/C0e80 ratios may suggest that there is a high tendency for PBDEs to migrate to deeper soil, presenting an increased risk for groundwater contamination. Surprisingly, the results implied that the transfer tendency of BDE-209 to deeper soil is higher than for other PBDE congeners in the more contaminated areas (i.e., e-waste site, paddy, and peanut fields). BDE-209 is a highly hydrophobic compound with a high logK_{ow} (9.97) and low water solubility (4.17 x 10^{-9} mg/L). Once BDE-209 interacts with soil, it binds strongly with soil particles or colloids, with little to no dissolution in soil water. Thus, the transfer of BDE- 209 to deep soil layers depends mostly on the transport associated with fine particulates and colloids via a preferential flow mechanism. A number of studies (McGechan and Lewis, 2002; Petersen et al., 2003; de Jonge et al., 2004; McCarthy and McKay, 2004) have shown that soil particulates and colloids can facilitate the transports of various contaminants, including atrazine (Laird et al., 1994) and phenanthrene (Magee et al., 1991), via a preferential flow phenomenon. The high irrigation frequency in paddy and peanut fields may also enhance the leaching of PBDEs via preferential flow. The preferential flow hypothesis, however, requires further research to be substantiated. Besides differences in physicochemical properties among PBDE congeners, the relatively higher mobility of BDE-209 in soil may also be attributed to a higher con- centration or environmental burden of BDE-209 in comparison to other PBDEs. High concentrations of BDE-209 in soil may enhance the difference in fugacity between soil matrices, and thereby in- crease the opportunity or tendency of BDE-209 to partition from bulk soil to fine soil particles; this may also lead to increased transport of BDE-209 with fine soil particles. The high mobility of BDE-209 is also evidenced by the relatively high concentration of BDE-209 in the 30 - 40-cm layer of the reference core, accounting for 14.1% of the total BDE-209. Differences in land use patterns may also influence the leaching of PBDEs to deep soil layers. The higher C_{30-80}/C_{0-80} ratios of PBDEs in the paddy field compared with those in the peanut field may be the result of a higher irrigation rate in the paddy field, which could facilitate the leaching of PBDEs to deeper soils, compared to the peanut field. In the peanut field, water movement in soil is dominated by a transient infiltration mechanism that is driven by instant rainfall or occasional irrigation, which can result in the rapid mobilization and transport of an initial peak of colloids (DeNovio et al., 2004). The increase in colloid mobilization may also enhance the vertical transport of organic chemicals adsorbed to those colloids. In the paddy field, water movement is dominated by a steady-state unsaturated flow as a result of frequent flooding. Therefore, it is likely that the transport of colloids and their associated organic chemicals in a paddy field is different from that in a peanut field (Cousins et al., 1999).

Composition of PBDEs in soil cores

BDE-209 was the most dominant PBDE congener found in soil cores, accounting for more than 84% of the total PBDEs, with the exception of surface soil at the e-waste site (61%, see Fig. 3). This is consistent with the fact that deca-BDE mixtures, of which BDE-209 is the major component, are the most widely PBDEs still being produced and used as commercial flame retardants (Wang et al., 2011b). A similar pattern was found in previous studies on soils and sediments near our study site in South China, in which BDE-209 was also the most dominant PBDE congener (Chen et al., 2006; Wang et al., 2011b). BDE-183 was the second most abundant PBDE congener measured in this study, especially in samples from the e-waste site, accounting for 28% of the total PBDEs. The higher portion of BDE-183 at the e-waste site compared to the other sites indicates additional input of octa-BDE mixtures from e-waste products (Zou et al., 2007).

Generally, the composition of PBDEs did not display any significant or consistent trend with soil depth (Fig. 3). Since the sur- face layer (0 - 20 cm) could be significantly influenced by tillage patterns or human activities, PBDEs detected in this depth should be excluded when considering variations in composition with soil depth. PBDE profiles were similar among different soil layers (>20 cm in depth) for the e-waste or reference sites respectively, which indicates that nonselective transport may be the dominant mechanism involved in the movement of PBDEs in soils in areas that experience less anthropogenic influence. This may be attributed to constant heavy rainfall (annual precipitation >2200 mm) and soil with relatively low total organic carbon (0.26 - 0.92%), which can result in the rapid mobilization and transport of an initial peak of colloids and their associated organic compounds. However, for soils in the paddy and peanut fields, significant changes in the relative abundance of PBDE congeners were observed between two adjacent layers, especially for low molecular weight PBDEs such as BDE-47 or BDE-99 (Fig. 3). PBDE compositions between adjacent soil layers were similar at the e-waste and reference sites but different at both of the farmland sites, which was probably due to differences in farming activities, such as tillage patterns and/or irrigation frequency.

This study found a lower abundance of the less brominated PBDE congener (i.e., BDE-28, 47, 100, 99) and a higher abundance of the more brominated congener (i.e., BDE-183 and 209), compared to a study conducted in the same area 4 years ago by Wang et al. (2011b). The differences between studies can be attributed to the high volatility associated with less brominated PBDEs, as they would have preferentially volatilized over the more brominated PBDEs, and the change in PBDEs over time indicates that levels of the less brominated PBDEs have been decreasing in topsoil since the banning of unregulated e-waste recycling in this area.

Factors influencing the vertical distribution of PBDEs in soil

Many factors can influence the vertical distribution of POPs in soil, such as climate condition, TOC, DOC, and land use types or farming patterns. Since the sample collection sites were close in proximity (<10 km apart), it is unlikely that climate contributed to the differences in the distributions of PBDEs in the soil cores we collected. Past studies have found that differences in land use can lead to differences in the concentration or composition of POPs in topsoil (Toms et al., 2008; Wang et al., 2010, 2011a), particularly in agricultural areas where soil and associated organic compounds are heavily influenced by plant roots and their exudates, as well as farming activities (Saison et al., 2004). We also found that different types of land use, in particular differences in farming activities such as crop type, tillage patterns, and irrigation frequency, can influence the vertical distribution of PBDEs in the soil (Figs. 2 and 3). Differences in the biogeochemistry of soil, such as the TOC or DOC content, may also affect the vertical distribution of PBDEs in soil (Andrade et al., 2010). The vertical distributions of TOC and DOC in the soil cores from the four sites in this study are presented in Fig. 4. Similar to PBDEs, the distributions of TOC and DOC also decreased with soil depth, and we found significant correlations between the concentration of total PBDEs, PBDEsexc209, and BDE-209 and soil TOC (all p values < 0.01) and DOC (all p values < 0.05). Although the statistics did not automatically imply a causal correlation, it still suggested that organic carbon had a significant influence on the vertical distribution of PBDE congeners in soil. The correlation between PBDEs and DOC was less significant than that for TOC suggests that non-dissolved organic carbon (NDOC) in soil may have a greater impact on the adsorption or retention of PBDE congeners than DOC. In conclusion, the biogeochemical properties of soil and the factors that can influence these properties, such as farming patterns or land use types, seem to be the main factors that control the vertical distribution of organic chemicals in soil.

CONCLUSIONS

The unregulated recycling and disposal of e-waste has led to serious environmental problems for the surrounding agricultural areas in South China. The results of this study demonstrated that the transfer of PBDEs in moist paddy field soil was higher than that in dry soil. Different land use types, in particular differences in farming activities, can affect the vertical transport of organic pollutants like PBDEs, especially for paddy fields that experience frequent flooding. The results of our study also suggest that PBDEs may preferentially adsorb to NDOC in soil than DOC. The transfer of POPs in contaminated soils at the e-waste recycling area, especially to deeper soil layers, may pose a potential risk for groundwater contamination. Therefore, strict control and management of the contaminated area is highly recommended to avoid secondary pollution. Further studies are urgently necessary for a comprehensive risk assessment of e-waste recycling sites and their impact on surrounding areas.

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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.2014.04.025.

FIGURES

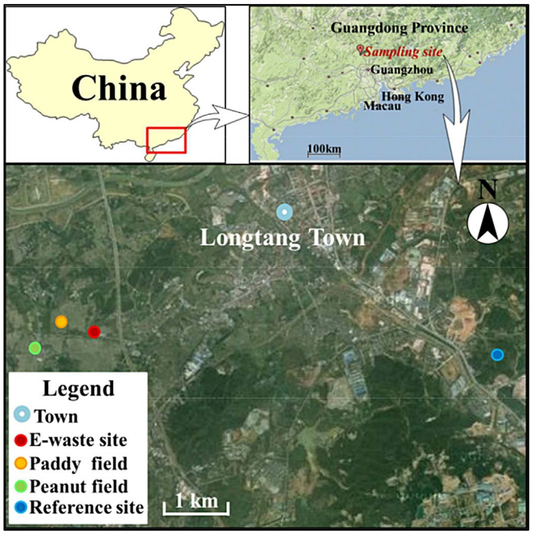

Fig. 1. Sampling locations.

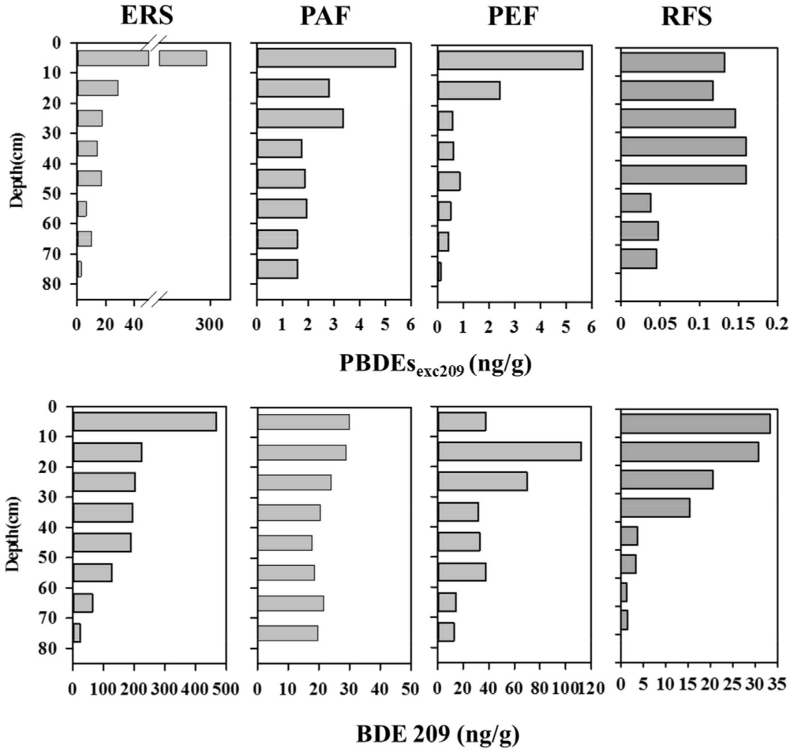

Fig. 2. Vertical distributions of PBDE concentrations in different soil cores. (ERS: E-waste recycling site; PAF: Paddy field; PEF: Peanut field; RFS: Reference site).

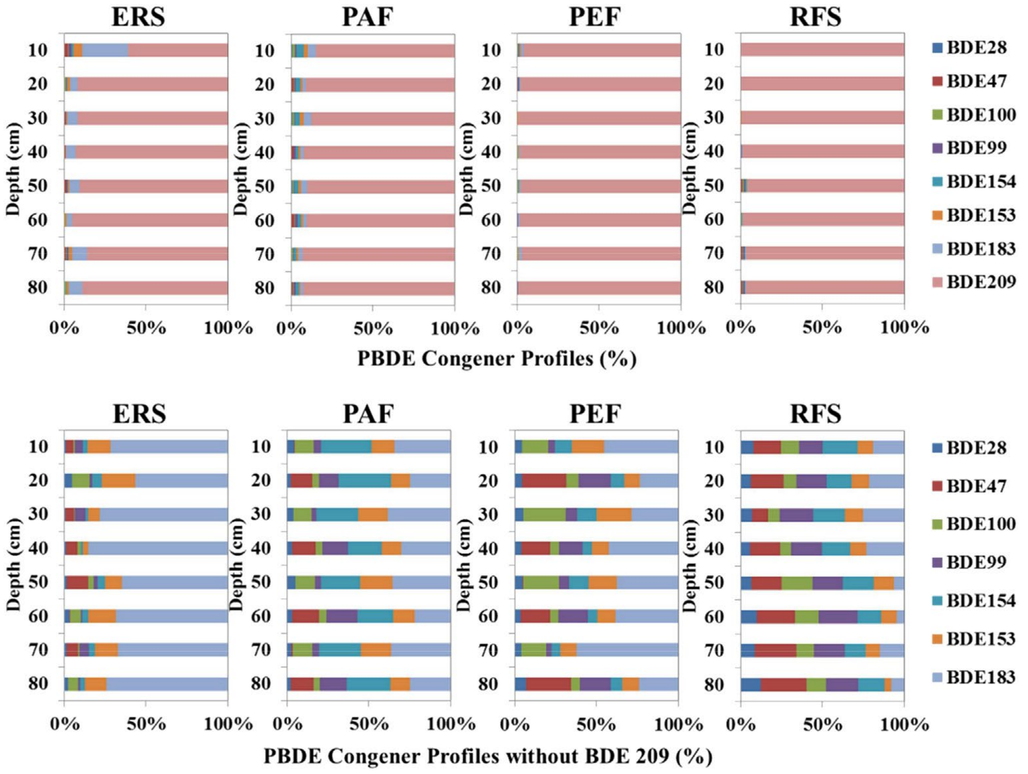

Fig. 3. Compositions of PBDE congeners with or without BDE-209 in different soil cores. (ERS: E-waste recycling site; PAF: Paddy field; PEF: Peanut field; RFS: Reference site).

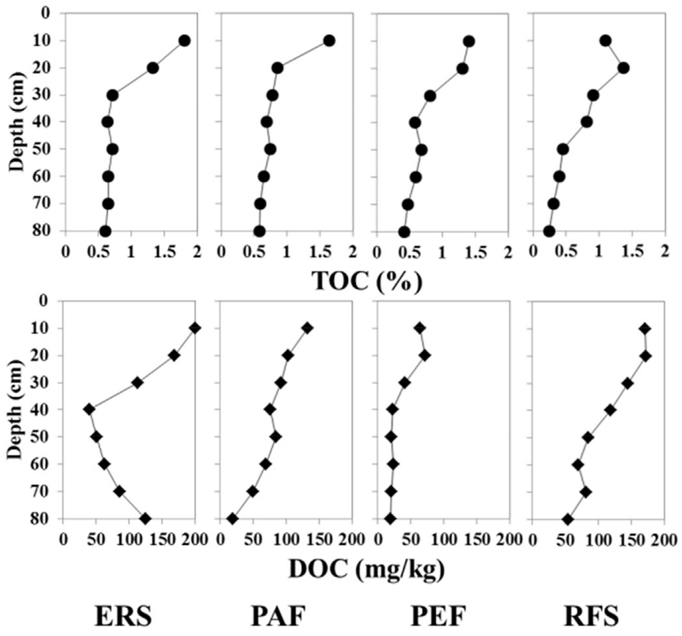

Fig. 4. Vertical distributions of total organic carbon and dissolved organic carbon in different soil cores. (ERS: E-waste recycling site; PAF: Paddy field; PEF: Peanut field; RFS: Reference site).

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