Environmental Pollution 159 (2011) 2443–2448

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Characterization of PBDEs in soils and vegetations near an e-waste recycling site in South China

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ARTICLE INFO

Article history:
Received 1 May 2011
Received in revised form
21 June 2011
Accepted 22 June 2011

Keywords:
E-waste
PBDEs
Soil
Vegetation
South China

ABSTRACT

The concentration and composition of PBDEs in the soils and plants near a typical e-waste recycling site in South China were investigated. The total concentration of PBDEs (ΣPBDEs) in soil ranged from 4.8 to 533 ng/g dry wt. The ΣPBDEs in vegetation were from 2.1 to 217 ng/g dry wt. For the vegetable, the highest concentration of 19.9 ng/g dry wt. was observed in the shoot of *Brassica alboglabra* L. BDE 209 was the predominant congener in all samples. In comaprison with other e-waste contaminated sites in China, lower concentrations of PBDEs and higher concentrations of PCBs were observed in both soils and plants suggesting different e-waste types involved in the present study. The PBDEs contaminated vegetables around the e-waste dismantling site may pose a potential health risk to the local inhabitants.

1. Introduction

Uncontrolled electronic-waste (e-waste) recycling has led to serious environmental problems due to the toxic contaminant release during the disposal activitives (Halluite et al., 2005; Wu et al., 2008; Luo et al., 2011). Polybrominated diphenyl ethers (PBDEs), used as brominated flame retardants in electronic circuit boards, are among the toxic chemicals emitted or formed during the recycling operations (Wang et al., 2005). Rude e-waste processing was recognized as one of the important pathways by which PBDEs enter the environment (Wong et al., 2007).

It is estimated that 50–80% of the global e-waste is legally or illegally imported to Asia each year, and 90% of which is destinated to China, making China to be the largest dumping site of e-waste in the world (Chen et al., 2009). Driven by the profit, rude e-waste recycling techniques, such as manual disassembling, open incineration and acid dipping, are extremely active, and have become a new important source of environmental pollution in a few locations of South China (Bi et al., 2007; Leung et al., 2008). High levels of heavy metals (Cu 11,140, Pb 4500, and Zn 3690 mg/kg), and persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs) (3206 ng/g), polychlorinated biphenyls (PCBs) (1443 ng/g) and PBDEs (44,473 ng/g), were detected in the soil, water and ambient environment around e-waste recycling sites, indicating a severe risk to the local ecosystem and inhabitants' health (Wong et al., 2007; Zhao et al., 2009b; Luo et al., 2011). Strikingly high concentration of PBDEs was observed in the blood of e-waste recycling workers, especially BDE 209 (3436 ng/g lipid wt.) (Qu et al., 2007). Moreover, most of these persistent substances can undergo long-range transport through air or water, and threaten the ecosystem and organisms far away from the e-waste recycling sites. Some research suggested that the PBDEs in marine sediments (Mai et al., 2005; Wurl et al., 2006) and *Katsuwonus pelamis* (Ueno et al., 2004) from South China Sea might originate from the disposal of e-waste in Qingyuan or Guiyu of Guangdong Province. Although literatures concerning PBDEs in air, dust, soil, sediment, and biota samples from the e-waste recycling sites in South China are increasing (Leung et al., 2007; Luo et al., 2007; Wong et al., 2007; Liu et al., 2008; Wu et al., 2008), little research has evaluated the PBDE levels in vegetations at these locations, especially in the vegetables commonly consumed by the local residents.

The present study was carried out in Longtang Town of north Guangdong Province, one of the important e-waste recycling areas in South China. Intensive e-waste recycling processes were active, and millions of tones of e-waste were processed annually. In general, most of the uncontrolled e-waste processing sites were

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doi:10.1016/j.envpol.2011.06.030

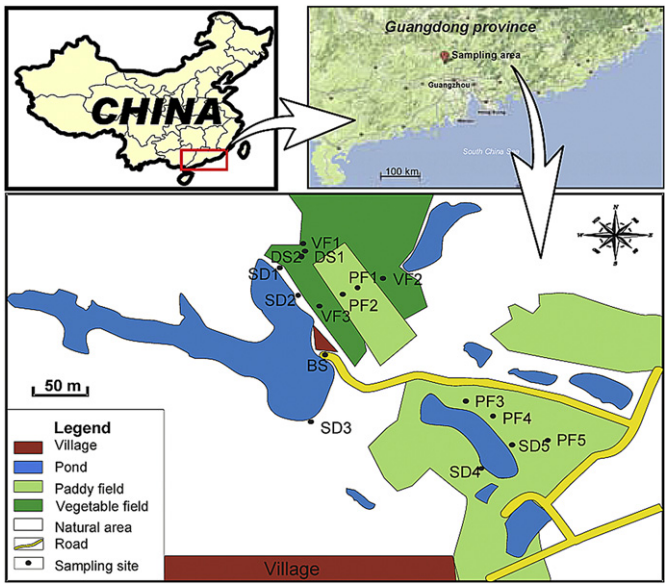

Fig. 1. Map of the sampling locations. (BS, burning site; PF, paddy field; VF, vegetable field; DS, deserted soil; SD, pond sediment).

located on or within 500 m away from the agricultural fields where vegetables and rice were planted. Food produced from these soils was mainly consumed by the local residents, and a potential health risk might be involved (Zhao et al., 2009b). The purpose of the present research was to investigate the effect of uncontrolled e-waste recycling activities on the contamination of the surrounding soils and vegetations by PBDEs. Emphasis was placed on the local vegetables which played an important role in the daily exposure of PBDEs to the local community. The results may be useful for designing management measures and for protecting the residents from potential health hazards in the e-waste affected areas.

2. Materials and methods

2.1. Sampling site

The sampling site is located in Guangdong Province, South China [23° 34′ N, 113° 0′ E]. Intensive uncontrolled e-waste processing operations made many e-waste open burning sites and electronic scraps scattered in or close to agricultural fields. Meanwhile, agricultural activities, such as rice and vegetable planting, are still going on in this area. As shown in Fig. 1, all the sampling locations in the present study can be classified into five different groups: e-waste open burning site (BS), vegetable field (VF), paddy field (PF), deserted soil (DS), and pond sediment (SD).

2.2. Soil and vegetation sampling

All samples were collected in the September, 2007. Top soils (0–15 cm) from e-waste burning site and surrounding vegetable fields, paddy fields, deserted places, and top sediments (0–5 cm) from pond areas were collected. Wild plants, vegetables, rice stalks and the soils where they were grown were sampled as well. Each sample was a composite of 5 subsamples. All the samples were wrapped with aluminum foil, put in polythene zip-bags, and transported to the laboratory. Each individual plant sample was separated into shoot and root subsamples. The fresh plant samples were first washed with tap water, and then rinsed 3 times with deionized water. Soil and plant samples were freeze-dried, ground with agate mortar, and stored at −20 °C until further chemical analysis.

Table 2
Concentrations of PBDE congeners in plant samples (ng/g dry wt.).

Congener	Wild plant $n = 10$		Vegetable $n = 10$		Paddy stalk $n = 2$	
	Mean	Range	Mean	Range	Mean	Range
BDE28	5.7	1.1–17.1	1.5	0.3–4.5	0.7	0.7
BDE47	5.0	1.7–15.4	1.9	0.4–6.5	0.9	0.9–1.0
BDE100	4.0	0.8–13.8	0.6	n.d.–1.5	0.6	0.5–0.6
BDE99	3.6	0.9–11.5	0.7	0.3–1.5	0.7	0.7–0.7
BDE154	6.3	0.8–23.6	0.5	n.d.–1.0	0.7	0.6–0.7
BDE153	3.1	0.6–9.4	0.5	n.d.–0.9	0.8	0.8–0.9
BDE183	3.6	0.8–11.0	0.5	n.d.–1.1	2.1	2.1–2.2
$\Sigma PBDEs_{exc209}$	31.3	7.4–89.4	6.2	1.5–16.1	6.5	6.4–6.6
BDE209	25.1	0.6–128	5.7	0.6–13.4	8.0	7.5–8.5
ΣPBDEs	56.4	12.5–217	11.9	2.1–21.3	14.5	13.9–15.1

2.3. Sample extraction and analysis

Briefly, about 20 g freeze-dried soil samples spiked with surrogate standards (PCB 30 and PCB 209) were extracted with dichloromethane (DCM) in a Soxhlet apparatus for 48 h with activated copper added to remove the sulfur. About 5 g freeze-dried plant samples homogenized with 5 g anhydrous sodium sulfate were spiked with surrogate standards, and extracted with DCM/acetone (3:1, v/v) and activated copper for 72 h. The extracts of soil or plant were concentrated to about 0.5 mL after solvent-exchange to hexane. The fractionated soil extracts were cleaned by passing through a multi-layer silica gel/alumina column containing anhydrous Na_2SO_4, 50% (w/w) sulfuric acid–silica gel, neutral silica gel (3% deactivated) and neutral alumina (3% deactivated) from the top to the bottom with an eluant of 20 mL hexane/DCM (1:1, v/v). The plant extracts were firstly washed with concentrated sulfuric acid for 5 times, and then purified with the multi-layer silica gel/alumina column (Wang et al., in press). After being concentrated to approximately 50 μL under a gentle stream of nitrogen, a known amount of BDE 77 was added to all the samples as the internal standard prior to analysis.

2.4. Instrumental analysis

GC-ECNI-MS (Agilent GC7890 coupled with 5975C MSD) applied with a DB5-MS capillary column (30 m × 0.25 mm i.d., and 0.25 μm film thickness) was used for the determination of 7 BDE congeners (BDE 28, 47, 99, 100, 153, 154, and 183). BDE 209 was analyzed separately by a CP-Sil 13 CB column (12.5 m × 0.25 mm i.d., and 0.2 μm film thickness). Temperatures were all set to 150 °C for MSD source and quadrupole.

2.5. QA/QC

A procedural blank, a spiked blank consisting of all chemicals, and a duplicated sample were run with each batch of 10 samples to assess potential sample contamination and the repeatability of analysis. Results showed no target compounds were detected in laboratory blanks except BDE 209. Method detection limit (MDL) was calculated according to US EPA method 5055. MDLs for 7 PBDEs

Table 1
Concentrations of PBDE congeners in soil samples (ng/g dry wt.).

Congener	BS $n = 5$		PF $n = 14$		VF $n = 10$		DS $n = 4$		SD $n = 6$	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
BDE28	29.8	15.0–62.0	0.4	0.2–0.6	0.7	0.3–1.1	0.3	0.2–0.4	10.1	0.2–43.1
BDE47	23.1	14.5–44.6	0.6	0.3–0.8	1.2	0.5–1.8	0.5	0.4–0.6	9.0	0.2–31.2
BDE100	19.7	11.0–28.8	0.3	0.2–0.5	0.5	0.2–1.4	0.3	0.3–0.5	7.8	0.2–29.7
BDE99	16.5	8.2–25.6	0.4	0.3–0.8	0.7	0.2–1.8	0.4	0.3–0.5	7.6	0.2–20.7
BDE154	16.7	7.8–25.4	0.4	0.2–1.0	0. 5	0.2–1.1	0.3	0.3–0.5	7.0	0.2–22.2
BDE153	15.7	5.8–27.4	0.4	0.2–1.3	0.8	0.3–2.1	0.3	0.2–0.5	6.0	0.2–17.7
BDE183	21.3	7.5–40.0	0.6	0.2–1.9	1.2	0.5–3.0	0.3	0.2–0.5	6.9	0.2–21.6
$\Sigma PBDEs_{exc209}$	143	77.3–249	3.2	1.7–6.6	5.4	3.0–12.3	2.5	2.0–3.5	54.7	1.5–186
BDE209	154	66.7–284	12.4	8.0–18.7	28. 8	12.9–44.9	24.0	13.2–42.2	65.2	3.2–200
ΣPBDEs	296	151–533	15.6	9.7–21.7	34.1	17.0–51.7	26.5	15.2–45.7	120	4.8–386

Table 3
Concentrations and tissue-to-soil ratios of PBDEs in vegetables (ng/g dry wt.).

Congener	*Raphanus sativus* L.[a]	*Daucus carota* L.[a]	*Colocasia esculenta* L. *Schott*[a]	*Brassica Chinensis* L.[b]	*Lactuca sativa* L. var.romana Gars[b]	*Pisum sativum* L.[b]	*Chrysanthemum coronarium* L.[b]	*Lactuca sativa* L. var. longifolia Lam.[b]	*Allium ascalonicum* L.[b]	*Brassica alboglabra* L.[b]
BDE28	0.4	0.5	0.3	1.4	0.8	1.7	2.4	2.0	1.0	1.6
BDE47	0.4	0.7	0.4	1.2	1.7	1.7	2.0	2.7	1.5	2.0
BDE100	n.d.	0.3	0.3	0.4	0.6	0.6	0.6	0.9	0.5	0.6
BDE99	0.3	0.4	0.3	0.4	0.7	0.7	0.8	1.2	0.8	0.8
BDE154	n.d.	0.3	0.3	0.4	0.6	0.5	0.6	0.9	0.5	0.7
BDE153	0.4	0.3	0.3	n.d.	0.6	0.6	0.6	0.9	0.6	0.3
BDE183	n.d.	0.3	0.4	0.4	0.7	n.d.	0.8	1.0	0.6	0.5
$\Sigma PBDEs_{exc209}$	1.5	2.7	2.3	4.2	5.8	5.7	7.8	9.4	5.5	6.5
BDE209	0.6	5.1	4.9	4.2	4.9	3.9	5.3	8.4	4.4	13.4
ΣPBDEs	2.1	7.8	7.2	8.3	10. 7	9.7	13.0	17.8	9.9	19.9
Ratio[c] of $\Sigma PBDEs_{exc209}$	0.287	1.02	0.664	1.55	0.470	2.02	1.48	3.052	2.04	2.42
Ratio[c] of BDE209	0.029	0.113	0.266	0.092	0.124	0.090	0.145	0.234	0.098	0.298
Ratio[c] of ΣPBDEs	0.082	0.164	0.329	0.174	0.206	0.210	0.313	0.478	0.207	0.417

[a] Root (include tuber).
[b] Shoot.
[c] Ratio = Concentration of vegetable/Concentration of soil.

(BDE 28, 47, 99, 100, 153, 154 and 183) and BDE 209 are 5.3 and 6.0 pg/g, respectively. The average surrogate recoveries for PCB 30 and 209 in soil samples were 75.8 ± 21.9% and 86.7 ± 30.5%, respectively; while those in plant samples were 86.4 ± 16.2% and 82.5 ± 17.6%, respectively. All the results reported in the study were deducted by the blanks, but not corrected by the surrogate recovery rates. All data were expressed on a dry-weight basis (ng/g dry wt.).

2.6. Stastical analysis

Principal component analysis (PCA) has been widely applied to discriminate the different origins of environmental pollutants. 8 PBDE congeners analyzed were treated as variables, while all the samples were treated as cases. Individual PBDE congeners that were below the estimated analytical detection limit were set at one-half of the detection limit. The eigenvectors were normal-varimax rotated to facilitate the interpretation of the results. Statistical analysis was carried out with SPSS 13.0 for Windows Release 13.0.

3. Results and discussion

3.1. Levels and congeners distribution of PBDEs

3.1.1. Levels of PBDEs in the soil samples

Table 1 presents the level of the 8 PBDE congeners measured in the soil samples (dry-weight basis). The ΣPBDEs of all soil samples ranged from 4.8 to 533 ng/g with an average of 78.0 ng/g, while the concentrations of BDE 209 were from 3.2 to 284 ng/g with an average of 46.3 ng/g. The highest concentration of PBDEs was found in the soil from the e-waste burning site due to the extensive e-waste recycling activitives, and the average concentration of ΣPBDEs at this site was above 1 order of magnitude higher than those from other agricultural fields, such as vegetable fields and paddy fields. The concentrations of PBDEs showed a clear decreasing trend with the distance from the e-waste burning site. It was obvious that the diffusion of PBDEs from the point pollution source made a dominant contribution to PBDE contamination in the surrounding areas (Luo et al., 2009). The influence of point pollution source to the surrounding environment has been termed the "halo effect" (Pier et al., 2003). Zhao et al. (2009c) also found that PBDEs from the e-waste recycling area diffused into the ambient regions, and resulted in a halo pattern of PBDE contamination at least 74 km in radius. In addition, except for the burning site, the sediments from ponds around the burning site showed the highest concentration of ΣPBDEs, followed by the soils from vegetable fields, deserted fields and paddy fields (Table 1). Soils used for different crops showed different PBDE concentrations even within the same distance from the e-waste burning site. For example, the concentration of ΣPBDEs in vegetable fields was 2 times higher than that in paddy fields, which may be ascribed to the variable cultivation activities or the distinct plant species. It was reported that plants could take up PBDEs from soil directly and pumpkin root had the highest PBDE concentrations among the plants tested (Huang et al., 2011).

As anticipated, BDE 209 was the dominant congener accounting for 36–91% of the total PBDEs in the soils. Meanwhile, BDE 47 was also the major congener followed by BDE 209. The result indicated that the commercial Deca-BDE and Penta-BDE were the key contaminants in this region as reported on other e-waste affected sites in China (Leung et al., 2007). This finding was consistent with the fact that commercial "deca-" product (mainly consisted of BDE 209) is one of the most highly used flame retardants across the world, followed by "penta-" products (e.g. BDE 47 and 99) (Birnbaum and Staskal, 2004).

The concentration of PBDEs from the paddy filed soils were comparable to the paddy soils from Guiyu (Wong et al., 2007; Leung et al., 2007), and Qingyuan (Luo et al., 2009), but the PBDE concentrations from the e-waste burning site soils were lower than those from Guiyu (Wong et al., 2007), and Taizhou (Ma et al., 2009). The PCB concentrations in this study area were also analyzed in a companion paper (Wang et al., in press), and relatively higher concentrations of PCBs (7.4–4000 ng/g) were discovered compared with other e-waste recycling site (4.7–102 ng/g) (Leung et al., 2006). Low concentrations of PBDEs and high concentrations of PCBs might attribute to the different e-waste types processed in this site. A number of dismantled capacitors and wire cables (mostly containing PCBs) were observed all over the sampling area.

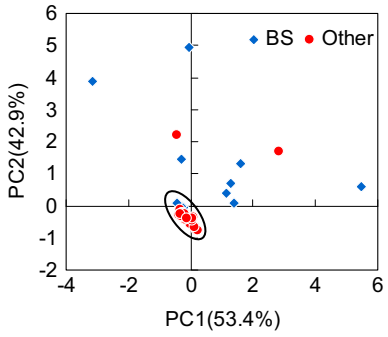

Fig. 2. Two-dimensional principal component score plot. (BS: Burning site samples; Other: Other site samples).

Table 4
Correlation coefficient matrix for PBDEs concentrations in soil samples outside the e-waste burning site ($n = 34$).

	BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE183	BDE209
BDE28	**1.000**	**0.974**	**0.993**	**0.863**	**0.945**	**0.912**	**0.940**	**0.725**
BDE47		**1.000**	**0.992**	**0.954**	**0.993**	**0.979**	**0.988**	**0.742**
BDE100			**1.000**	**0.916**	**0.977**	**0.953**	**0.972**	**0.733**
BDE99				**1.000**	**0.980**	**0.993**	**0.974**	**0.693**
BDE154					**1.000**	**0.994**	**0.994**	**0.728**
BDE153						**1.000**	**0.994**	**0.721**
BDE183							**1.000**	**0.765**
BDE209								**1.000**

Bold means correlation is significant at the 0.01 level.

This was consistent with the report that PCBs-enriched components like capacitors and wire cables were recycled in the present study area Qingyuan, and PBDE-enriched devices like computers and television sets dominated in Guiyu (Yang et al., 2008). However, the average ΣPBDEs of soil in the current study was still higher than those from a foam manufacturing plant (76 ng/g) in U.S. (Hale et al., 2002) and an urban area (9.6 ng/g) in Japan (Hayakawa et al., 2004).

3.1.2. Levels of PBDEs in the plant samples

The levels of 8 PBDE congeners in the plant samples are summarized in Table 2. The concentrations of PBDEs in vegetables are listed in Table 3.

The concentrations of ΣPBDEs in all the plant samples ranged from 2.1 (vegetable) to 217 ng/g (*Neyraudia reynaudiana* from the burning site), with an average of 32.2 ng/g. The wild plant sample from the open burning site had the highest PBDE concentration, followed by paddy stalk and vegetable. The high PBDE levels in the wild plants from the burning site could be attributed to the direct air deposition during the e-waste recycling process, such as open burning. Among the vegetables, *Brassica alboglabra* L. had the highest concentrations of ΣPBDEs and BDE 209. High concentration of PBDEs in the vegetable sample clearly demonstrated that PBDEs had already entered into food chains due to the wide contamination in the surrounding environment of e-waste recycling site. Similar to the soils, BDE 209 and 47 were still the most predominant congeners in the plant samples.

In comparison with other studies, the concentrations of PBDEs in wild plants were comparable to those in tree and shrub leaves (17.1–64.2 ng/g) (Ma et al., 2009), and bark sample of *Cedrus deodara* (25.3 ng/g) (Wen et al., 2009) around e-waste recycling sites, but lower than the metasequoia bark (244 ng/g) (Liu et al., 2008), and *Cinnamomum camphora* leaves (12.8–400 ng/g) collected from other e-waste recycling sites (Zhao et al., 2009c). However, the concentrations of PBDEs in vegetable were much higher than those collected from e-waste recycling site in Zhejiang Province (Zhao et al., 2009a), which may pose a potential risk to the consumers.

The tissue-to-soil ratios of vegetable were also calculated (ratio = $C_{vegetable}/C_{soil}$) and shown in Table 3. The ratio of $\Sigma PBDEs_{exc209}$ was much higher than the ratio of BDE 209, indicating that the lower brominated congeners were more removable than the higher ones. In addition, the ratios of root or tuber were generally lower than the ratios of shoot among various vegetables. This result suggested that PBDEs in shoot samples may mostly originate from the atmosphere instead of the soil. Among the vegetables measured, *Lactuca sativa* L. (var. longifolia Lam) had the highest tissue-to-soil ratio of $\Sigma PBDEs_{exc209}$, while *B. alboglabra* L. had the highest ratio of BDE 209. This implied those two species may have a higher ability to take up PBDEs from the surrounding environment than other species.

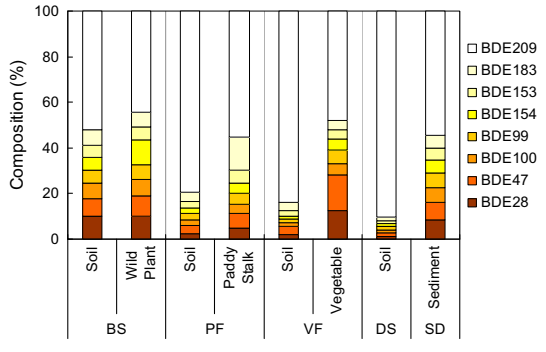

Fig. 3. Compositions of PBDE congeners. (BS, burning site; PF, paddy field; VF, vegetable field; DS, deserted soil; SD, pond sediment).

3.2. Principal component analysis of PBDE concentrations

The PCA (PC1 vs PC2) results of PBDEs in soils and plants are plotted in Fig. 2. The first two principal components (PCs) explained about 53.4% and 42.9% of the total variance, respectively. The samples outside the e-waste burning site were closed to each other in the score plot with only two exceptions (pond sediments), indicating that PBDEs in these soils may derive from the same source – dispersion by the ash or gas emission from the open burning activity. This was supported by the significant correlation among various PBDE congeners in soils collected outside the burning site (Table 4).

3.3. PBDE congeners in soil and plant samples

It is crucial to disclose congener/homologue-specific information in order to understand some valuable difference of contaminants on their origin, environmental fate and behavior (Duarte-Davidson et al., 1997). The PBDE composition in the vegetable soil was generally similar to those in the paddy soil and deserted soil, but different from soil of the e-waste burning site (Fig. 3). The potential fractionation of PBDE composition between the burning site and the surrounding sampling locations suggested PBDE congeners in the nearby soils were not directly from the e-waste release, but may be the result of more complex environmental processes, such as leaching, volatilization, dry/wet deposition, advective transport, and soil burial etc. Meanwhile, the distribution of PBDEs was not completely dependent on the molecular weight of congeners, especially for BDE 209. As reported, lower brominated PBDE congeners are mostly in the gaseous phases, while higher brominated congeners tend to be associated with particles (ter Schure and Larsson, 2002; de Boer et al., 2003). Therefore, lower brominated PBDEs may undergo a greater distance through long-range atmospheric transport to areas outside the e-waste burning site than the higher brominated PBDEs. The different PBDE compositions could also be influenced by the environmental and/or

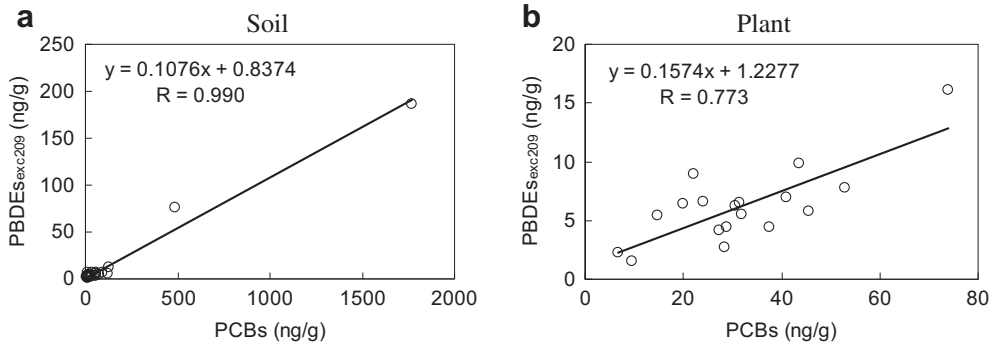

Fig. 4. Relationships between ΣPBDEs$_{exc209}$ and ΣPCBs in soil and plant samples outside the e-waste burning site. (a - Soil; b - Plant).

biologic processes, such as photolysis, debromination, biodegradation, and plant uptake. Previous research has indicated that aerobic microbes from the contaminated soils preferentially utilized low brominated BDEs as carbon sources (Schmidt et al., 1992; Vonderheide et al., 2006), and BDE 209 was vulnerable to anaerobic bacteria (Gerecke et al., 2005).

BDE 209 was the dominant congener in the samples from the current study, which was consistent with the fact that it is the major commercial PBDE product added into plastic products commonly used in high-tech and other electrical appliances (Zou et al., 2007). However, BDE 209 proportion in soil of the e-waste burning site was lower than those of the ambient areas, which was similar to the result of Luo et al. (2009) in this area. Two major reasons could explain this scenario. First, BDE 209 was more readily debrominated to lower BDE congeners under the changes of pressure and temperature during the rude recycling operations (Thuresson et al., 2006). BDE 209 in the burning site soils could be debrominated by the burning activity, which makes the proportion of BDE 209 to the total PBDEs reduced. Second, the background value of BDE 209 could also affect the proportion. A high level of BDE 209 (1.7 ng/g, accounting for 98% of Σ_{22}PBDEs) had been found in the rural background soil from a non-point pollution site in Guangdong Province (Luo et al., 2009). Therefore, the BDE 209 background value might influence the BDE 209 proportion of the surrounding areas to a bigger extent than that of the burning site. Meanwhile, BDE 209 was the dominant congener in the plant samples of this study, which supported the notion that BDE 209 could eventually be bioaccumulated in food chains through complex biogeochemical process. Schecter et al. (2004) gained a similar observation that BDE 209 was detected in many meat products in U.S. (such as chicken and pork). Chen et al. (2009) had proposed that the percentage of BDE 209 in the e-waste processing site could be used to validate where the e-waste comes from. However, the different behaviors between BDE 209 and other PBDEs in the recycling process resulted in the various proportion of BDE 209, which made it impossible to be used in determining whether the e-waste came from the domestic or abroad. In this case, it is suggested the concentrations of Dechlorane Plus (DP) (Yu et al., 2010) and/or Hexabromocyclododecanes (HBCDs) (Gao et al., 2011) should also be taken into consideration in evaluating the potential source of the e-waste.

In this study, similar PBDE patterns were found between wild plants and their corresponding soils at the e-waste burning site (Fig. 3). However, the PBDE patterns between plants and soils from other sampling sites, such as vegetable garden and paddy field, were quite different. Beside the background value of BDE 209 in soil, biologic factors from plants and their associated microbes were probably responsible for this observation as well. Some plants could take up POPs directly from soil, and certain microbes within the rhizosphere could degrade the target compounds in soil (Liste and Alexander, 2000; Mattina et al., 2004; Huang et al., 2011). Ultimately, the pattern of PBDEs in the soil could be changed correspondingly.

3.4. Correlation between ΣPBDEs$_{exc209}$ and ΣPCBs

PCB concentrations in the samples were also analyzed in a companion paper (Wang et al., in press). The correlation of PCBs and PBDEs in samples outside the e-waste burning site is plotted in Fig. 4. Significant correlations were found between ΣPBDEs$_{exc209}$ and ΣPCBs in soil and plant samples outside the burning site ($R = 0.990$, $p < 0.01$ for soil in Fig. 4a, and $R = 0.773$, $p < 0.01$ for plant in Fig. 4b), which was in agreement with the results of Wu et al. (2008) and Liu et al. (2008), respectively. The possible explanations were as follows: firstly, the two types of substances (PCBs and PBDEs) were acquired from the same source (e-waste recycling activities) for the soils around the open burning site; secondly, the uptake and/or bioaccumulation rates of PBDEs and PCBs by the plants outside the burning site in this study were comparable. However, Leung et al. (2006) found a strong negative correlation between PCBs and PBDEs at another e-waste recycling site ($R = -0.992$). The different results may be due to the difference of soil properties, contamination levels and compound congeners studied.

4. Conclusions

The inappropriate recycling and disposal of e-waste became an important source for a number of toxic chemicals, including PBDEs. This study is one of the little research on the contamination of PBDEs in vegetable near the e-waste recycling site in China. The results demonstrated that past uncontrolled e-waste recycling had resulted in the occurrence and migration of PBDEs into the surrounding environment. The paddy and vegetable fields near the e-waste dismantling site were all contaminated with PBDEs. The concentration of PBDEs showed a clear decreasing trend with the distance from the e-waste burning site. Meanwhile, in comparison with other e-waste contaminated sites, lower concentrations of PBDEs and higher concentrations of PCBs were observed in the present study area, suggesting different e-waste types involved. The different behaviors between BDE 209 and other PBDEs in the recycling process made it impossible to use the single percentage of BDE 209 in determining whether the e-waste came from the domestic or abroad. In addition, PBDEs has entered the food chain, in particular the vegetables planted in the ambient area. Therefore, vegetables growing in the e-waste recycling area may pose a potential risk to the local ecosystem and residents and need further risk assessment in the future.

Acknowledgments

This study was supported by the Joint Funds of the National Natural Science Foundation of China and the Natural Science Foundation of Guangdong Province, China (NSFC-GDNSF U0933002), the National Natural Science Foundation of China (Nos. 40821003 and 40739001) and the Research Grants Council of the Hong Kong SAR Government (PolyU 5212/08E).

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