RESEARCH ARTICLE

Distribution of metals and brominated flame retardants (BFRs) in sediments, soils and plants from an informal e-waste dismantling site, South China

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Abstract Brominated flame retardants (BFRs, including polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol-A (TBBPA)) and metals (Cu, Zn, Pb, Cd, Ni, Hg and As) in sediments, soils and herb plants from unregulated e-waste disposal sites were examined. The metal concentrations, ∑PBDE and TBBPA concentrations in all samples from the examined e-waste dismantling sites were relatively high in comparison with those of rural and urban areas around the world. The PBDE and TBBPA levels in soils significantly decreased with increasing distance from the e-waste dismantling sites, indicating that PBDEs and TBBPA had similar transport potential from the e-waste dismantling process as a point source to the surrounding region. BDE-209 and TBBPA predominated in all samples, which is consistent with the evidence that the deca-BDE and TBBPA commercial mixtures were extensively used in electronic products. Metals, PBDEs and TBBPA displayed significant positive correlations with TOC, whereas the correlations with pH were insignificant, indicating that TOC was a major factor governing the spatial distribution, transportation and fate in sediments and soils. A significant relationship between log-transformed metals and BFR concentrations indicated common pollution sources. Moreover, cluster analysis and principal component analysis further confirmed that the metals and BFRs had a common source, and penta- and deca-BDE commercial products may be two sources of PBDEs in this region.

Introduction

Along with the accelerating update of electronic information technologies and their decreasing lifespans, a significant amount of electronic items are becoming obsolete and are being discarded in various parts of the world (Leung et al. 2006). Electronic waste (e-waste) is a heterogeneous mixture of metal, plastics, glass and ceramics that often contains a range of toxic chemicals, including brominated flame retardants (BFRs), mercury (Hg), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn) and other potentially harmful substances (Wong et al. 2007; Robinson 2009; Li et al. 2011a; Yao et al. 2013). If not disposed of appropriately, such wastes always trend toward release into the environment and can become a point source of metal and organic contamination, causing adverse effects to both the environment and human health.

BFRs have aroused extensive concerns over their persistence, bioaccumulation and potential adverse effects on wildlife and human (Birnbaum and Staskal 2004). It is well known that polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol-A (TBBPA), as BFRs, have been widely used in electronic products over the past three decades. In

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computers, the three major PBDE commercial formulations (penta-, octa- and deca-BDE) are mainly used in printed circuit boards, plastics, wires/cables and components such as connectors. The domestic production capacities of technical TBBPA and deca-BDE in 2006 were approximately 38,000 and 20,000 t, respectively (Xiao 2006). PBDEs have been found in both abiotic and biotic environmental samples (Sjödin et al. 2003) due to their extensive usage and environmental persistence.

In general, BFRs are relatively hydrophobic and lipophilic compounds that have low water solubility and low vapour pressures (Tittlemier et al. 2002). Studies have demonstrated that large proportions of PBDEs and TBBPA released into the environment will end up in sediment or soil (Watanabe and Sakai 2003; Nyholm et al. 2010). In addition, the contaminated sediment or soil can become a second source of pollution via re-emission and transport (Zou et al. 2007). Although literature concerning metal and BFR levels in various environmental samples and in human samples from e-waste recycling sites has already been published (Wong et al. 2007; Ni et al. 2010), to the best of our knowledge, only a few studies focused on the transport of metals, PBDEs and PCBs in soil, and biological samples have been reported. For example, Zhao et al. (2009) reported that PBDEs could be transported from e-waste recycling sites up to a distance of 74 km using *Cinnamomum camphora* leaves as biomonitors. Li et al. (2011b) reported that the transport range of PBDEs and PCBs was 40 km, with metals remaining at the original site without transport to the surrounding areas. Another study reported that the transport range of metals was only a few metres (Fujimori and Takigami 2014). However, the available data on the occurrence and transport of TBBPA in sediments, soils and plant leaves are minimal in China, despite the extensive use of TBBPA. Most published data for TBBPA in biota comes from Europe, and TBBPA levels have been demonstrated to be quite low or undetectable (for example, the TBBPA concentration in mosses from the Arctic was 0.019 ng/g ww (De Wit et al. 2006)), which also provides evidence of long-range transport of TBBPA. Furthermore, previous studies have suggested that TBBPA results in strong acute toxicity to organisms. Therefore, more studies on the transport of TBBPA from the potential point source (e-waste dismantling site) to surrounding regions and possible bioaccumulation in herb plant samples are urgently needed.

The present study was conducted in a small village in the Longtang area, which is an e-waste processing area. The local residents have worked in the e-waste recycling process for approximately three decades. Currently, more than one million tonnes of e-wastes are disassembled inappropriately in simple households each year. The e-wastes are composed of printed circuit boards, electric capacitors, electric generators, cable wires and other items, etc. In addition, the local residents still are also involved in traditional agricultural activities, such

as growing rice and planting vegetables, in the vicinity of e-waste workshops (Luo et al. 2011). The Longtang area has a typical subtropical monsoon climate, with high temperature and rainfall and flat terrain. The meteorological conditions accelerate the transport of contaminants via atmospheric dry/wet deposition.

Atmospheric pollutants (metals and persistent organic pollutants (POPs)) can be transported and accumulated in soil, sediment and vegetation through gas absorption/volatilisation and dry/wet deposition. Sediment is an environmental sink of organic compounds and plays an important role in the distribution and fates of these contaminants in aquatic environments. For terrestrial ecosystems, soil is the initial recipient for atmospheric pollutants and also the major route of entry of POPs into agricultural and wildlife food chains. In addition, herb plants have been used as bioindicators to investigate the long-range transport of POPs due to aerial portions of the vegetation can receive the bulk of the POP burden from the atmosphere (Hassanin et al. 2005). To better understand the distribution of metals and BFRs (particularly TBBPA) in the ambient environment caused by the illegal e-waste disposal, the current study investigated the distribution and short-range transport of contaminants (metals and two brominated retardants, PBDEs and TBBPA) in the aquatic and terrestrial environments (surface sediment, soil and plant samples) surrounding the e-waste dismantling site in Longtang. Moreover, we also examined the significance of the correlation between total organic carbon (TOC) and pH with the levels of metals, PBDE and TBBPA, and we also aimed to identify similarities of the contaminant and PBDE pollution patterns through cluster analysis and principal component analysis.

Materials and methods

Sampling area and collection

The study area is situated in Longtang (23° 34′ N, 113° 0′ E), Qingyuan. The illegal e-waste dismantling workshops are scattered around the agriculture fields. Printed circuit board scraps have been dumped beside the river or piled up in the near hills. e-Waste debris, river sediments, soils and herb plants (*Setaria viridis* L. Beauv. and *Arachis hypogaea* Linn.) were collected from all or some of both e-waste dismantling sites and farmland in March and May 2012. A total of 56 samples were collected from 10 sampling sites (Fig. 1). More detailed descriptions of the samples and sampling locations are presented in Table S1 in the Supporting Information. S1 represents the control site as the samples were collected from upstream of the discharge of the e-waste dismantling sites.

The sediment, soil and herb plant samples were collected from the river and riverbank, which were close to the e-waste dismantling sites (Fig. 1). The soil and plant samples from
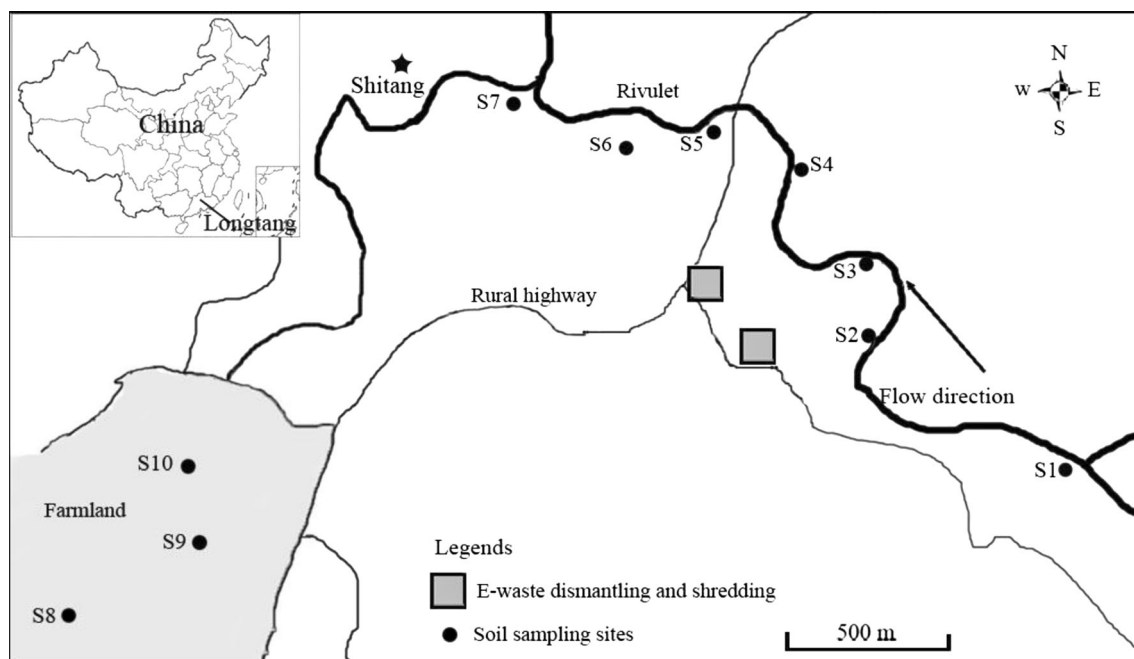
Fig. 1 The sampling locations in Shitang, Qingyuan and Guangdong

these locations were designated as soils-E and plants-E, respectively. The river flows from S1 to S7 and ultimately to the Longtang River. Farmland soils and peanut crops were collected from S8 to S10, which were located far from the e-waste dismantling sites and denoted as soils-F and plant-F, respectively. Surface sediments were collected with a stainless steel columnar sampler (K-BTM, Cole-Parmer, USA) and a precleaned stainless steel shovel for the surface soil samples (0–5 cm) from an area of approximately 10 m^2 in each sampling location. The samples were freeze-dried, sieved through a stainless steel mesh with 0.2-mm pore size, ground and stored at −20 °C until chemical analysis. *S. viridis* and peanut crop plants were collected from the e-waste dismantling sites and farmland, respectively. Plants were first carefully washed with tap water to remove any adhering soil particles and then thoroughly rinsed with distilled water and dried with filter paper, which was followed by being freeze-dried before being ground into a homogeneous mixture with a mortar and pestle.

Standards and reagents

Acetone, n-hexane, dichloromethane (DCM) and isooctane were purchased from Shanghai Chemical Company (Shanghai, China). All chemicals used were of reagent grade with purity >99.8 %. Reference standards for PBDEs (BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-203, BDE-206, BDE-207, BDE-208 and BDE-209), and TBBPA were purchased from Accustandard Inc. (New Haven, CT). The ^{13}C PCB-208 internal standard solution was obtained from Welington Laboratories,

TerraChem Inc. (Shawnee Mission, KS), as well as the ^{13}C-PCB-141, PCB-209, ^{13}C-TBBPA and ^{13}C-BDE-209 standard solutions. Anhydrous sodium sulphate, hydrogen peroxide, nitric acid, perchloric acid and sulphuric acid were obtained from Shanghai Chemical Company (Shanghai, China). Neutral silica gel (100–200 mesh) and alumina (80–100 mesh) were extracted with a mixture of dichloromethane and acetone (1:1 *v/v*) for 72 h and heated at 180 and 120 °C for 12 h, respectively. Sodium sulphate was boiled at 650 °C for 4 h prior to use.

Analysis methods

The analysis method for the BFRs in solid samples followed previous reports (Zhou et al. 2012; Zhou et al. 2014). Briefly, sediments or soils of less than 5.0 g of dry mass were spiked with recovery surrogates (24 ng of ^{13}C-PCB 141, 10 ng of ^{13}C-BDE-209 and 20 ng of ^{13}C-TBBPA) and extracted with 200 mL of hexane/acetone (1:1 *v/v*) for 8 h in a Soxhlet apparatus (Buchi, Switzerland), with added activated copper granules to remove sulphur. The extract was filtered and concentrated to 1 mL using a rotary evaporator and subsequently cleaned up with a multilayer silica column, i.e. a 10-mm i.d. glass column containing a series of silica and alumina (Wang et al. 2011). The purified extract was collected and carefully evaporated to 200 μL under a gentle stream of nitrogen. Various chemicals were analysed in two separate fractions: one fraction was used for testing PBDEs and another fraction for testing TBBPA. The first fraction was spiked a known amount of internal standards ^{13}C-PCB 208 and re-dissolved in 200 μL of isooctane before instrumental analysis. Then, 100 μL of BSTFA +1 % TMCS was added to the

second fraction of extracts, and derivatisation was performed according to the reports on the TBBPA derivatisation method of Xie et al. (2007). Then, the spiked internal standards were adjusted to 200 μL prior to GC-MS analysis. Plant samples of 5.0 g were mixed with Na_2SO_4 and subjected to extraction according to the soil and sediment sample extraction method described above. The extracts were rotary-evaporated to dryness and re-dissolved with 10 mL of n-hexane (three times) and then treated with amounts of sulphuric acid treatment overnight. The organic phase was gathered and then concentrated to 1 mL by passage through a multiple silica column. The subsequent operation was the same as described above.

Instrumental analysis of the PBDEs and TBBPA derivatives was conducted with a gas chromatograph 7890N coupled with a mass spectrometer 5975C (Agilent Technologies, Wilmington, DW, USA) operating with a negative chemical ionisation (NCI) source in the selective ion monitoring (SIM) mode. For tri- to hepta-BDE congeners and TBBPA derivatives, a DB-5ms column (30 m×0.25 mm×0.25 μm, J&W Scientific, CA, USA) was used to separate tri- to hepta-BDEs (BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153 and BDE-183) and TBBPA. The samples were injected in a splitless mode with a volume of 1 μL with a 6-min solvent delay time. Helium was used as a carrier gas at a flow rate of 1.5 mL/min. The column temperature started at 100 °C (held for 1 min), increased to 220 °C at a rate of 30 °C/min and held for 1 min, before being increased to 250 °C at a rate of 3 °C/min and held for 1 min. A DB-5HT column (15 m×0.25 mm× 0.10 μm, J&W Scientific, CA, USA) was used to separate octa- to deca-BDEs (BDE-203, BDE-208, BDE-207, BDE-206 and BDE-209). The column temperature started at 100 °C, increased to 325 °C at 10 °C/min and was held constant for 10 min. Ions at m/z 79 and 81 were monitored for PBDEs (except for BDE-209) and TBBPA, whereas ions at $m/z=79$, 81, 484.7 and 486.7, and 79, 81, 494.7 and 496.7 were monitored for BDE-209 and ^{13}C-BDE-209, respectively. In addition, ions at m/z 474 and 476 were used for ^{13}C-PCB-208.

For the metal analysis, microwave-assisted digestion (MARS-5, CEM, Matthews, CN, USA) was used according to previous studies (Zhou et al. 2013). A total of 0.2 g of sediment/soil samples were weighed and digested with a mixture of nitric acid (HNO_3) and perchloric acid ($HClO_4$). A total of 0.1 g of plant samples were digested with 4 mL of HNO_3 (65 %) and 1 mL of hydrogen peroxide (H_2O_2) (30 %) in a microwave digestion system and diluted to 10 mL with deionised water. All sample solutions were clear. Concentrations of Cu, Zn, Cd, Pb, As and Ni were determined by inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer NexION 300Q, Waltham, MA, USA). Hg was determined by atomic fluorescence spectrometry (AFS-9230, Titan Instruments Co., Ltd., Beijing, China). For quality control, a blank digest was also performed using the same method.

TOC and pH

The analytical method used to detect TOC in sediment and soil samples was reported previously (Wang et al. 2011). Briefly, less than 3 g of the dried sample was treated with 10 % HCl to remove inorganic carbon, washed with deionised water three times, and dried overnight at 105.1 °C. The TOC content was determined with an element analyser (TOC-VcPH, Shimadzu Corp., Kyoto, Japan). The pH values were measured in a KCl/water solution at a soil/solution ratio of 1:2.5 (m/v) (Shepherd and Walsh 2002).

Quality assurance and quality control (QA/QC)

A fraction of samples from different matrices were spiked with surrogate standards prior to solvent extraction to ensure method accuracy. The average recoveries for ^{13}C-PCB 141, ^{13}C-BDE-209 and ^{13}C-TBBPA in the sediment and soil samples were 94.2, 78.6 and 77.2 %, respectively. A procedure blank was included for each set of eight field samples, and all blank controls contained no detectable amounts of the target substances. The recoveries of 13 PBDE congeners and TBBPA in all samples were in the range of 78.5–117.3 and 81.3–109.5 %, respectively. The limit of detection (LOD) was defined as a signal/noise (S/N) ratio of 3. The LODs for the PBDE congeners except for BDE-209, BDE-209 and TBBPA were in the range of 2 to 25, 500 and 25 pg/g dw, respectively. For metals, the LODs of Cu, Zn, Pb, Cd, Ni, Hg and As were 0.5, 1.5, 0.07, 0.03, 0.3, 0.001 and 1.0 μg/L, respectively. The reported data were not corrected for the surrogate recoveries. The accuracy of the metal analytical method was controlled using certificated reference materials (CRMs) from the China National Center for Standard Materials, including for soil (GBW07405) and plant (GBW07604(GSV-3)) samples. The measurements agreed well with certified values, with satisfactory reproducibility illustrated by the standard deviation. The recoveries of these seven metals were 98.6–104.1 and 92.3–105.3 % for soil and plant, respectively (Table S2 in Supporting Information). For metals, the sample duplicates and standard reference solution at regular intervals were analysed.

Statistical analysis

When the contaminant concentration in various matrices was lower than the limit of quantitations (LOQs), it was considered undetected and calculated as a half of the LOQ. One-way analysis of variance was applied to examine significant differences in different sites. Data on contaminant concentrations were log-transformed and then tested for normality (Kolmogorov-Smirnov test) and for homogeneity of variance (Levene's test). If the data failed that test, we analysed the data using non-parametric tests. Principal component analysis (PCA) was performed with SPSS 18.0 for Window (SPSS

Table 1 Concentration of metals and BFRs in e-waste, sediment, soil and plant samples from the e-waste dismantling site and farmland site (ng/g dw)

	Compounds	e-Waste	Sediment	Soil-E	Soil-F	Plant-E	Plant-F	Optimum[a]	Action[a]	Grade II[b]	Background value[c]
Metals	Cu	7,163.18	3,392.65 (277.62–5,837.87)	2,159.32 (1,411.66–2,968.39)	102.24 (78.82–128.24)	96.14 (29.74–176.57)	6.84 (6.00–7.31)	36	190	50	17
	Zn	161.7	2,183.02 (350.61–3,719.6)	1,365.96 (485.77–2,088.83)	104.35 (85.31–126.01)	137.69 (102.98–226.06)	106.09 (90.85–122.50)	140	720	200	47.3
	Pb	161.49	1,170.12 (105.11–1,918.50)	576.32 (291.48–957.75)	53.40 (40.65–66.64)	3.03 (0.40–5.50)	0.23 (0.20–0.30)	85	530	250	36
	Cd	18.32	11.07 (3.5–14.98)	6.33 (0.07–11.54)	0.09 (0.06–0.12)	0.34 (0.20–0.52)	0.13 (0.10–0.20)	0.8	12	0.3	0.056
	Ni	41.25	133.62 (61.47–170.43)	78.14 (54.45–110.07)	39.34 (36.46–43.93)	n.d.	n.d.	35	210	40	14.4
	Hg	0.28	4.08 (0.79–9.00)	1.38 (0.11–3.42)	0.12 (0.10–0.14)	0.17 (0.02–0.39)	0.02 (0.01–0.04)	0.3	10	0.3	0.078
	As	44.97	290.44 (104.65–514.00)	80.22 (25.70–184.98)	23.17 (22.48–24.15)	8.63 (2.67–15.41)	0.94 (0.83–1.03)	29	55	30	8.9
	Total metals	7,591.172	7,185.0 (1,100.55–11,954.74)	4,267.67 (2,277.39–6,276.24)	322.72 (264.29–389.25)	245.99 (146.52–422.30)	114.26 (98.34–130.84)				
BFRs	BDE-15	63.71	10.59 (0.87–27.62)	3.55 (0.52–7.58)	0.67 (0.30–1.22)	1.38 (0.23–4.07)	0.68 (0.44–0.96)				
	BDE-28	222.97	9.24 (0.95–24.31)	7.15 (2.05–11.56)	0.29 (0.20–0.34)	0.58 (0.03–2.33)	0.41 (0.33–0.55)				
	BDE-47	710.13	53.35 (4.61–156.47)	49.52 (9.36–108.23)	1.12 (0.43–2.40)	2.79 (0.25–10.5)	1.13 (0.97–1.46)				
	BDE-100	67.92	10.61 (0.63–28.41)	9.69 (1.44–25.86)	0.84 (0.29–1.44)	0.39 (0.02–1.68)	0.37 (0.16–0.52)				
	BDE-99	668.25	77.38 (5.88–245.21)	79.68 (11.72–103.67)	1.00 (0.38–1.85)	3.04 (0.37–11.70)	1.66 (0.86–3.03)				
	BDE-154	13.90	14.56 (1.02–40.75)	9.83 (1.78–21.52)	0.32 (0.02–0.97)	0.38 (0.02–1.20)	0.40 (0.27–0.49)				
	BDE-153	138.82	27.81 (3.72–72.05)	23.31 (4.39–39.77)	0.59 (0.10–1.19)	1.14 (0.11–4.71)	0.73 (0.41–1.27)				
	BDE-183	115.19	33.15 (1.46–93.54)	18.47 (3.74–38.06)	0.24 (0.10–0.43)	0.52 (n.d.–1.91)	n.d.				
	BDE-203	6.50	6.51 (0.79–19.96)	3.69 (0.97–6.73)	0.12 (0.07–0.17)	0.36 (n.d.–0.56)	n.d.				
	BDE-208	21.04	5.72 (0.86–10.59)	3.34 (1.10–5.76)	0.12 (0.09–0.18)	0.32 (n.d.–0.67)	n.d.				
	BDE-207	336.07	85.62 (14.26–156.41)	53.98 (16.667–88.33)	1.48 (0.50–2.27)	4.18 (n.d.–9.07)	n.d.				
	BDE-206	123.10	24.91 (2.74–49.96)	16.82 (3.11–27.72)	0.25 (0.12–0.47)	0.89 (n.d.–1.96)	n.d.				
	BDE-209	18,386.06	2,404.75 (383.78–4,449.43)	1,994.44 (347.16–3,340.39)	162.43 (112.81–252.17)	39.12 (3.32–76.31)	16.28 (14.97–18.15)				
	∑PBDE	20,873.65	5,313.94 (482.87–5,313.94)	2,273.47 (421.20–3,713.23)	115.81 (115.82–264.81)	52.06 (4.84–124.19)	21.66 (18.96–23.27)				
	TBBPA	1,939.01	384.22 (24.69–913.64)	295.83 (84.0–646.06)	81.75 (29.98–165.79)	42.26 (n.d.–64.46)	17.17 (15.30–20.85)				
	BFRs	22,812.66	3,148.44 (507.56–6,168.73)	2,569.29 (541.2–4,209.23)	251.22 (145.80–430.61)	87.27 (4.84–180.08)	38.82 (34.26–43.51)				

Metals' unit as mg/kg, BFRs' unit as ng/g dw

n.d. not detected

[a] Dutch standard from VROM

[b] China standards from SEPA

[c] Background value of Guangdong Province from CNEMC

Inc., Chicago, IL, USA). To provide reliable data on PBDE congeners, we removed the congeners detected in <70 % of samples and replaced of "below the detection limit" results with a value of half the detection limit for congeners. For linear regression analysis, the contaminant concentrations in various environment matrices were first log-transformed and were then plotted against each other. The correlations between the contaminant concentrations in sediment/soil with TOC and pH were determined with Pearson correlation test, using $P<0.05$ as the level of statistical significance.

Results and discussions

Concentrations

Metals The concentrations of the involved metals (including Cu, Zn, Pb, Ni, Cd, Hg and As) were measured in all samples together with some relative quality criteria and are summarised in Table 1. Using the New Dutch list action value (VROM 2001), as China does not have its own regulatory guideline for sediments, Cu, Zn and Pb were the primarily contaminants in the sediment from the e-waste dismantling site. For example, the mean contents of Cu, Zn and Pb exceeded their corresponding action values by 17.9, 3.0 and 2.2 times, respectively, and the mean contents of Cd and Hg exceeded their optimum values by approximately 13.8 and 13.6 times, respectively. In addition, the metal levels in the soils-E samples were similar to the sediments and were higher than those of e-waste debris. Therefore, it is very likely that metal contamination in this study area mainly came from acid processing rather than manual dismantling and dumping.

Using the Chinese soil standards (SEPA 1995), soils were primarily contaminated by Cu and Cd, exceeding the grade II standard of soil quality (pH <6.5) by more than 43 and 21 times, respectively, and Cu also exceeded the Dutch Standard action value. The mean concentrations of metals (except for Cu) in farmland soils were 10–20 times lower than those in the soils-E samples and were also lower than the grade II standard but above the soil background value of Guangdong Province (CNEMC 1990). These results suggest that e-waste dismantling activities had only minor impacts on the surrounding soil. Based on the metal concentrations in sediments and soils, it was evident that the sediment and soil samples collected from the e-waste dismantling sites were highly contaminated with metals, particularly Cu, Cd, Pb and Zn. The present levels of metals were consistent with those in samples collected from simple household e-waste recycling workshops in the same area (Liu et al. 2013), and other areas (such as Taizhou (Chen et al. 2010) and Wenling in Zhejiang (Tang et al. 2010)) displayed slightly lower values than those in samples collected from e-waste open burning sites in Guiyu (Wong et al. 2007) and incineration sites in Qingyuan (Luo et al. 2011). These findings highlight that the serious metal contamination in the Longtang area has resulted from e-waste dismantling activities.

Metal levels in *S. viridis* and peanut crop plants varied greatly and are also given in Table 1. The Ni levels in plants were below the corresponding LOQs for Ni. The mean concentrations of total metals in the plants-E samples were two times higher than those in the plants-F samples (Fig. 2a). This may have resulted from the elevated levels of metals in the soil near the e-waste recycling sites. The deposition of atmospheric pollutants may be another possible reason (Bi et al. 2009). Zn displayed the highest content among the metals, and the mean concentrations in *S. viridis* and peanut plants were 143.87 and 110.87 mg/kg, respectively. One potential explanation was that Zn could be taken up and mainly accumulated in plant leaf tissue.
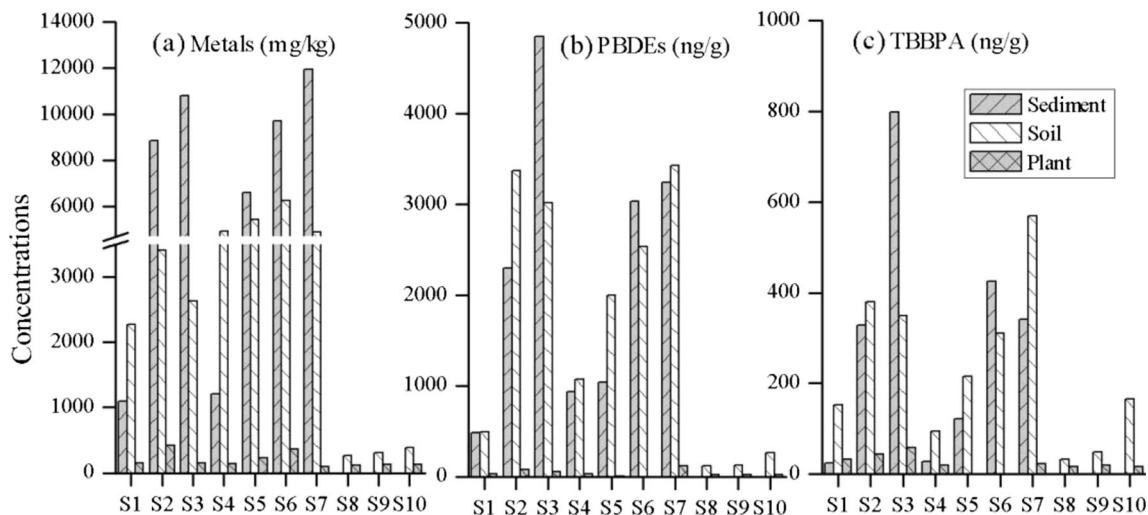

Fig. 2 The concentrations of total contaminants in sediment, soil and plants from the different sampling sites

BFRs A total of 13 BDE congeners including di- to deca-BDE and TBBPA were measured in e-waste debris, sediment, soil and minority plant samples, and their concentrations are also summarised in Table 1. The levels of total BFRs in the surface soils-E samples were consistent with those in the sediment, with a mean of 3,148.44 and 2,569.29 ng/g dw, respectively. BFRs were also found in the farmland soil, although the concentrations (with a mean of 251.22 ng/g) were approximately ten times lower than those in the soils-E samples. Furthermore, BFR levels were also relatively higher in the plants-E samples than those in the plants-F samples. e-Waste debris was found to contain high levels of total BFRs compared with the environmental samples, with the levels of 22,812.66 ng/g. These results indicate that BFRs in the ambient environment could be derived from the e-waste dismantling scrap.

PBDEs constituted the most prevalent group of BFRs in the e-waste debris, sediments, soils-E and plants-E samples, with average contributions of 91.5, 89.7, 87.6 and 64.1 %, respectively (Fig. 3a). $\sum$PBDE (was defined as sum of all PBDE congeners) concentrations ranged from 482.87 to 5,313.94 ng/g in sediments, comparable to those in soils (ranging from 421.20 to 3,713.23 ng/g dw) and lower than those in e-waste debris (20,873.65 ng/g). The $\sum$PBDE concentrations in farmland soils ranged from 115.82 to 264.81 ng/g. The distribution profiles of PBDEs in the two types of plant samples indicated that a slightly higher concentration of $\sum$PBDE (52.06 ng/g dw) was found in the plants-E samples compared with that in the plant-F samples (21.66 ng/g).

The average $\sum$PBDE concentrations of farmland soils were comparable to those from Qingyuan (Gao et al. 2011; Liu et al. 2013), approximately four times higher than those from a rural area of Guangdong Province (Luo et al. 2009). These levels from the e-waste dismantling site were relatively lower than those from Qingyuan (25,478.84 ng/g) (Luo et al. 2009) and from some other e-waste sites in China (Leung et al. 2007; Wong et al. 2007; Ma et al. 2009; Wang et al. 2014) However, their levels in the current study were still higher than those from San Francisco Bay (2–8 ng/g) (Klosterhaus et al. 2012) and from Tokyo Bay, Japan (Minh et al. 2007). These comparisons suggest that serious PBDE contamination had been induced by the e-waste manual dismantling and mechanical crushing processes. This variation could be ascribed to the different distances from the potential pollution source and the recycling methods.

TBBPA was detected in quantifiable levels in all sediment and soils-E samples, and the levels ranged from 24.69 to 913.64 ng/g dw, which are significantly higher than those from Lake Chaohu (Yang et al. 2012), and consistent with the previous reported values in soils and sediments in the same regions (Zhang et al. 2009; He et al. 2010). In addition, they are lower than those from estuaries close to BFR manufacturer in England (2.4–9750 ng/g) (Morris et al. 2004). Because of the extensive use of TBBPA in Asia (Xiao 2006) and most electronic items

containing circuit boards being produced in China, as expected, the highest levels of TBBPA were observed in the e-waste debris samples (1,939.01 ng/g dw). The TBBPA concentration in farmland soils ranged between 29.98 and 165.79 ng/g (with an average of 81.75 ng/g), which is higher than that in samples from an industrialised region (0.025–78.6 ng/g) of East China (Tang et al. 2014) and industrial soils (3.4–32.2 ng/g) in Spain (Sánchez-Brunete et al. 2009).

Low amounts of TBBPA in biological samples, often below LOQs, have been reported by several studies (Morris et al. 2004; Harrad et al. 2010). Some possible explanations are that TBBPA has a lower bioaccumulation potential compared with other BFRs as PBDEs and that polar nature of TBBPA results in a greater level of metabolism and elimination inside the organisms. The mean concentrations of TBBPA in examined plant samples were relatively low in the *S. viridis* and peanut crop plants with levels of 42.26 and 18.67 ng/g dw, respectively (Table 1). The concentration of TBBPA in this study was slightly higher compared with the previous reported data on leaves of camphor trees in the same region (He et al. 2010). Compared with these Chinese data, the present levels of TBBPA in all samples were at the high end of the reported levels in China.

These results clearly indicated that the levels of metals, $\sum$PBDE and TBBPA in the sediment, soil and plant samples near the e-waste dismantling sites were significantly higher than those from farmland samples (Fig. 2b, c, $P<0.05$). These findings revealed that these pollutants released by e-waste activities were likely to be directly or indirectly transferred to aquatic and terrestrial ecosystems. Atmospheric transport and deposition may play a more important role in moving PBDEs and TBBPA from contamination sources to remote regions. In addition, the mean concentrations of TBBPA were lower than those of $\sum$PBDE in surface sediment, and similar distribution patterns of BFRs were also found in both soils-E and plants-E samples. This could be mainly attributed to the primary use of TBBPA as a reactive flame retardant, which is likely to restrict its emission from products into the environment. TBBPA may bind to organic matter such as humus substances, due to the presence of the phenolic group. This formation might not be extracted with the current extraction method and the degradation of TBBPA in the atmospheric transport process.

Composition profiles

Metals The composition profile of metals was clearly different from site to site and is shown in Fig. S1. Copper is a main component of electric wires and cables, and our results confirmed that the elevated levels and relative high contribution of Cu in total metals were found in sediment and soil (25–62 %). Galvanisation in the surface electric items and Pb-Sn soldering in printed circuit boards are applied in an attempt to prevent oxidation. As expected, the proportion of Zn and Pb
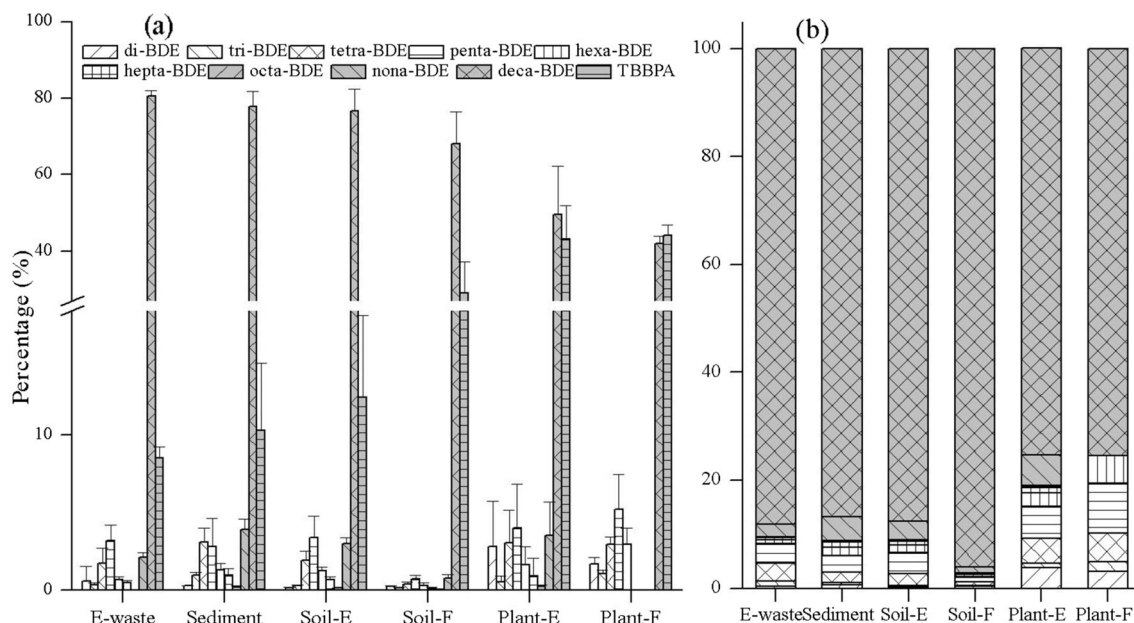
Fig. 3 The BFR profiles (**a**) and PBDE profiles (**b**) in the environmental samples from Longtang area. *Soil-E* represents the soil from the e-waste area; *Soil-F* represents the farmland soil; *Plant-E* represents plants near the e-waste area; and *plant-F* represents plants from the farmland

was 30 and 15 %, respectively. These results indicated that the contaminated soil could be derived from the transport and deposition of dust particles and ash of plastic cables and plastic chips containing toxic metals (Wong et al. 2007). We observed that elevated proportions and higher concentrations of As in farmland soil might be derived from the pesticides used. Zn was the dominant element in plant leaves, most likely due to the different bioaccumulation potential of metals in plants and the herb plants preferential bioaccumulation of Zn. The composition of metals in soil samples followed the same trend as the sediment. These results imply a similar transport and distribution of metals in the sediment and soil in the Longtang area.

BFRs BDE-209 and TBBPA contributed more than 80 % to the total BFRs in all samples (Fig. 3a), indicating that the deca-BDE commercial mixture and TBBPA commercial products may be the major BFRs used in electronic products. Furthermore, a noticeable difference in BFR profiles between plant samples and other samples was observed in Fig. 3a. The plant samples contained a much lower proportion of BDE-209 and a higher proportion of di- and penta-BDE, suggesting that there might be further debromination of PBDEs inside plants, or that less-brominated congeners were more likely to be taken up efficiently by plants (Mueller et al. 2006). The congener profiles of PBDEs in all sediment and soil samples from each site displayed some similar trends in Fig. 3b. As expected, BDE-209 dominated in all congeners, accounting for over 90 %, which is consistent with the levels in e-waste debris (approximately 90 %). These results could be attributed to the extensive usage of deca-BDEs in the electrical and

electronic products in China and the strong binding affinity of BDE-209 with sediment or soil particles. The relatively higher contributions of nona- and tetra- through penta-BDEs (main ingredient of penta-BDE commercial mixtures) and lower contributions of hepta- and octa-BDEs in total congeners were observed. These results indicate that the commercial deca- and penta-BDEs were the dominant contaminants in this study area. This finding is consistent with the evidence that the deca- and penta-BDE commercial mixtures are the most frequently used flame retardants in electronic products. In addition, a different profile was obtained for plant samples, when compared with the soil samples, in which contained a significantly higher content of less-brominated congeners (di- through hexa-BDEs). These differences might be ascribed to the preferential plant uptake of less-brominated congeners, and biotic debromination of highly brominated congeners to less-brominated congeners inside plants. In addition, the profile pattern of lower concentrations of BDE-209 and higher concentrations of di- through hexa-BDEs in farmland samples from farther from the e-waste dumping site is attributable to possible debromination of highly brominated congeners and/or redistribution between particles of various sizes during atmospheric transportation.

To identify the main origin of PBDEs in the study area, a comparison to some characteristic ratios of PBDE congener profiles in environmental samples to penta-BDE and deca-BDE commercial products that are widely used in various literature reports was conducted (Leung et al. 2007; Chen et al. 2013), including the BDE-47/(BDE-47 + BDE-99) and nona-BDEs/(nona-BDEs + deca-BDEs) ratios, which were plotted for each site (Fig. S3a). The BDE-47/(BDE-47 +

BDE-99) ratio in e-waste debris was 0.51, which is consistent with the ratios in the technical mixture (La Guardia et al. 2006), whereas the ratios in the environmental samples were between the ratios in the penta-BDE commercial mixture (0.44 and 0.50). The degradation of the highly brominated compounds in environmental samples led to the presence of the extensive various PBDE congener profile in environmental samples. Although nona-BDEs were not detected in the majority of plant samples, the evidence indicated relatively higher nona-BDEs/(nona-BDEs + deca-BDEs) ratios in plants (ranging from 0.04 to 0.15) than in the technical mixture (Fig. S3b). This further proves the degradation of the highly brominated compounds inside plants. In addition, the ratios of e-waste debris mostly resemble that of Saytex 102E (0.03) (La Guardia et al. 2006), suggesting that the e-waste contained complex plastics and cables that were mainly composed of deca-BDE commercial mixtures Saytex 102E as flame retardants. Moreover, the nona-BDEs/(nona-BDEs + deca-BDEs) ratios in sediments (0.04–0.06) and soils (0.02–0.09) were higher than that in deca-BDE commercial mixtures (0.03). These results further confirm the different transport behaviour of PBDE congeners in different environments.

Transport of contaminants

As e-wastes (which contain metals, PBDEs and TBBPA) are shredded mechanically, metals, PBDEs and TBBPA can be stripped off the e-wastes in the dismantling process and then diffused from the e-waste dismantling site (act as emission source) to the aquatic and terrestrial environment through direct discharge and air transport and dry/wet deposition. Sediment has a tendency to bind to organic matter and can generally be transported as suspended particles, causing the accumulation of metals, PBDEs and TBBPA in the downstream environment. The highest metal and $\sum$PBDE concentrations in sediment were found in S3, which is a bend in the river at which the slow flow rate could concentrate pollutants. Figure 2 also shows that the distributions of predominant metals (Cu, Pb and Zn) were uneven in sediments from site to site. The different distribution of metals in the sediment could be attributed to the different source inputs, distance from pollution source, hydrodynamic process and deposition conditions. In addition, there was no good linear relationship between PBDEs and TBBPA in sediment versus the distance, and their transport in aquatic environment could be attributed to the hydraulic conditions (such as flow direction and river bend) and deposition rate.

Pollutant concentrations in the terrestrial environment displayed a declining trend as a function of the distance. We plotted the logarithms of the pollutant concentrations against those of distances from the emission source. The log-linear regression equation exhibited a good linear relationship of $\sum$PBDE concentrations in soils versus distances (R^2=0.61, P<0.01, Fig. 4), suggesting that the PBDEs in soils from the

surrounding areas mainly came from the e-waste dismantling sites via short-range air transport. However, the relationship between $\sum$PBDE and TBBPA concentrations in plants was not significantly correlated with the distance. Furthermore, the data on individual PBDE congeners can fit well to a log-linear regression relationship (Fig. S4), and the slopes of the regression lines were −1.22, −1.13, −1.08 and −0.94 for the di- to penta-BDE, hexa- to hepta-BDE, octa- to nona-BDE and BDE-209, respectively. The slopes of the regression lines for the four groups were close to the previous slope of the relationship of PBDEs to distance (Zhao et al. 2009). There was no distinct difference in the slopes for the highly brominated and less-brominated PBDEs, indicating that the transport of the highly brominated PBDEs might not differ from that of less-brominated PBDEs at short-range scale, which is consistent with the previous studies on the short-range transport of PBDEs (Li et al. 2011b; Luo et al. 2013). This differs from the long-range transport of PBDEs.

As shown in Fig. 4, a clear declining trend of the concentration of TBBPA in soils with increasing the distance was also observed (P<0.01). These results indicate that TBBPA had transport potential to the surrounding areas. Moreover, the slopes of the log-linear regression equation for $\sum$PBDE (−0.96) were slightly greater than that for TBBPA (−0.67) (Fig. 4). This result indicates that the transport potential of TBBPA might be slightly different from that of PBDEs, which most likely can be attributed to the differences in physicochemical properties, including, according to reports, the high water solubility (0.17 to 4.2 mg/L) and low vapour pressure (4.72×10^{-9} Pa at 25 °C) of TBBPA (Kuramochi et al. 2008) versus those of PBDEs. TBBPA and highly brominated congeners preferentially sorbed to suspended particles, so their transport potential was mainly controlled by transport behaviour of the particles. These findings suggest that TBBPA in soils might mainly be transported via wet deposition of particles. This reflects that mild temperatures and humid weather conditions may influence the transport behaviour. Overall, it was obvious that the concentrations of $\sum$PBDE and TBBPA in the soils displayed a distinct decreasing trend with increasing distance from the e-waste dismantling site. These findings indicate that the diffusion of PBDEs and TBBPA from the point pollution source made a dominant contribution to PBDEs and TBBPA contamination in the surrounding areas.

However, metals in the terrestrial environment displayed no linear relationship with the distance. The results further confirmed that metals had less transport potential to the surrounding area because of their low vapour pressures, which is consistent with a previous report by Li et al. (2011b).

Correlation

The relationships between the concentration of metals, PBDEs and TBBPA were examined and are summarised in
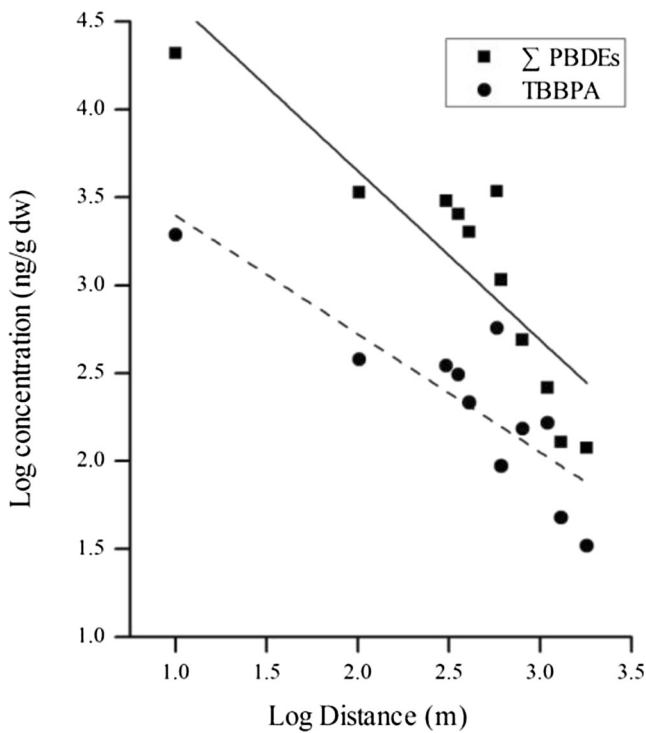
Fig. 4 The relationship between the logarithm of concentration of total PBDEs and TBBPA concentration in soil versus that of distance from the e-waste dismantling site (m) PBDEs $y=-0.96\times+5.57$, $R^2=0.74$, TBBPA $y=-0.67\times+4.07$, $R^2=0.70$

Table S2. A strong correlation ($P<0.05$) between Cu, Pb, Zn, Ni and Cd indicates that these metals came from a common source. However, Hg and As were not significantly associated with other metals. This finding suggests there was a discrete contamination source of the seven metal pollutants in the study regions.

Interestingly, strong positive correlations between the total concentration of PBDEs and TBBPA were also found in all samples (Table S3). There was a moderate positive linear relationship between the concentrations of ∑PBDE in the plants and soils ($P<0.05$, $R^2=0.43$, Fig. S3) and with a much higher proportion of less-brominated PBDEs in plants than in the soils, and foliar uptake from the air mainly contributed to the accumulation of PBDEs in plants. There was no significant linear relationship for TBBPA. These findings indicate similarities in the input pathways of PBDEs and TBBPA into the local environment but differences in their environmental behaviours. The metal concentrations in plants were not correlated with their concentration in soils, which is consistent with previous results (Fu et al. 2008). These findings suggest that the accumulation of metals, TBBPA and PBDEs in plants might be attributed to polluted soil and aerial deposition during the e-waste dismantling process.

The TOC value in the sediment and soils for each site varied widely, with a range of 2.02 to 13.44 %. It is well known that sediment/soil, due to high organic carbon content,

can accumulate significant concentrations of hydrophobic organic contaminants, such as PBDEs and TBBPA (Gouin and Harner 2003). To determine the TOC and pH influence on the distribution of metals and BFRs, Pearson correlation analysis was performed, and the correlation coefficients are listed in Table 2. The correlation coefficients between metals and TOC in the soil samples were relatively high (0.96 for Cu, 0.92 for Zn, 0.90 for Ni, 0.86 for Pb and 0.84 for Cd). There was a significant correlation only between Zn, Pb and Ni, and TOC in the sediment samples. Significant correlations between TBBPA and TOC and between individual PBDE congeners and TOC were also found (see Table 2). These findings suggest that TOC played an important role in the distribution of contaminants. Organic carbon was reported to associate with both metals and lipophilic organic contaminants and, therefore, to play a role in their mobility and fate in soils and sediments (Bradl 2004; Bayen 2012). However, TOC does not solely explain the distribution of contaminants in sediments and soils.

Table 2 Correlations between metals and BFRs in sediments/soils and TOC, pH

Samples	Sediments		Soils	
Parameter	TOC	pH	TOC	pH
Cu	0.74	−0.42	0.96**	−0.57
Zn	0.83*	−0.64	0.92**	−0.58
Pb	0.85*	−0.55	0.86**	−0.62
Cd	0.75	−0.39	0.84**	−0.56
Ni	0.91**	−0.49	0.90**	−0.57
Hg	0.67	−0.36	0.51	0.36
As	−0.48	0.63	0.53	0.21
Total metals	0.79*	−0.50	0.95**	−0.58
BDE-15	−0.11	0.54	0.90**	−0.49
BDE-28	0.73	−0.23	0.97**	−0.57
BDE-47	0.76*	−0.41	0.92**	−0.55
BDE-100	0.68	−0.39	0.87**	−0.56
BDE-99	0.73	−0.44	0.89**	−0.55
BDE-154	0.46	−0.31	0.92**	−0.56
BDE-153	0.85*	−0.45	0.96**	−0.56
BDE-183	0.86*	−0.60	0.96**	−0.54
BDE-203	0.84*	−0.52	0.95**	−0.52
BDE-208	0.97**	−0.55	0.96**	−0.54
BDE-207	0.95**	−0.55	0.98**	−0.53
BDE-206	0.89**	−0.53	0.97**	−0.54
BDE-209	0.87*	−0.54	0.97**	−0.53
∑PBDEs	0.86*	−0.54	0.97**	−0.53
TBBPA	0.89**	−0.51	0.84**	−0.53

**Correlation is significant at the 0.01 level (two-tailed)

*Correlation is significant at the 0.05 level (two-tailed)

In general, metals enter into soil/rivers and tend to bind cohesively to soil/sediment particles. However, metals bound to soil/sediment particles can be remobilised in an acidic environment. Various studies have reported that pH value plays an important role in determining metal behaviours (Equeenuddin et al. 2013). The pH value in the samples in the present study was relatively low (4.7–6.6) and comparable to reported data (Tang et al. 2010). Uncontrolled acid waste discharge along the riverbank or into the river could have decreased the pH of the soil/river. However, the metals had a poor negative correlation with pH value. It was also found that the concentration of PBDEs and TBBPA in the sediments and soils presented nonsignificant negative correlations (*P*>0.05) with pH value (Table 2). These results suggest that pH did not play a significant role in terms of the distribution and dispersion of metals, PBDEs and TBBPA.

In general, the chemicals associated with e-waste were released into the environment as a mixture. It is not uncommon that metals and organic pollutants coexist in the ambient environment (Tang et al. 2010; Zhang et al. 2014). Relationships between the total concentration of metals and BFRs in environmental samples were analysed. To eliminate the unit variation, the concentration was logarithmically calculated. A strong positive correlation between metals and BFRs were found in sediment and plant samples (*r*=0.80 and 0.70, respectively), which indicated that the metals and BFRs came from a similar source in the Longtang region. This inference is further supported by the tightness of the cluster analysis.

Cluster analysis and source attribution

Cluster analysis was conducted to identify the similarity of the concentrations of metals and BFRs. The ward method and correlation for distance measure were used to obtain the clusters. Figure 5a shows that the two main groups can be distinguished with the dendrogram from the cluster analysis results. The first group can be divided into two subgroups. The first subgroup includes Cu, Zn and PBDEs, which were the main contaminants in all samples, and significantly correlated with each other. The second subgroup includes Ni, Cd, Pb and TBBPA. These contaminants were associated with each other and presented low to moderate contamination. The second major group included As and Hg. As and Hg did not appear to be associated with other variables. These results confirmed the assumption that a point source of Hg and As existed in this study area. In other words, the results from the cluster analysis confirmed the hypothesis that suggested that the contaminants might have a common source and could be mainly derived from the e-waste dismantling activities in Longtang. For example, mechanical crushing and manual dismantling resulted in metal and BFR contamination in the ambient environment.

PCA was also performed to clarify the general distribution patterns of PBDEs by comparing compositions of environmental samples and that of PBDEs commercial mixtures (Fig. 5b). This plot highlights the similarities within sample types, despite the variations in sampling locations for each sample. Of the total variance within the dataset, PC1 and PC2 accounted for 35.1 and 25.9 %, respectively. Highly positive PC1 values were found for the penta-BDEs commercial mixture, and positive PC2 values were displayed by the octa-BDE formulation.
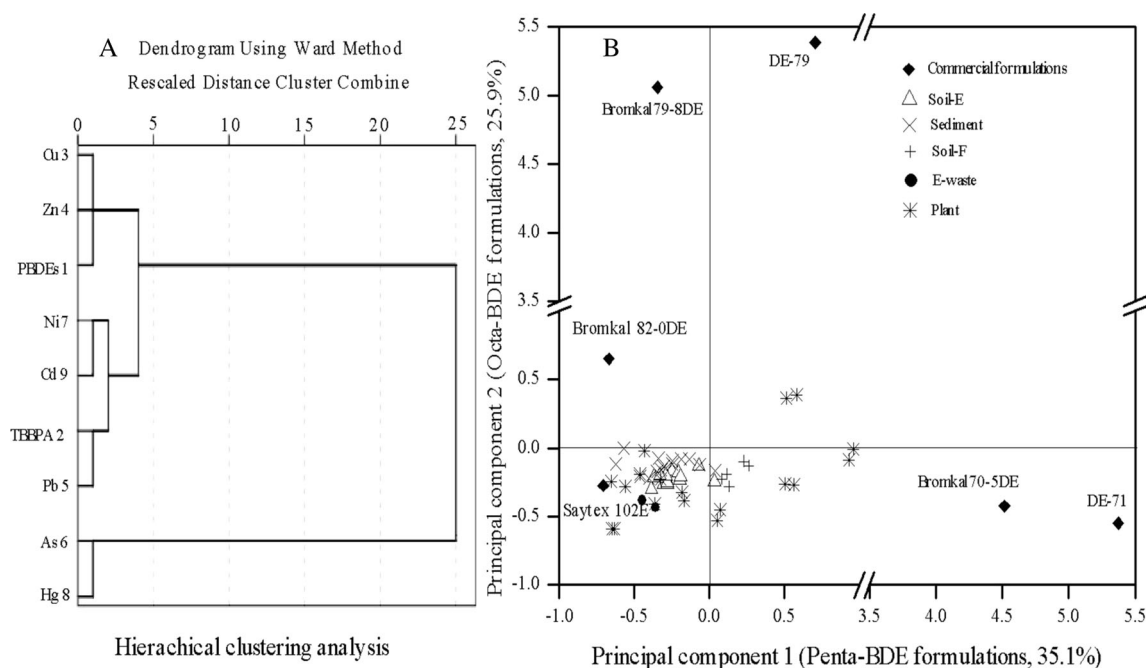

Fig. 5 Hierachical clustering analysis of metals and BFRs (**a**) and plot of PCA scores for PC1 and PC2 (**b**)

Highly negative values for both PC1 and PC2 were displayed by the deca-BDE formulation. Even more remarkable was the similarity in sample scores along the first two PCs among e-waste debris, sediment and soil samples, and which were characterised by strongly negative values of both PC1 and PC2 (Fig. 5b). The e-waste debris, sediment and soils-E samples displayed greater negative values of PC1 than farmland soil samples, which implies that the e-waste dismantling could constitute a major source of deca-BDE in those samples. The plant samples projected on PC1, influenced by a combination of penta-BDE and deca-BDE formulation. Most samples centralised near the origin of the PCA plot, suggesting that the contamination could be influenced by inputs from more than one PBDE commercial mixtures in the Longtang area.

Conclusion

The elevated concentrations of metals, PBDEs and TBBPA in all samples in the vicinity of the sampled e-waste dismantling sites in Longtang confirmed that the e-waste was the predominant source of metals and BFR contamination of the local environment. Indeed, when comparing the results with the action value from the New Dutch list, Cu, Zn and Pb were the primary contaminants in sediment and soils-E samples. The composition profile of BFRs was generally similar in the e-waste debris and environmental samples. The relative contributions of TBBPA and BDE-209, BDE-207, BDE-99 and BDE-47 in all samples were dominant in the total BFRs. Metals had lower mobility than BFRs and remained in their original locations, and PBDEs and TBBPA obviously decreased with increasing distance from the point source. A significantly positive correlation among the concentration of metals, PBDEs and TBBPA was observed, suggesting that these substances could have a common source, and there was a significant correlation between TOC, most metals and all PBDE congeners and TBBPA. TOC played an important role in controlling the contaminant levels. According to the results of the correlation analysis, PCA and cluster analysis, we observed that Cu, Zn, Pb, Ni, Cd, PBDEs and TBBPA were the main contaminants and that these contaminants have a common source, i.e. the e-waste dismantling process. Overall, TOC and proximity to the point sources were major factors controlling the distribution of contaminants. Because the distribution and transport of metals and BFRs in the environment are very complicated, more research is needed to investigate the combination of metals and organic pollutants (BFRs).

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