RESEARCH ARTICLE

Characterization of heavy metals and brominated flame retardants in the indoor and outdoor dust of e-waste workshops: implication for on-site human exposure

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Abstract Forty-four indoor and outdoor dust samples were collected from e-waste workshops and were analyzed to characterize the heavy metals and brominated flame retardants (BFRs) as well as on-site human exposure. The results showed that the most abundant Polybrominated diphenyl ethers (PBDE) congener from three sites was deca-BDE, and it was penta-BDE for the other site. A significant and positive association was found between BDE-209 and decabromodiphenyl ethane (DBDPE). The high percentage of nona-BDE indicated the debromination of deca-BDE during e-waste recycling. The ratio comparison of BDE-47 to (BDE-100+BDE-99) indicated that the outdoor dust went through more physiochemical processes. The enrichment factors for Cu and Pb were high in both the indoor and outdoor samples. Cd significantly exceeded the Chinese soil guideline grade III. The PCA results combined with the enrichment factor (EF) values suggested common sources and behaviours of Cu, Pb and Sb in the indoor dust. Co, Cr, Ni, Zn and Mn in the outdoor samples were more likely affected by crust. Strong correlations were found only for Pb and Sb with polybrominated diphenyl ethers (PBDEs). The hazard index for on-site human exposure to Pb was at a chronic risk. Despite the low deleterious risk of BFRs, concern should be given to DBDPE; the chronic toxicity of which is not known.

Keywords Heavy metals · Brominated flame retardants · Indoor dust · Outdoor dust · On-site human exposure

Introduction

The quantity of discarded electronic equipment (e-wastes) has been rapidly increasing around the world as a consequence of newer generations and constant upgrades of electronics (Robinson 2009). It was estimated that 50 million tons of e-wastes are produced annually (Ni et al. 2009). Massive quantities are transported to developing countries. Approximately 80 % of e-waste collected in the western USA was exported to Asia, 90 % of which were sent to China coastal areas through illegal imports for recycling (Schmidt 2006).

Bromine flame retardants (BFRs) are commonly used in electronic products to meet fire regulations. Polybrominated diphenyl ethers (PBDEs) were the most extensively used BFRs in recent decades. Commercial penta- and octa-BDEs have been found to pose high health risks to humans and wildlife (Hites 2004), which resulted in them being banned in some regions of the world (EU 2003, Renner 2004). However, commercial deca-brominated diphenyl ether (BDE) mixtures were also banned in the European Union and parts of the USA, although they are still widely used in many countries (Betts 2008). The restrictions and bans for the use of PBDEs have caused manufacturers to seek non-PBDEs BFRs. For instance, decabromodiphenyl ethane (DBDPE) is now used as an alternative for deca-BDE in various products. Because DBDPE has been recently detected in the environment and wildlife (Kierkegaard et al. 2004, Shi et al. 2009), it should receive more attention.

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In addition to BFRs, metal is also an important hazardous substance that is released from e-waste recycling. Previous studies at e-waste recycling sites in Asia have revealed hazardous metal pollution in various environmental media including the air, soil, water, sediments and food (Chen et al. 2011, Li et al. 2011, Luo et al. 2011, Wong et al. 2007a, b, c, Zheng et al. 2013). Metals have great potential to accumulate in vital organs of the human body. Pb and Cd are associated with a number of adverse health effects such as cardiovascular, nervous system, blood and bone diseases (Jarup 2003). Excessive Cu may lead to toxic effects in humans (Brewer 2010).

Among the various environmental media, dust has been found to have high levels of BFRs from different regions of the world (Harrad et al. 2008, Wilford et al. 2005). Metal concentrations in dust were also at high levels at e-waste sites (Wong et al. 2007a, c). Dust is a significant medium and exposure pathway of toxic substances. Significant association was found between the PBDE concentration in breast milk and dust, indicating the prominent role of dust in exposure (Wu et al. 2007). The concentration of Pb in human blood was also strongly associated with the Pb concentration in dust (Lanphear et al. 1997). BDE-209 and Pb were found in the blood of e-waste workers and toddlers living in e-waste areas. The amounts were 3436 ng/g lipid weight and 100 μg/L for the workers and toddlers, respectively (Huo et al. 2007, Wen et al. 2008).

Taizhou has been involved in e-waste recycling for decades. In recent years, a large fraction of e-waste recycling shifted to remote areas. Simple household recycling workshops run by families are the most common form. High concentrations of BFRs and metals in this area have been reported in environment media and the human body (Jiang et al. 2014, Tang et al. 2010, Zhang et al. 2011). However, e-waste workshops have a steady accumulation of BFRs and metals due to the recycling activities, which cause adverse effect on human body, and could be the point source for the surrounding environment. Given their potential impact on human health, particularly on young people, understanding dust BFRs and metals as well as the associated exposure of people in workshops is urgent. Therefore, the present study aimed to investigate the characterization of heavy metals and BFRs in dust directly collected from the workshops, and the on-site human exposure of these two types of contamination was also assessed. Such a survey is also needed for local governments to make more strict regulations.

Materials and methods

Research area

A large composite sample of dust was procured in October 2013 from family-run workshops involved in abandoned recycling for decades from remote areas of Wenling City,

southeast of Zhejiang Province, China. The location and the information of the sampling sites are shown in Fig. 1 and Table S1. Site E was chosen as the reference site and was located in a village far from other sites and without any e-waste recycling.

Sample collection and preparation

Multiple ground surface dust samples both inside and outside of the workshops and reference site (indoor and outdoor dust mentioned later) were collected using plastic brushes and dustpans with a gentle sweeping motion. A total of 47 composite samples were collected, 24 indoor and 23 outdoor. The mass of each sample ranged from 15 to 30 g. After each sampling, the brushes and dustpans were cleaned with paper towels. All samples were stored in paper bags, which were previously heated at 50 °C overnight to remove volatiles after collection and sealed in polyethylene bags (Ziploc) at <4 °C for transport to the laboratory. All of the samples were air-dried at room temperature to a constant weight and then sieved (<75 μm) prior to chemical analyses.

Chemical analysis

BFRs analysis

For the measurement of PBDE and DBDPE, each sample (0.5 g) was spiked with the surrogate standards $^{13}C_{12}$-PCB-141 and $^{13}C_{12}$-BDE-209 and extracted with 100 ml of acetone/dichloromethane (1:1, v/v) for 8 h in a soxhlet apparatus (Buchi, Switzerland). The extracts were condensed to near dry and solvent-exchanged to 1 mL of hexane. The cleanup was conducted on a multi-layer silica gel column, and 40 mL of n-hexane/dichloromethane (1:1, v/v) was added to elute the target substances. The fractions were concentrated to 1 mL. A known amount of injection internal standard, $^{13}C_{12}$-PCB-208, was added before instrumental analysis. Detailed information of the analysis conditions for the BFRs is shown in Supplementary Material.

Heavy metals analysis

Each sample (0.250 g) was digested according to the USEPA Method 3052, with modifications. An acid mixture of HNO_3, HCl and HF (3:1:1, $v/v/v$), along with the samples, was added into polytetrafluoroethylene vessels for microwave digestion (Ethos A, Milestone, Italy). After digestion, the extracts were filtered into 25-mL volumetric flasks. The concentrations of Co, Cr, Mn, Cu, Ni, Pb, Sb, Zn and Cd were determined by inductively coupled plasma mass spectrometry (ICP-MS) (NexION300, PerkinElmer, USA).
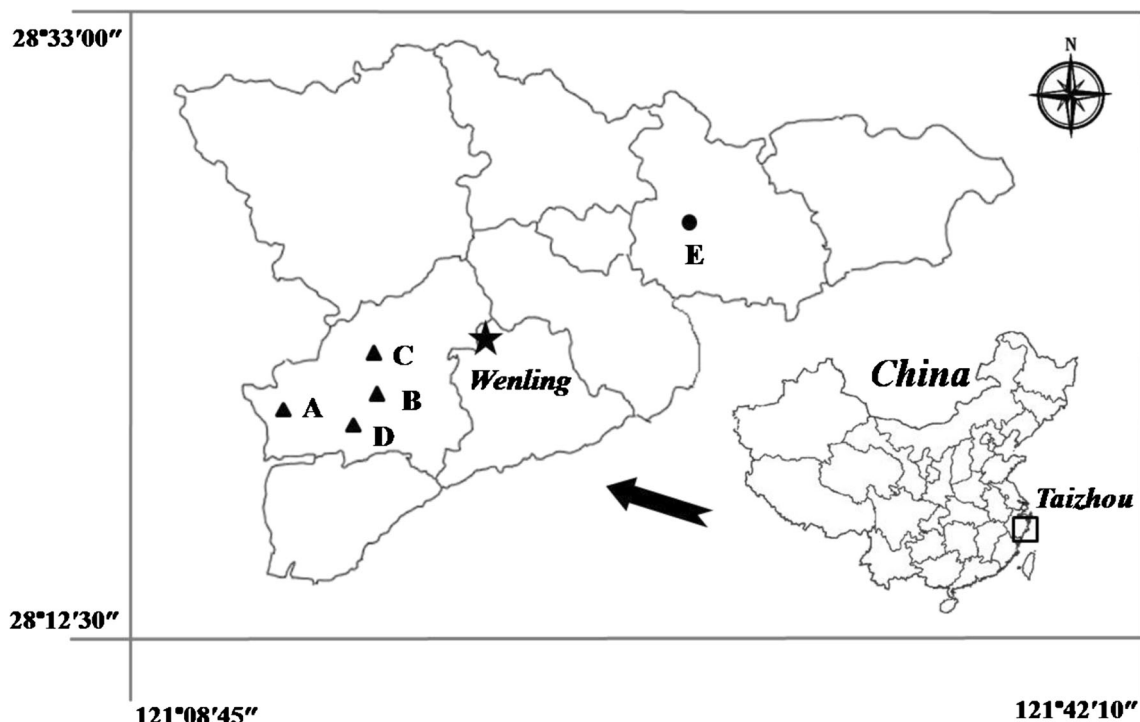
Fig. 1 Map of the study area and sampling sites

Quality control and quality assurance

Each sample was duplicated for accuracy and reproducibility. The recoveries of ^{13}C-PCB-141 and ^{13}C-BDE-209 were in the range of 88–107 and 78–98 %, respectively, for dust samples. A procedure blank and a solvent blank were run for each batch of ten samples. No target substances were detected. The limit of detection (LOD) was defined as a signal/noise (S/N) ratio of 3, and it ranged from 0.1 to 4.5 ng/g for PBDEs and 4.5 ng/g for DBDPE.

To confirm the accuracy of the analytical methods for metals, a certified reference material GSS-5 (Institute of Geophysical and Element Prospecting, People's Republic of China) was analyzed. The results were in good agreement (98–108 %) with certified values.

Enrichment factors for metals

The enrichment factor (EF) is defined by the following equation:

$$\mathrm{EFs} = \frac{(C_x/C_{Mn})_{sample}}{(C_x/C_{Mn})_{background}} \tag{1}$$

where C_x is the concentration of metals in dust and background, and C_{Mn} is the concentration of Mn. The background metal concentration in Zhejiang Province was obtained from

CNEMC (1990). Mn was abundant in the crust and had a small concentration range in this study, so it was selected as the reference element in the EF calculations.

Enrichment factor: EF <2 minimal enrichment, EF =2–5 moderate enrichment, EF =5–20 significant enrichment; EF =20–40 very high enrichment; and EF >40 extremely high enrichment (Li et al. 2010).

Statistical analysis

All statistical analyses were performed using SPSS 16.0 for Windows (SPSS, Inc.). For data less than the LOD, a value of one half of the LOD was assigned. The probability distribution tests through the Kolmogorov-Smirnov test for all the data were normal. ANOVA tests were used for statistical comparisons between more than two groups. Pearson regressions were used to test the correlations between contaminants. PCA is an effective analytical tool to minimize the set of original variables and extract a small number of latent factors or principal components for analyzing the relationships between observed variables and samples. Statistical significance was set at $p < 0.05$.

Exposure and risk assessment

Risk assessment with regard to exposure to contaminated dust by ingestion was performed to estimate the non-cancer toxic

(chronic) risk. The exposure doses were calculated according to the equation as follows (USEPA 1997):

$$ADD = \frac{C \times IngR \times EDF}{BW} \qquad (2)$$

Non-cancer toxic risk was determined by calculating the hazard quotient (HQ),

$$HQ = \frac{ADD}{RfD} \qquad (3)$$

If HQ ≤1, noncancerous effect are unlikely, whereas for HQ >1, adverse health effects might be possible. HQ >10 is considered to be a high chronic risk. The detailed definition and parameters for these two equations are listed in the Supplementary Material.

Results and discussion

BFRs and metal concentrations in dust

The mean and range of the concentrations for BFRs and metals are shown in Table 1 and Table S2. Among the five sampling sites, the highest mean concentrations of PBDEs in both the indoor and outdoor dust were at site A at 46,600 and 9000 ng/g, respectively. However, with the exception of nona- and deca-BDE, samples from site D provided evidence of a significant emission source of low bromated PBDE to the environment. The sum of the eight PBDE congeners (BDE-28, 47, 100, 99, 154, 153, 183 and 203) was 14,400 and 6250 ng/g for the indoor and outdoor samples, respectively. The mean concentration in indoor samples from sites A to D was 27,400 ng/g, which is comparable to those detected in workshops from the Guiyu and Taizhou area; the values of which were 14,800 and 30,700 ng/g, respectively (Leung et al. 2011, Ma et al. 2009). The mean concentration in outdoor samples was 7060 ng/g, which is higher than those from e-waste areas from south China (Leung et al. 2011). DBDPE was also detected in 43 of the 47 dust samples. The highest concentrations were detected in the samples from site A, which were 9200 and 1130 ng/g for the indoor and outdoor samples, respectively. The mean value (4800 ng/g) of the in indoor samples from sites A to D was higher than those detected in e-waste storage facilities (1300 ng/g) and work-shops (3030 ng/g) from south China (Muenhor et al. 2010, Zheng et al. 2011). A summary of the BFRs concentrations compared with other studies is shown in Table S3. In general, the BFR concentrations in our study were much higher than those reported in non-recycling areas (Ali et al. 2011, 2013, Fromme et al. 2014, Takigami et al. 2009), indicating that the high level of BFRs contamination resulted from e-waste recycling. For the reference site, BDE-209 was the major

component, and the mean values were 226 and 103 ng/g for the indoor and outdoor samples, respectively. This was expected due to the still common use of commercial deca-BDE in China. The BFR concentrations in indoor samples were significantly higher than those in the corresponding outdoor samples ($p<0.001$).

For metal concentrations, soil guidelines (Table S4) were applied to evaluate the extent of contamination due to the lack of guidelines in dust. Of the nine metals investigated in the indoor dust samples, the Cu and Pb levels were extremely elevated. The highest concentration of Pb was found in samples collected from site D, and the mean value was 17,230 mg/kg. It was an order of magnitude lower than those detected in workshops in southeastern China, but it was comparable for Cu concentration (Leung et al. 2008). The Cu and Pb concentrations exceeded the New Dutch List action value (VROM 2001) by 11–69 and 5–54 times, respectively. The Co and Cr concentrations were all below the action value. The Zn and Ni concentrations exceeded the action value, with the exception of two samples of Zn and all samples of Ni at site B. The mean Cd concentrations were below the action value. However, all Cd concentrations significantly exceeded the Chinese guidelines, even for grade III (industrial activity) (SEPA 1995), with a range from 3.3 to 20.5 mg/kg. The Sb concentrations were all above the action value, with the exception of two samples, and the highest concentration was 244 mg/kg.

For the outdoor dust, the metal concentrations were significantly lower than the corresponding indoor samples ($p<0.01$). The Cu and Pb concentrations in the outdoor samples were above the New Dutch List action value, with the exception of two samples for Pb, and the highest concentrations were 1790 and 6960 mg/kg, respectively. They were higher than those from non-recycling areas (Han et al. 2006, Lu et al. 2010). The mean Sb concentration exceeded the action value by 1.8 times, and the concentration ranged from n.d. to 112 mg/kg. The Cd concentrations in the outdoor samples were also above the less stringent Chinese grade III value, with one sample not detected. The Co, Cr, Ni and Zn concentrations were within the action value or with little impact.

Mn was also analyzed in both the indoor and outdoor samples. Moreover, Cu, Pb, Ni, Zn and Cd were also detected in samples from the reference site. In contrast to the recycling area, the metal concentrations in the outdoor samples were higher, indicating the influence of other human activities. A summary of the metal concentrations compared with other studies is shown in Table S5.

Profiles, relationships and debromination for BFRs

In general, deca-BDE accounted for the major proportion of the total PBDE in samples from sites A, B and C, with 80.8,

Table 1 Mean concentrations of BFRs (ng/g) and metals (mg/kg) in the dust from five sampling sites

BFRs		BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-203	BDE-208	BDE-207	BDE-206	BDE-209	DBDPE	$\sum_8$PBDEs[a]	$\sum_{12}$PBDEs
A	In	228	1806	109	2088	114	546	1170	412	586	962	924	37,600	9200	6480	46,600
	Out	89.6	561	36.8	605	55.3	223	209	83.0	143	346	283	6360	1130	1870	9000
B	In	153	989	86.7	1176	97.2	273	570	226	371	585	442	23,500	5200	3570	28,500
	Out	26.9	401	20.4	381	18.2	99.3	169	69.5	165	244	213	3370	790	1190	5200
C	In	59.0	473	49.6	580	61.6	187	365	102	143	424	368	10,300	2900	1880	13,100
	Out	9.52	267	18.5	201	26.9	73.0	110	47.8	82.0	102	94.0	1840	440	750	2870
D	In	752	4949	539	5740	418	540	1452	46.4	81.6	201	219	1170	210	14,400	16,100
	Out	340	2310	256	2021	246	336	649	87.1	103	250	216	1690	340	6250	8500
A–D	In	285	1966	183	2310	163	393	891	211	314	575	528	19,600	4800	6410	27,400
	Out	116	860	80.8	770	86.2	184	275	72.5	124	240	205	4050	670	2450	7060
E	In	—[b]	8.61	—	10.3	—	—	—	—	—	—	3.88	226	—	—	249
	Out	—	—	—	45.4	—	—	—	—	—	—	—	103	—	—	103

Metals		Co	Cr	Mn	Cu	Ni	Pb	Sb	Zn	Cd
A	In	32.5	141	782	5150	360	9630	52.3	1360	10.8
	Out	18	48.2	559	675	64	1450	17.9	383	5.3
B	In	21.3	85.9	637	4220	130	6720	39.3	951	9.5
	Out	11.1	47.5	543	601	55.5	860	10.1	163	4.2
C	In	52.6	193	958	6760	553	5120	24.2	1290	12.7
	Out	20.2	107	717	1260	197	624	7.7	203	4.8
D	In	39.6	133	817	9450	401	17,230	165	939	7.2
	Out	17.9	81.4	578	950	171	3640	71.6	251	4.9
A–D	In	36.7	142	808	6290	374	9520	67	1160	10.2
	Out	17	69.9	600	867	122	1890	27.1	257	4.8
E	In	3.9	8.2	403	19.1	12.8	33.4	—	59.2	—
	Out	9.8	29.7	491	45.4	—	97.2	—	89	—

[a] Sum of BDE-28, 47, 100, 99, 154, 153, 183 and BDE-203

[b] Not detectable

82.5 and 78.6 % for indoor and 73.6, 69.9 and 67.3 % for outdoor dust, respectively. The profiles were similar to those observed in studies elsewhere (Cao et al. 2013, Wang et al. 2010). This was mostly attributable to the high use of commercial deca-BDE in older electronic products around the world. However, the composition of PBDE congeners detected in samples from site D could be commonly found in commercial penta-BDE products. The concentrations were significantly higher than other sites ($p<0.01$). BDE-47 and BDE-99 attributed 30.7 and 35.7 % for indoor samples and 24.4 and 26.5 % for outdoor samples, respectively. The characteristics of PBDE homologues in dust were highly affected by the types of e-wastes and specific recycling activity. Heating or burning can lead to a high concentration of low brominated congeners in the workshops (An et al. 2011), which might cause the high percentage of penta-BDE in the dust from site D.

As shown in Fig. 2, similarities were found in the composition of PBDE congeners between the indoor and outdoor samples. However, the elevated total percentage of tri- through hepta-BDE in the outdoor dust from the former three sites suggested that less brominated PBDE congeners were more likely to escape the workshop than the higher ones due to their relatively high vapour pressures (Jones-Otazo et al. 2005) and depositing along with fine particles (Wei et al. 2009). On the contrary, a decline of this percentage was observed in the composition at site D. It was due to the long-range atmospheric transport (LRAT) of PBDEs (Melymuk et al. 2012), especially for low brominated congeners after heating and exhaustion. A previous study confirmed that tri- through hexa-BDE presented significant proportions in the atmosphere of rural sites away from the e-waste areas (Tian et al. 2011). Moreover, the mean concentrations of octa- through deca-BDE, except for BDE-206 in outdoor samples, were higher than their corresponding indoor concentrations at site D. This implied that the decline of this percentage was

also driven by the high contamination of high brominated PBDEs from other emission sources at this sampling site.

A significant and positive association between BDE-209 and DBDPE ($r^2=0.907$, $p<0.001$) was found in the linear correlation examination of all dust samples (Fig. S1). This implied similar emission sources of BDE-209 and DBDPE and was consistent with the use of DBDPE as an alternative to deca-BDE. The mean ratio of DBDPE to BDE-209 (0.21) was higher than the calculated values obtained from e-waste storage facilities (0.04) but lower than those found in workshops from south China (0.32) (Muenhor et al. 2010, Zheng et al. 2011). The presence of DBDPE indicated that there were e-wastes containing "novel" BFRs in our study areas.

Figure 3a shows the ratios of BDE-208:BDE-183 and BDE-208:BDE-209. It was reported that the former ratio in the octa-BDE and the latter ratio in the deca-BDE formulation was under 0.45 and 0.08 %, respectively (La Guardia et al. 2006). In fact, these two ratios in our dust samples from e-waste workshops were all substantially exceeded and implied the occurrence of debromination of BDE-209 to BDE-208. Deca-BDE was confirmed to undergo photo degradation under light to form nona-BDE (Bezares-Cruz et al. 2004). This decomposition may occur during large-scale and long-term e-wastes recycling activities. However, it is also possible that debromination may have occurred during the manufacturing of PBDE-containing products (Chen et al. 2010). In addition to BDE-208, the other nona-BDEs (BDE-206 and BDE-207) in our study were also considerable. This suggested that there were different degradation products for deca-BDE to nona-BDE (Söderström et al. 2004).

Moreover, penta-BDE (BDE-99 and BDE-100) was confirmed to further debrominate to tetra-BDE (BDE-47) under solar irradiation (Söderström et al. 2004). A comparison of the BDE-47 to (BDE-100+BDE-99) ratios between the indoor and outdoor samples is exhibited in Fig. 3b. The standard deviation of this ratio in outdoor dust was 0.15 in comparison

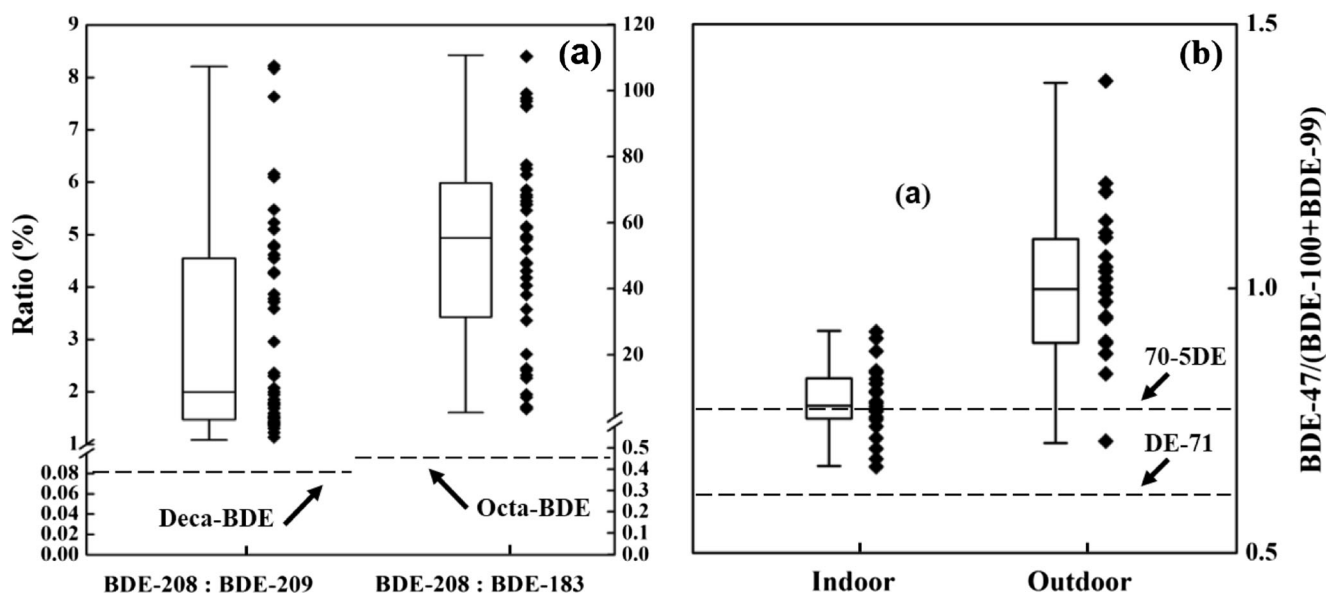**Fig. 2** Congener profiles of PBDEs in the indoor and outdoor dust from four sampling sites
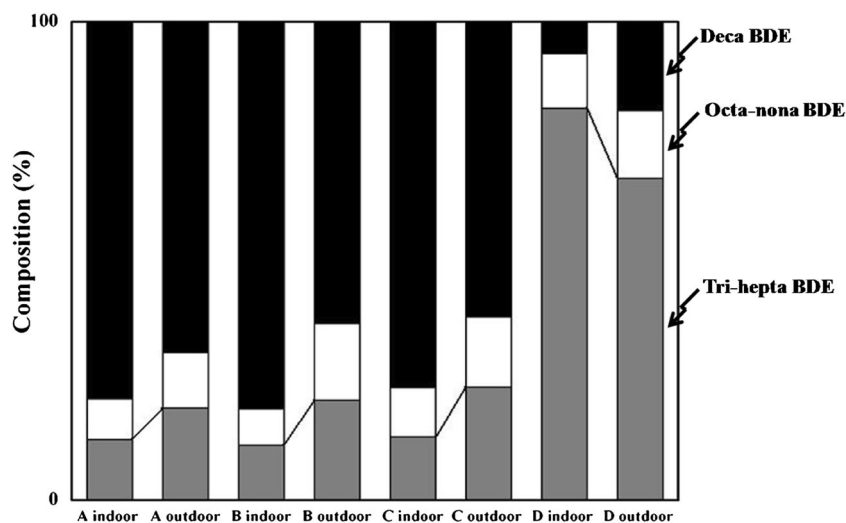
Fig. 3 Comparison of PBDE congener ratios in the indoor and outdoor dust with those in commercial BDE products

with 0.06 for indoor dust. In addition, these ratios in the outdoor samples deviated more from those in two commercial penta-BDE products. To some extent, these results suggested that the PBDE in outdoor dust went through more physio-chemical processes, such as debromination and volatilization. However, further studies are required to fully understand the degradation of these brominated congeners in the indoor and outdoor dust.

EFs, contamination profiles comparison and statistical analysis

The EF values calculated by Eq. (1) are plotted in Fig. 4. The EFs for Co and Cr in both indoor and outdoor samples were all lower than 1, indicating a predominant source of crustal soils
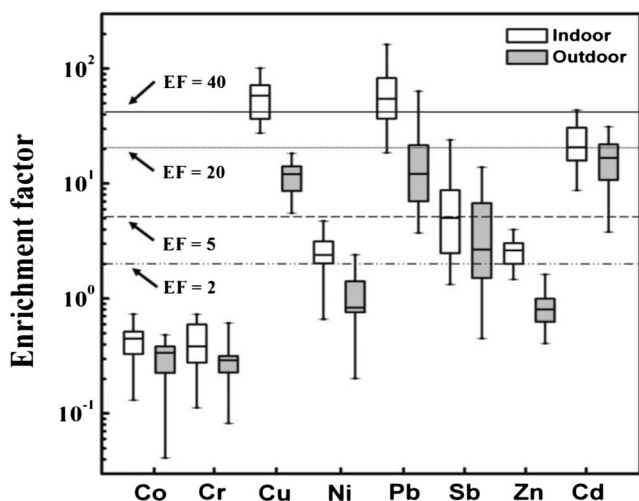

Fig. 4 The enrichment factors of metals in the indoor and outdoor dust samples

rather than other anthropogenic sources (Liu et al. 2003). Elements Ni (2.47) and Zn (2.63) in indoor dust, with mean EF values higher than 2, had moderate enrichment and were derived from e-waste recycling activities. However, these two metals in the outdoor samples were lower than 2, with the exception of two samples for Ni. The mean EFs of element Sb were 6.40 and 3.70 for indoor and outdoor samples, respectively. Elements Cu, Pb and Cd in the outdoor samples showed "significant enrichment" with mean EF values of 11.6, 19.6 and 16.2, respectively. However, the values for these three metals in the indoor samples were significantly higher ($p < 0.01$) than other metals. The EFs of Cd were within the grade "very high enrichment" with a mean value 23.0. Cu and Pb had "extremely high enrichment", with mean EF value 56.5 and 64.8, respectively.

Figure S2 shows the comparison of the profiles for PBDEs in indoor dust samples and e-waste. For DBDPE, the comparison was not conducted due to the lack of general data in e-waste. The mean percentage from sites A to C (9.84, 3.25, 80.6 and 6.27 % for penta-, octa-, deca-BDE and other congeners, respectively) was similar to those detected in e-waste (5.5, 9.1, 80.8 and 5.4 %, respectively) (Li et al. 2013). For site D, the penta- BDE composition was similar to that in two commercial products, which indicated that the e-waste in the workshops was the source of PBDEs in the dust. However, the metal profile in the dust was different from that in typical e-waste (Fig. S3), indicating the complex mechanism of the metals in the dust emitted from e-waste. The percentages of Mn and Pb in the dust were higher than those in general e-waste. However, it was in line with our selecting Mn as the reference metal due to its high concentration in the crust. Pb was a highly enriched metal, and its calculated content in general e-waste was underestimated.

The differences and similarities of the BFRs profiles in the dust were examined by PCA, which implied a composition characteristic of their sources and subsequent environmental behaviour. Two clusters are exhibited in Fig. 5a. The higher molecular weight PBDE congeners and DBDPE had high loadings on PC2 and lower loadings on PC1 for in the indoor samples. Figure 5b shows that the PCA result for outdoor samples was similar to the indoor result. However, octa- and nona-BDE had higher loadings on PC1 than those in indoor PCA result, indicating the similar trend to the less brominated PBDEs emitted from the workshops.

The metals in the dust were also examined by PCA. The first two principal components explained 66.0 and 22.8 % of the total variability of the metals in indoor dust, respectively (Fig. 5c). Through PCA, the metals were classified into two clusters. Group Cu, Pb and Sb had high loadings on PC2, and group Co, Cr, Mn, Ni, Zn and Cd had high loadings on PC1, indicating a common source and behaviour of the metals within groups from e-waste recycling activities. Figure 5d shows the first two principal components of the data from the outdoor dust samples, and the result of which was similar to the PCA for the indoor samples. In fact, Pb, Sb, Cu and Cd all had positive scores on PC2. A previous study confirmed that the principal component axis could be interpreted as the indicator of pollution or crust (Fujimori et al. 2012). Thus, combined with the EF calculations in Fig. 4, Pb, Sb, Cu and Cd were concluded to be the pollution metals emitted from e-waste recycling, whereas Co, Cr, Ni, Zn and Mn were more likely affected by the crust in outdoor samples.
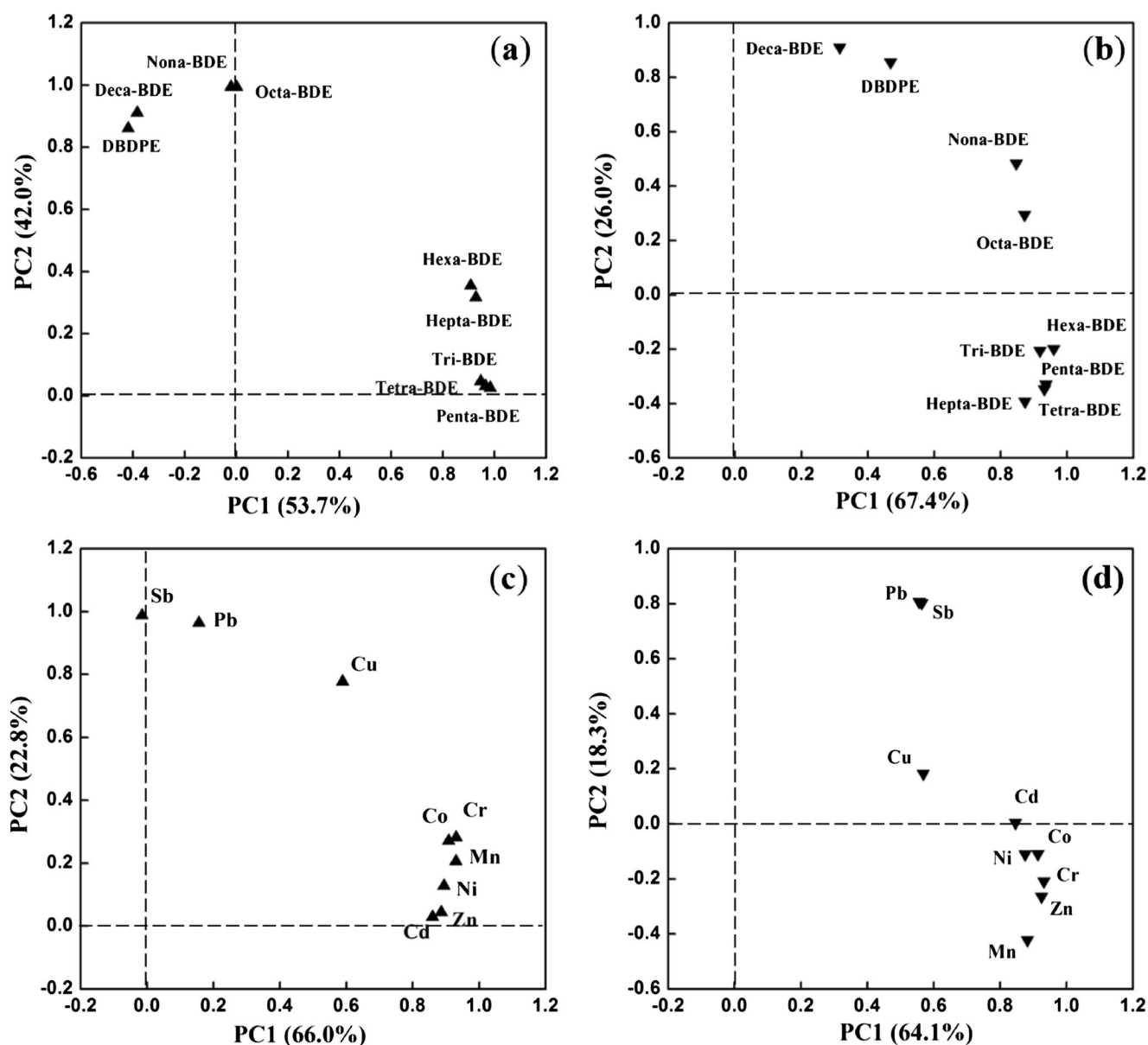

Fig. 5 Loading plots of the principal component analysis (PCA) for BFRs and metals in the (a), (c) indoor and (b), (d) outdoor dust samples

Table 2 Pearson correlation coefficient matrix between BFRs and metals

	Co	Cr	Mn	Cu	Ni	Pb	Sb	Zn	Cd	Penta-	Octa-	Deca-	DBDPE
Co	1												
Cr	0.919**	1											
Mn	0.911**	0.871**	1										
Cu	0.727**	0.772**	0.862**	1									
Ni	0.933**	0.893**	0.922**	0.797**	1								
Pb	0.596**	0.592**	0.619**	0.872**	0.541**	1							
Sb	0.436**	0.427**	0.400**	0.701**	0.363*	0.922**	1						
Zn	0.803**	0.775**	0.865**	0.834**	0.786**	0.646**	0.353*	1					
Cd	0.797**	0.837**	0.791**	0.692**	0.708**	0.503**	0.273	0.843**	1				
Penta-BDE[a]	0.367*	0.317*	0.346*	0.665**	0.292	0.866**	0.894**	0.313*	0.199	1			
Octa-BDE	0.505**	0.510**	0.519**	0.759**	0.430**	0.874**	0.762**	0.636**	0.489**	0.844**	1		
Deca-BDE	0.276	0.411**	0.400**	0.379*	0.258	0.327*	0.028	0.694**	0.649**	0.038	0.501**	1	
DBDPE	0.368*	0.483**	0.479**	0.426**	0.361*	0.348*	0.035	0.769**	0.693**	0.040	0.514**	0.952**	1

[a] Penta-BDE: sum of BDE-47, 100, 99, 154 and 153; octa-BDE: sum of BDE-183 and BDE-203; and deca-BDE: BDE-209

*$p = 0.05$ (correlation is significant; two-tailed); **$p = 0.01$ (correlation is significant; two-tailed)

The relation between BFRs and metals in the dust samples was examined by a single PCA (Fig. S4). Three clusters were found in the PCA for indoor dust. Pb and Sb were in the same cluster with the low molecular weight PBDEs. Whereas for the PCA for outdoor dust, two clusters, "metals" and "BFRs," indicated no relation between these two contaminants.

Moreover, Pearson's correlation coefficients are presented in Table 2 for the BFRs and metals for all dust samples.

Significant positive correlations (in italics) were found for some pairs for metals and BFRs respectively. However, strong correlations between metals and BFRs were only found in Pb and Sb with penta-BDE and Pb with octa-BDE. This was consistent with the result of single PCA for the indoor dust we discussed and might indicate similar characteristics of emission source for Pb, Sb and low brominated commercial BDE during e-waste recycling.

Table 3 Hazard quotient for BFRs and metals in the dust

	RfD	Adults			Toddlers		
		HQ$_{mean}$	HQ$_{median}$	HQ$_{95thpercentile}$	HQ$_{mean}$	HQ$_{median}$	HQ$_{95thpercentile}$
BFRs[a]							
Penta-BDE	2.00E-03	2.09E-03	1.38E-03	6.89E-03	5.79E-03	8.79E-03	2.76E-02
Octa-BDE	3.00E-03	3.06E-04	2.38E-04	7.26E-04	9.98E-04	1.29E-03	2.66E-03
Deca-BDE	1.00E-02	1.75E-03	1.39E-03	4.36E-03	5.84E-03	7.33E-03	1.78E-02
DBDPE	3.33E-01	1.12E-05	9.25E-06	2.82E-05	3.89E-05	4.70E-05	1.18E-04
Metals							
Co	2.00E-02	1.53E-03	1.49E-03	2.71E-03	6.42E-03	6.27E-03	1.14E-02
Cr	3.00E-03	3.93E-02	3.15E-02	7.71E-02	1.65E-01	1.32E-01	3.24E-01
Mn	4.60E-02	1.64E-02	1.65E-02	2.05E-02	6.91E-02	6.93E-02	8.60E-02
Cu	4.00E-02	1.31E-01	1.29E-01	2.27E-01	5.50E-01	5.40E-01	9.95E-01
Ni	2.00E-02	1.64E-02	1.49E-02	3.34E-02	6.89E-02	6.25E-02	1.40E-01
Pb	3.50E-03	2.27E+00	2.03E+00	5.44E+00	9.52E+00	8.52E+00	2.28E+01
Sb	4.00E-04	1.40E-01	8.67E-02	4.69E-01	5.86E-01	3.64E-01	1.97E+00
Zn	3.00E-01	3.21E-03	3.14E-03	5.19E-03	1.35E-02	1.32E-02	2.18E-02
Cd	1.00E-03	8.48E-03	7.42E-03	1.59E-02	3.56E-02	3.12E-02	6.66E-02

[a] Penta-BDE: sum of BDE-47, 100, 99, 154 and 153; octa-BDE: sum of BDE-183; and BDE-203 and deca-BDE: sum of BDE-208, 207, 206 and 209

On-site exposure and health assessment

To perform a preliminary evaluation of human exposure to dust ingestion, we assumed 100 % absorption of dust intake, which is in line with other studies (Jones-Otazo et al. 2005). To be more acceptable for on-site (recycling work place) exposure and health assessment, the exposure duration fraction (EDF) in our study was assigned as the time people spent in workshops rather than the common calculated parameters used in most previous studies (Leung et al. 2008, Wang et al. 2010), which might result in an overestimation. Moreover, the mean concentration derived from the four sampling sites was used in the assessment.

The calculated hazard quotients of the BFRs and metals for adults and toddlers are shown in Table 3. The average exposures of penta-, octa-, deca-BDE and DBDPE via dust ingestion for both adults and toddlers were several orders of magnitude lower than their corresponding RfD values. The HQ range of the three PBDE congeners in this study suggested the likelihood of the low health risk of PBDEs exposure. For DBDPE, acute toxicity of such alternative flame retardants was low (Harju et al. 2008), whereas little is known about its chronic toxicity. Therefore, more toxicological research is required on account of the exposure dose via dust.

The HQ for metals were all lower than one, which indicated no adverse effects, except for Pb; the values of which were 2.27 and 9.52 for adults and toddlers, respectively. Notably, the value for Pb was close to 10 for toddlers, suggesting the high chronic risk of Pb. For Sb and Cu, the HQ was also considerable, with values 0.14 and 0.13 for adults and 0.59 and 0.55 for toddlers, respectively. However, there are adverse health effects for toddlers when using the 95th percentile concentrations, 1.00 and 1.97 for Cu and Sb, respectively.

Our results highlight the human exposure to BFRs and metals via dust during workshop and work time. However, the evaluated exposure was only an indication of the estimates. This was due to the small number of dust samples analyzed, the substantial inter-individual variation depending on the time spent in workshop and the quantity of dust ingested.

Conclusions

The uncontrolled e-waste recycling activities conducted in family-run workshops in recent decades have resulted in notable contamination of BFRs and heavy metals in house dust and the corresponding outdoor dust. We provided evidence that e-waste workshops could be regarded as the point source of BFRs and some metals because they could be emitted from workshops with the dust. We found that the composition of BFRs varied with type of e-wastes and

recycling activities. BDE-209 had a strong correlation with DBDPE. The occurrence of PBDE debromination was also observed in all dust samples. The EF calculations showed a strong enrichment of heavy metals, especially for Cu, Pb and Cd. The source of elements Co, Cr, Ni and Zn in outdoor dust was affected by the crust. Significant positive correlations were found for Pb and Sb with PBDEs. The exposure through dust ingestion for BFRs was at low risk, whereas it was notable that toddlers were at high chronic risk of Pb. Further studies on BFRs and heavy metals in the air and particle phase are required to elucidate the human exposure in family-run e-waste workshops.

References

Ali N, Harrad S, Goosey E, Neels H, Covaci A (2011) "Novel" brominated flame retardants in Belgian and UK indoor dust: implications for human exposure. Chemosphere 83:1360–1365

Ali N, Ali L, Mehdi T, Dirtu AC, Al-Shammari F, Neels H, Covaci A (2013) Levels and profiles of organochlorines and flame retardants in car and house dust from Kuwait and Pakistan: implication for human exposure via dust ingestion. Environ Int 55:62–70

An T, Zhang D, Li G, Mai B, Fu J (2011) On-site and off-site atmospheric PBDEs in an electronic dismantling workshop in south China: gas-particle partitioning and human exposure assessment. Environ Pollut 159:3529–3535

Betts K (2008) Does a key PBDE break down in the environment? Environ Sci Technol 42:6781

Bezares-Cruz J, Jafvert CT, Hua I (2004) Solar photodecomposition of decabromodiphenyl ether: products and quantum yield. Environ Sci Technol 38:4149–4156

Brewer GJ (2010) Copper toxicity in the general population. Clin Neurophysiol 121:459–460

Cao Z, Yu G, Chen Y, Liu C, Liu K, Zhang T, Wang B, Deng S, Huang J (2013) Mechanisms influencing the BFR distribution patterns in office dust and implications for estimating human exposure. J Hazard Mater 252–253:11–18

Chen SJ, Ma YJ, Wang J, Tian M, Luo XJ, Chen D, Mai BX (2010) Measurement and human exposure assessment of brominated flame retardants in household products from South China. J Hazard Mater 176:979–984

Chen A, Dietrich K, Huo X, Ho S (2011) Developmental neurotoxicants in e-waste: an emerging health concern. Environ Health Perspect 119:431–438

CNEMC (1990) Background values of soil elements in China. China Environmental Science Press, Beijing

EU (2003): The ban of marketing the penta- and octa-BDE mixtures. Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 Amending for the 24th Time Council Directive 76/769/EEC Relating to Restrictions on the Marketing and Use of Certain Dangerous Substances and Preparations.

Fromme H, Hilger B, Kopp E, Miserok M, Volkel W (2014) Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and "novel" brominated flame retardants in house dust in Germany. Environ Int 64:61–68

Fujimori T, Takigami H, Agusa T, Eguchi A, Bekki K, Yoshida A, Terazono A, Ballesteros FC (2012) Impact of metals in surface matrices from formal and informal electronic-waste recycling around Metro Manila, the Philippines, and intra-Asian comparison. J Hazard Mater 221–222:139–146

Han Y, Du P, Cao J, Posmentier ES (2006) Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci Total Environ 355:176–186

Harju M, Heimstad ES, Herzke D, Sandanger T, Posner S, Wania F (2008): Emerging "new" brominated flame retardants in flame retarded products and the environment. Report 2462, Norwegian Pollution Control Authority, Oslo, Norway.

Harrad S, Ibarra C, Abdallah M, Boon R, Neels H, Covaci A (2008) Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and offices: causes of variability and implications for human exposure. Environ Int 34:1170–1175

Hites RA (2004) Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environ Sci Technol 38:945–956

Huo X, Peng L, Xu XJ, Zheng LK, Qiu B, Qi ZL, Zhang B, Han D, Piao ZX (2007) Elevated blood lead levels of children in Guiyu, an electronic waste recycling town in China. Environ Health Perspect 115:1113

Jarup L (2003) Hazards of heavy metal contamination. Br Med Bull 68: 167–182

Jiang H, Lin Z, Wu Y, Chen X, Hu Y, Li Y, Huang C, Dong Q (2014) Daily intake of polybrominated diphenyl ethers via dust and diet from an e-waste recycling area in China. J Hazard Mater 276:35–42

Jones-Otazo HA, Clarke JP, Diamond ML, Archbold JA, Ferguson G, Harner T, Richardson GM, Ryan JJ, Wilford B (2005) Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. Environ Sci Technol 39:5121–5130

Kierkegaard A, Bjorklund J, Friden U (2004) Identification of the flame retardant decabromodiphenyl ethane in the environment. Environ Sci Technol 38:3247–3253

La Guardia MJ, Hale RC, Harvey E (2006) Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ Sci Technol 40:6247–6254

Lanphear BP, Roghmann KJ (1997) Pathways of lead exposure in urban children. Environ Res 74:67–73

Leung AO, Duzgoren-Aydin NS, Cheung K, Wong MH (2008) Heavy metals concentrations of surface dust from e-waste recycling and its human health implications in southeast China. Environ Sci Technol 42:2674–2680

Leung AO, Zheng J, Yu CK, Liu WK, Wong CK, Cai Z, Wong MH (2011) Polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in surface dust at an E-waste processing site in Southeast China. Environ Sci Technol 45:5775–5782

Li X, Feng L (2010) Spatial distribution of hazardous elements in urban topsoils surrounding Xi'an industrial areas, (NW, China): controlling factors and contamination assessments. J Hazard Mater 174: 662–669

Li J, Duan H, Shi P (2011) Heavy metal contamination of surface soil in electronic waste dismantling area: site investigation and source-apportionment analysis. Waste Manag Res 29:727–738

Li Y, Duan YP, Huang F, Yang J, Xiang N, Meng XZ, Chen L (2013) Polybrominated diphenyl ethers in e-waste: level and transfer in a typical e-waste recycling site in Shanghai, Eastern China. Waste Manag 34:1059–1065

Liu Q-T, Diamond ML, Gingrich SE, Ondov JM, Maciejczyk P, Stern GA (2003) Accumulation of metals, trace elements and semi-volatile organic compounds on exterior window surfaces in Baltimore. Environ Pollut 122:51–61

Lu X, Wang L, Li LY, Lei K, Huang L, Kang D (2010) Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China. J Hazard Mater 173:744–749

Luo C, Liu C, Wang Y, Liu X, Li F, Zhang G, Li X (2011) Heavy metal contamination in soils and vegetables near an e-waste processing site, South China. J Hazard Mater 186:481–490

Ma J, Addink R, Yun S, Cheng J, Wang W, Kannan K (2009) Polybrominated dibenzo-p-dioxins/dibenzofurans and polybrominated diphenyl ethers in soil, vegetation, workshop-floor dust, and electronic shredder residue from an electronic waste recycling facility and in soils from a chemical industrial complex in eastern China. Environ Sci Technol 43:7350–7356

Melymuk L, Robson M, Helm PA, Diamond ML (2012) PCBs, PBDEs, and PAHs in Toronto air: spatial and seasonal trends and implications for contaminant transport. Sci Total Environ 429:272–280

Muenhor D, Harrad S, Ali N, Covaci A (2010) Brominated flame retardants (BFRs) in air and dust from electronic waste storage facilities in Thailand. Environ Int 36:690–698

Ni HG, Zeng EY (2009) Law enforcement and global collaboration are the keys to containing e-waste tsunami in China. Environ Sci Technol 43:3991–3994

Renner R (2004) Government watch: in US, flame retardants will be voluntarily phased out. Environ Sci Technol 38:14A–15A

Robinson BH (2009) E-waste: an assessment of global production and environmental impacts. Sci Total Environ 408:183–191

Schmidt CW (2006) Unfair trade e-waste in Africa. Environ Health Perspect 114:A232

SEPA (1995): (State Environmental Protection Administration). Environmental Quality Standards for Soils (GB 15618–1995).

Shi T, Chen SJ, Luo XJ, Zhang XL, Tang CM, Luo Y, Ma YJ, Wu JP, Peng XZ, Mai BX (2009) Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China. Chemosphere 74:910–916

Söderström G, Sellström U, de Wit CA, Tysklind M (2004) Photolytic debromination of decabromodiphenyl ether (BDE 209). Environ Sci Technol 38:127–132

Takigami H, Suzuki G, Hirai Y, Sakai S (2009) Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. Chemosphere 76:270–277

Tang X, Shen C, Shi D, Cheema SA, Khan MI, Zhang C, Chen Y (2010) Heavy metal and persistent organic compound contamination in soil from Wenling: an emerging e-waste recycling city in Taizhou area. China J Hazard Mater 173:653–660

Tian M, Chen SJ, Wang J, Zheng XB, Luo XJ, Mai BX (2011) Brominated flame retardants in the atmosphere of E-waste and rural sites in southern China: seasonal variation, temperature dependence, and gas-particle partitioning. Environ Sci Technol 45:8819–8825

USEPA (1997) Exposure Factors Handbook; EPA/600/P-95/002Fa, b, c; Environmental Protection Agency. Office of Research and Development, Washington, DC

VROM (2001): The New Dutch List. Intervention values and target values: soil quality standards; Netherlands Ministry of Housing, Spatial Planning and Environment, Department of Soil Protection: The Hague, Netherlands.

Wang J, Ma YJ, Chen SJ, Tian M, Luo XJ, Mai BX (2010) Brominated flame retardants in house dust from e-waste recycling and urban areas in South China: implications on human exposure. Environ Int 36:535–541

Wei H, Turyk M, Cali S, Dorevitch S, Erdal S, Li A (2009): Particle size fractionation and human exposure of polybrominated diphenyl

ethers in indoor dust from Chicago. Journal of environmental science and health. Part A, Toxic/hazardous substances & environmental engineering 44, 1353–61

Wen S, Yang FX, Gong Y, Zhang XL, Hui Y, Li JG, Liu AL, Wu YN, Lu WQ, Xu Y (2008) Elevated levels of urinary 8-hydroxy-2'-deoxyguanosine in male electrical and electronic equipment dismantling workers exposed to high concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans, polybrominated diphenyl ethers, and polychlorinated biphenyls. Environ Sci Technol 42: 4202–4207

Wilford BH, Shoeib M, Haner T, Zhu J, Jones KC (2005) Polybrominated diphenyl ethers in indoor dust in Ottawa, Canada: implications for sources and exposure. Environ Sci Technol 39:7027–7035

Wong CS, Duzgoren-Aydin NS, Aydin A, Wong MH (2007a) Evidence of excessive releases of metals from primitive e-waste processing in Guiyu, China. Environ Pollut 148:62–72

Wong CS, Wu SC, Duzgoren-Aydin NS, Aydin A, Wong MH (2007b) Trace metal contamination of sediments in an e-waste processing village in China. Environ Pollut 145:434–442

Wong MH, Wu SC, Deng WJ, Yu XZ, Luo Q, Leung AO, Wong CS, Luksemburg WJ, Wong AS (2007c) Export of toxic chemicals—a review of the case of uncontrolled electronic-waste recycling. Environ Pollut 149:131–140

Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, La Guardia M, McClean MD, Webster TF (2007) Human exposure to PBDEs: associations of PBDE body burdens with food consumption and house dust concentrations. Environ Sci Technol 41:1584–1589

Zhang X, Ruan X, Yan M, Zhao Y, Wei W, Qin Z, Yang Y, Xu H, Li Y (2011) Polybrominated diphenyl ether (PBDE) in blood from children (age 9–12) in Taizhou, China. J Environ Sci 23:1199–1204

Zheng J, Luo XJ, Yuan JG, Wang J, Wang YT, Chen SJ, Mai BX, Yang ZY (2011) Levels and sources of brominated flame retardants in human hair from urban, e-waste, and rural areas in South China. Environ Pollut 159:3706–3713

Zheng J, Chen KH, Yan X, Chen SJ, Hu GC, Peng XW, Yuan JG, Mai BX, Yang ZY (2013) Heavy metals in food, house dust, and water from an e-waste recycling area in South China and the potential risk to human health. Ecotoxicol Environ Saf 96:205–212