E-waste recycling induced polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzo-furans pollution in the ambient environment

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Abstract

Polybrominated diphenyl ethers (PBDEs) have been determined in 30 samples, including soil, biota and plant collected from an electronic waste recycling site and its vicinage towns. Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) were also simultaneously analyzed in 20 samples. PBDEs were detected in all soil samples and the highest was up to 789 ng/g dry weight (dw). The toxic equivalency (TEQ) of PCBs and PCDD/Fs detected in E-waste recycling site is significant higher than those in the vicinage samples. Biota and plant were also contaminated with high level of PBDEs, PCBs and PCDD/Fs in this area. High levels of the three kinds of organic compounds in the environmental samples showed that the E-waste recycling have induced serious environmental problems.
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1. Introduction

With the rapid development of electric technology, the production of electronic wastes (E-waste) including computer, cellular phone, television is rather striking. Many countries have to face up to the questions to deal with this toxic garbage. Much E-waste is being exported to developing countries, and especially for East and South Asia, such as China, India, and Pakistan. The imported E-waste to Asian countries is creating an increasingly large environmental problem in this region (de Wit, 2002; Martin et al., 2004). Various high toxic pollutants like polychlorinated biphenyls (PCBs) in capacitors/transformers, polybrominated diphenyl ethers (PBDEs), which is as brominated flame retardants in circuit board, and polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDDs/Fs) as the combustion products of PVC in electric wire, can be emitted or

formed during the recycling procedures (Wang et al., 2005). All these have led to the high level of pollution in the ambient environment, and further to threaten the ecosystem local and inhabitants' health (Wong et al., 2007; Yu et al., 2006; Deng et al., 2006; Danish Environmental Protection Agency, 1999). Approximately 10 folds higher levels of airborne PBDEs were monitored compared with the controls (Sjödén et al., 2001) and much higher levels of PBDEs in serum of workers in E-waste recycling factories might sound the alarm for the potential threaten posed by such vocation (Sjödén et al., 1999).

Because of the lack of related standardized rules in China, extensive emission of the pollutants occurs illicitly in some south areas due to the E-waste recycling and 90% of the E-waste exported to Asia goes to China (BAN et al., 2002). Millions of these wastes are recycled in the illegal workshops mainly based on the cheapest techniques including sort, firing, incineration, and acidic wash. High risks of the E-waste recycling directly threaten the workers' and local inhabitants' health without any protection. High levels of POPs including PCDD/Fs were

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Fig. 1. Sketch map for sampling sites.

reported in sediments, ash and human hair from E-waste recycling sites (Luksemburg et al., 2002; Soderstrom and Marklund, 2002). If the recycling and disposal is unregulated, there will be significant damage to the local environment and human health. Risk assessment is now urgent for the potential danger induced by E-waste illegal and improper E-waste treatment. However, limited data on the actual pollution situation are available due to the various restrictive factors. The actual pollution in the ambient environment around the recycling places should be evaluated for the safety of the local ecosystem.

PBDEs, PCBs and PCDD/Fs are recognized as three types of anthropogenic environmental pollutants with high toxicity (Darnerud et al., 2001; Martin et al., 2003). The majority of E-waste is recycled by basic methods, such as manual treatment and open incineration. Because their possible emission can occur during the recycling procedure of E-waste, growing concerns have been attracted to disclose the potential pollution in those areas. In this paper, a typical area as a famous base for E-waste recycling is selected to study the contaminations of PBDEs, PCBs and PCDD/Fs.

2. Materials and methods

2.1. Chemicals

Standard solutions of PCDD/Fs (1613-LCS (Labeled compound stock solution), 1613-ISS (^{13}C -1, 2, 3, 4-TCDD and ^{13}C -1, 2, 3, 7, 8, 9-HxCDD Internal Standard Spiking Solution) and 1613-PAR (Native PCDD/Fs, Precision and Recovery Stock Solution)), PCBs (WP-LCS (WHO ^{13}C -PCBs Surrogate Spiking Solution), WP-ISS (WHO ^{13}C -PCBs, Internal Standard Solution), MXP), and PBDEs (^{13}C -labeled MBDE-MXC, MBDE-139-IS) were obtained from Wellington Laboratories. Certified reference material WMF-01 (Reference fish tissue for organic contaminant analysis) was also purchased from Wellington Laboratories. All solvents were purchased from Tedia. Silica gel (0.063–0.100 mm) was obtained from Merck. Bio-Beams SX-3 was purchased from Bio-Rad.

2.2. Instrumentation

The analysis of PBDEs, PCDD/Fs and PCBs was performed on an Agilent 6890 gas chromatography coupled with an Autospec Ultima mass spectrometer operating with EI source in SIM mode. An aliquot of sample extract (2 μl) was injected with splitless mode into a DB-5MS fused silica capillary column (60 m $\times$ 250 μm i.d. $\times$ 0.25 μm film thickness) with helium (1.2 mL/min) as

carrier gas. Oven temperature programs in the range of 90–330 $^{\circ}\text{C}$ were used for the base-lined separation of the analytes. The detailed instrumental parameters could be referenced in our previous works (Liu et al., 2006a,b).

2.3. Sampling

Based on the careful field survey, a particular sampling activity was performed in August, 2005. As shown in Fig. 1, four towns located in South China were selected as the sampling places. Town A is a typical E-waste recycling site, which is composed by four villages (A01, A02, A03, and A04). Town B is closely adjacent to town A. Town C and D, served as the control places, are relatively far away from town A.

Three types of samples soils, plants and snails, were collected. Surface soil samples (about 100 cm in depth) were mainly gathered with a stainless steel sampler from farmlands and roadsides. Considering the relatively low volatilities and aqueous solubility of POPs like PBDEs, eventually leading to heavy of the environmental burden of these chemicals in soils (Palm et al., 2002), the soil samples studied here might represent the actual pollution level in the ambient environment. Several plants samples including such as metasequoia bark, paddy and snails named *Ampullaria gigas Spix* were also obtained for a glancing glimpse of POPs accumulation in organisms in these areas. All the collected samples as listed in Table 1 were kept frozen until analysis.

2.4. Sample pretreatment

The detailed pretreatment procedure for PBDEs, PCDD/Fs and PCBs has been described in our previous work (Liu et al., 2006a,b). The main steps are shown in the following: the freeze-dried samples were pulverized and spiked with ^{13}C -labeled surrogate standards. After 24-hour Soxhlet extraction with 1:1 dichloromethane (DCM): hexane, the acidic silica was added to remove lipid impurities. The organic layer was concentrated using a rotary evaporator, and 7 mL of hexane was added to redissolve the residue. A portion of concentrated sulphuric acid (8 ml) was subsequently added and vigorously shook for complete mix. The solution was then allowed to stand for an hour. The separated organic phase in the vial was sequentially subjected to acidic silica gel, acidic alumina and silver nitrate (AgNO_3) silica (10% w/w) for the separation of PBDEs from PCBs and PCDD/Fs. The separation of PCBs and PCDD/Fs was used florisil. Gel permeation chromatography (GPC) was used for further cleanup of PCBs and PCDD/Fs, respectively. The eluted sample was concentrated followed by the addition of ^{13}C -labeled internal standards, (WP-ISS (for PCBs), MBDE 139 (for PBDEs) and 1613-ISS (for PCDD/Fs), respectively) and final analysis by HRGC-HRMS. Based on the procedure above, total 19 PBDE congeners (BDE-7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183 and 209), 19 PCB congeners (CB-28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180, 189, 209) and 17 PCDD/Fs (2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD) were analyzed.

Table 1

The sample numbers and names collected from each sampling site

Sampling sites		Surface Soil	Plant	Snail (<i>Ampullaria gigas Spix</i>)
A	A01	4	1 metasequoia bark	0
	A02	2	0	0
	A03	9	0	1
	A04	2	0	0
B		2	1 paddy (stem and root)	1
C		2	0	0
D		1	1 leguminous plants	1

Fig. 2. PBDEs levels in surface soil, plant and snail samples.

2.5. Quality assurance/quality control (QA/QC)

The quality control was performed based on the description in the EPA methods 1614 draft, 1613B and 1668A. All analyses were carried out following the isotope dilution/high resolution gas chromatography/high resolution mass spectrometry/selected ion recording methods. Method blanks are analyzed with each batch of 9 samples to demonstrate freedom from contamination. Along with each batch of samples, laboratory blanks was analyzed under exactly the same conditions as the samples as well. Quality assurance of the method was also confirmed elsewhere (Liu et al., 2006a,b).

3. Results and discussions

All concentration reported below are on dry weight (dw) basis.

3.1. Pollution levels and profiles of PBDEs in E-waste recycling site

A total of 19 PBDE congeners including the mono-to deca-BDE were detected. Concentrations of Σ PBDEs in the surface soils were in the range of 0.40–789.49 ng/g (Fig. 2). The dominant congeners were BDE-47, 99, 153, 154, 183, and 209, which is accordant with the previous reports (Julander et al., 2005). The profiles of PBDEs in the surface soils in this area were well consistent with the dominant usage of deca-BDEs in electrical and electronic equipment. In Fig. 2, the mean concentrations of Σ PBDEs in soils from A, B, C and D were 142.32, 2.49, 0.57 and 0.48 ng/g, respectively, which clearly showed that the level of PBDEs in E-waste recycling town A was significant higher than those in the other towns. Also, PBDEs contents in soil from each village of town A were investigated, with the range from 2.4 to 789.5 ng/g. The results showed that there is high PBDE contamination in this town, which was also consistent with the results reported by Wang et al. (2005).

But when compared to the previous data on PBDEs pollution in E-waste sites (Cai and Jiang, 2006), it could be found that the levels obtained herein were relatively lower. The difference should be induced by the different samples investigated. The soil samples analyzed previously were directly collected in E-waste dumping and burning sites, while the samples studied herein were from roadside and farmland, which could offer more information on the pollution in the ambient environment around E-waste recycling sites. It could be also found in Fig. 2 that the soil samples from town B, which is located near E-waste recycling town, were contaminated with relatively higher levels of PBDEs. This implied the recycle of large amounts of E-waste could also affect in the ambient environment. The levels of PBDEs in soils from town C and D were comparable to the blank value of the method.

PBDEs in biota samples were also shown in Fig. 2. The profiles of PBDEs in these samples were similar to those in soils. For the plant samples, the highest concentration of PBDEs (244.08 ng/g) was found in the metasequoia bark from town A01. The paddy samples from town B were at the levels of 4.99–8.41 ng/g. The contents in stem were relatively higher than those in root. This was accord with the results in the previous report, which was probably strongly influenced by the air pollution of PBDEs. (Ohta et al., 2002). Little influence was found in the leguminous plants from town D (1.03 ng/g of PBDEs) because this place is relative far from E-waste sites. The snail (*Ampullaria Gigas Spix*) from town A, B and D contained 148.52, 14.59 and 0.79 ng/g, respectively, obviously showing the highest pollution of PBDEs existed in the samples from town A.

3.2. Pollution levels and profiles of PCBs in E-waste recycling site

19 PCB congeners in soil and bio-samples were analyzed in this work, which included six indicator PCBs (CB-28, 52, 101, 138, 153, and 180)

Fig. 3. PCBs levels in surface soil, plant and snail samples.

and twelve WHO-specified PCBs. Fig. 3 showed the results of Σ PCBs in surface soils. High contaminations of Σ PCBs were detected in site A, with concentrations from 0.31 to 21.06 ng/g (from 0.12 to 8.66 pg WHO-TEQ/g) (Fig. 3). In soils from site B and C, Σ PCBs were from 0.08 to 0.59 ng/g (from 0.03 to 0.38 pg WHO-TEQ/g). The profiles of PCBs were analyzed between site A and other two sites. Six indicator PCBs in soil in site A, B, C accounted for 71.7%, 88.7%, and 71%, respectively. But for site D, the concentrations of indicator PCBs were up to 92.1%. Pollutions of Σ PCBs in snails collected in site A, B, and C were from 3.27 to 11.66 ng/g (from 0.22 to 14.24 pg WHO-TEQ/g).

3.3. Pollution levels and profiles of PCDD/Fs in E-waste recycling site

The E-waste area is recognized to be contaminated with PCDD/Fs because of the open burning of wires to recover copper. Occurrence of PCDD/Fs in samples was shown in Fig. 4. OCDD was the main congener in the seventeen PCDD/Fs congeners. Also, relative high concentration of OCDF was found in the surface soils. It should be mentioned to that the concentrations of PCDD/Fs in a agricultural soil sample collected from town A (A04-3) with 46.11 pg WHO-TEQ/g and the determined concentrations of PCDD/Fs among these soil and biota samples were up to 53.39 pg WHO-TEQ/g, and 75.47 pg WHO-TEQ/g, respectively. The concentration of PCDD/Fs in snail of town A was comparable to those in other two towns (town B and D).

Among the analytical samples, tree bark was contaminated with the highest pollution of PCDD/Fs in the studied areas. High accumulation of PBDEs, PCBs and PCDD/Fs was all found in sample of tree bark,

indicating that tree bark can be used as passive samplers to monitor the pollution of these compounds in ambient airborne dust (Zhu and Hites, 2006). More evidence should be given to confirm its feasibility as a potential bioindicator for such persistent organic pollutants in further study.

3.4. Comparison the characters of the pollution of PBDEs, PCBs, and PCDD/Fs

Based on the results listed above, it could be found that E-waste recycling caused serious PBDEs pollution in the ambient environment. In town A, the samples, including the soils, plants and snails, were all detected very high concentrations of PCDD/Fs, PCBs, and PBDEs. Town B, which is located at the adjacent area of town A and as one of the main drags and trading places for the E-waste, were also contaminated by PBDEs.

The relationships were studied among the concentrations of Σ PCDD/Fs, Σ PCBs, and Σ PBDEs in the soil samples collected from town A. For sampling site A01, four samples (A01-1, A01-2, A01-3, A01-4) were selected. Although no linear relationship was found between the concentrations of Σ PCBs and Σ PBDEs, the same concentrations trend were found in these sites (Figs. 2 and 4). For sampling site A04, four samples (A04-3, A04-5, A04-6, A04-8) were also selected. Very good linear relationship among these three groups of compounds was found. The coefficients (R^2) of PBDEs vs PCBs, PBDEs vs PCDD/Fs, and PCBs vs PCDD/Fs were up to 0.999, 0.980, and 0.985, respectively. The results showed that the E-waste recycling could bring both serious PBDEs pollution and PCBs pollution.

Fig. 4. PCDD/Fs levels in surface soil, plant and snail samples.

Fig. 5. Total PCDD/Fs TEQ comparison.

As a whole, comparing to the percent of the WHO-TEQ of PCBs and PCDD/Fs, we found that the main WHO-TEQ of the surface soils in these sampling sites mainly came from the contributions of PCDD/Fs (Fig. 5). But for the plants samples and bio-samples, the contributions of PCBs for WHO-TEQ were higher than those in soils.

4. Conclusion

Very high concentrations of PBDEs, PCBs and PCDD/Fs were found in the soils, plants, and bio-samples in the electronic waste recycling site. Vicinage sites are also contaminated by these three kinds of compounds. Further investigation is expected, especially for the determination of dioxin-like compounds since heavy pollution of PCDD/Fs was found in agricultural soils in site A.

Since the E-waste recycling can affect the local environment so seriously, a more safe and scientific recycling operation of electronic wastes is anticipated to avoid damaging the local ecosystem and the local inhabitants' health. Fortunately, China is now preparing legislation on electronic waste. Related national-level legislations have been drafted to regulate the E-waste management. The E-waste management pilot will be built to follow a specialized disposal plant model (Hicks et al., 2005).

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References

- Cai ZW, Jiang GB. Determination of polybrominated diphenyl ethers in soil from e-waste recycling site. *Talanta* 2006;70:88–90.
- Danish Environmental Protection Agency. Brominated flame retardants: substance flow analysis and assessment of alternatives; 1999.
- Darnerud PO, Eriksen GS, Jóhannesson T, Larsen PB, Viluksela M. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environ Health Perspect* 2001;109:49–68.
- Deng WJ, Louie PKK, Liu WK, Bi XH, Fu JM, Wong HM. Atmospheric levels and cytotoxicity of PAHs and heavy metals in TSP and PM_{2.5} at an electronic waste recycling site in southeast China. *Atmos Environ* 2006;40:6945–55.
- de Wit CY. An overview of brominated flame retardants in the environment. *Chemosphere* 2002;46:583–624.
- Hicks C, Dietmar R, Eugster M. The recycling and disposal of electrical and electronic waste in China – legislative and market responses. *Environ Impact Assess Rev* 2005;25:459–71.
- Julander A, Westberg H, Engwall M, van Bavel B. Distribution of brominated flame retardants in different dust fractions in air from an electronics recycling facility. *Sci Total Environ* 2005;350:151–60.
- Liu HX, Zhang QH, Cai ZW, Li A, Wang YW, Jiang GB. Separation of polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzo-furans in environmental samples using silica gel and florisil fractionation chromatography. *Anal Chim Acta* 2006a;557: 314–20.
- Liu HX, Zhang QH, Song MY, Jiang GB, Cai ZW. Method development for the analysis of polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzo-furans in single extract of sediment samples. *Talanta* 2006b;70:20–5.
- Luksemburg WJ, Mitzel RS, Peterson RG, Hedin JM, Maier MM, Schuld M, et al. Polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDFs) levels in environmental and human hair samples around an electronic waste processing site in Guiyu, Guangdong Province, China. *Organohalogen Compd* 2002;55:347–9.
- Martin M, Richardson BJ, Lam PKS. Harmonisation of polychlorinated biphenyl (PCB) analyses for ecotoxicological interpretations of Southeast Asian environmental media: what's the problem? *Mar Pollut Bull* 2003;46: 159–70.
- Martin M, Lam PSK, Richardson BJ. An Asian quandary: where have all of the PBDEs gone? *Mar Pollut Bull* 2004;49:375–82.
- Ohta S, Ishizuka D, Nishimura H, Nakao T, Aozasa O, Shimidzu Y, et al. Comparison of polybrominated diphenyl ethers in fish, vegetables, and meats and levels in human milk of nursing women in Japan. *Chemosphere* 2002;46:689–96.
- Palm A, Cousins IT, Mackay D, Tysklind M, Metcalfe C, Alaee M. Assessing the environmental fate of chemicals of emerging concern: a case of the polybrominated diphenyl ethers. *Environ Pollut* 2002;117:195–213.
- Sjödin A, Hagmar L, Klasson-Wehler E, Kronholm-Diab K, Jakobsson E, Bergman A. Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environ Health Perspect* 1999;107:643–8.
- Sjödin A, Carlsson H, Thuresson K, Sjölin S, Bergman A, Ostman C. Flame retardants in indoor air at an electronics recycling plant and at other work environments. *Environ Sci Technol* 2001;35:448–54.
- Soderstrom G, Marklund S. PBCDD and PBCDF from incineration of waste-containing brominated flame retardants. *Environ Sci Technol* 2002;36: 1959–64.
- The Basel Action Network (BAN), The Silicon Valley Toxics Coalition (SVTC), Toxics Link India, SCOPE (Pakistan), Greenpeace China. Exporting harm: the high-tech trashing of Asia. Seattle, WA, and San Jose, CA; February 25th, 2002.
- Wang DL, Cai ZW, Jiang GB, Leung A, Wong MH, Wong WK. Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility. *Chemosphere* 2005;60:810–6.
- Wong Coby SC, Wu SC, Duzgoren-Aydin Nurdan S, Adnan Aydin, Wong Ming H. Trace metal contamination of sediments in an e-waste processing village in China. *Environ Pollut* 2007;145:434–42.
- Yu XZ, Gao Y, Wu SC, Zhang HB, Cheung KC, Wong MH. Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies. *Chemosphere* 2006;65:1500–9.
- Zhu LY, Hites RA. Brominated flame retardants in tree bark from north America. *Environ Sci Technol* 2006;40:3711–6.