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PBBs, PBDEs, and PCBs levels in hair of residents around e-waste disassembly sites in Zhejiang Province, China, and their potential sources

Gaofeng Zhao^a, Zijian Wang^{a,*}, Michael H. Dong^{b,1}, Kaifeng Rao^a, Jianping Luo^a, Donghong Wang^a, Jinmiao Zha^a, Shengbiao Huang^a, Yiping Xu^a, Mei Ma^a

^aState Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

^bCalifornia Department of Pesticide Regulation, California, USA

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ABSTRACT

This study was conducted to explore the exposure potential of Chinese residents to PBBs, PBDEs, and PCBs in e-waste disassembly sites in Zhejiang province. The contents of 23 PBB congeners, 12 PBDE congeners, and 27 PCB congeners in hair and in their potential sources, including soil and e-waste, were measured via GC-MS. The levels of PHAHs in the three subfamilies (i.e., the PBBs, PBDEs, and PCBs) were all considerably higher ($P < 0.05$) in hair samples collected from the disassembly sites than from the control site. The highest levels of PBBs ($57.77 \text{ ng g}^{-1} \text{ dw}$), PBDEs ($29.64 \text{ ng g}^{-1} \text{ dw}$), and PCBs ($181.99 \text{ ng g}^{-1} \text{ dw}$) in hair were all found in those from the disassembly site Xinqiu, which are respectively 2, 2, and 10 times more than those observed in hair from the control site Yandang. Among the three subfamilies of PHAHs, PCBs were the most predominant pollutants detected. PBBs, which have very limited information available in China, can be detected at a comparable level with PBDEs in these samples in the study. Therefore, these observations suggested that more attention should be given over the potential for environmental or occupational exposure to PHAHs present in e-waste. By and large, the PHAH levels measured in the hair samples were consistent with those detected in the soil. Hair analysis could thus be a valid screening tool for assessing human PHAHs exposure in and around e-waste disassembly sites.

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1. Introduction

Electronic waste, or otherwise known as “waste electrical and electronic equipment”, or “e-waste” for short, is a pressing pollution issue driven by the rapid increase of obsolete or end-of-life electronic goods, such as computers, printers, copying machines, television sets, and mobile phones, that are left in the environment (EU, 2003). Recently e-waste has become the fastest growing stream of all solid waste found in China in that huge amounts of such waste are constantly being generated

from (legal or illegal) imports and domestic use (Hicks et al., 2005). Both the demand for recycled materials and the potential economical benefit are factors promoting the development of the disassembly (recycling) industry of e-waste. A cluster of small villages in the littoral zone in the Zhejiang province has thus become a booming recycling center for e-waste, but nonetheless at the expense of having thousands of villager workers engaged in primitive recycling operations without the use of adequate protective equipment. Such primitive operations include, but are not limited to, stripping

* Corresponding author. Tel.: +86 10 62849107; fax: +86 10 62849140.

E-mail address: wangzj@rcees.ac.cn (Z. Wang).

¹ Contributing as well as participating in a personal capacity.

of metals in open pit acid baths, removing electronic components from circuit boards by heating over a grill, and recovering metals by burning cables (BAN et al., 2002). Yet as a result of these operations and through leakage, evaporation, runoff, and leaching, many toxic chemicals may be released into the local environment and eventually into the human body.

Polyhalogenated aromatic hydrocarbons (PHAHs) represent a large family of highly lipophilic and environmentally persistent substances, of which polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) are two subfamilies that were of great concern in the present study. These two subfamilies have been used extensively as flame retardants for many years (BSEF, 2001). PBDEs are used in ABS-plastics, high-impact polystyrene, epoxy resins, and rubber, and thus may appear in such e-waste products as obsolete or end-of-life printed circuit boards, cables, and television sets (WHO, 1997). PBBs were used as flame retardant additives in plastics, textiles, and other materials in the early 1970s. However, in 1974 the use of hexabromobiphenyl was banned in the United States shortly following an accident that resulted in a widespread contamination of farm products in Michigan (WHO, 1994a; US ATSDR, 2004). That accident also led to the discontinued production of the octabromobiphenyl and decabromobiphenyl formulations in 1979. It is likely that the hexabromobiphenyl congener is still being produced in some developing countries or in countries with economies in transition (POPRC, 2007a). When used as additives, PBDEs and PBBs are physically mixed into electronic products, not chemically bound to them. Therefore, under ideal conditions they would be more readily released into the local environment (US ATSDR, 2004). There are increasing concerns

over the export of e-waste to developing countries for fear of widespread releases of hexabromobiphenyl during recycling operations (POPRC, 2007a). It was largely due to these concerns that in 2006 the European Union and its member states proposed that commercial octabromodiphenyl ether and hexabromobiphenyl be listed as persistent organic pollutants in Annex A of the Stockholm Convention. Polychlorinated biphenyls (PCBs) were the third and last subfamily considered in the present study. Until they were banned in the United States in the late 1970s, PCBs had been widely used as coolants and insulators in electrical capacitors and transformers, and as plasticizers in paint and rubber sealant (Safe, 1994). Recent studies by Zhao et al. (2006, 2007a,b) suggested that obsolete transformers and electrical waste are important sources for the emission of PCBs into local environments. In addition to being highly lipophilic and persistent in the environment, all three PHAHs subfamilies are notably toxic and bioaccumulative (Hardy, 2000; McDonald, 2002). Animal studies (WHO, 1993, 1994a,b) showed that the PHAHs in these three subfamilies not only were they capable of disrupting endocrine functions but could also induce neurodevelopmental, hepatic, reproductive, and other adverse health effects. Accordingly, an exploratory effort was made in the present study to monitor the hair and environmental levels of 62 PHAHs in samples collected at a recycling cluster (center) and a control site. The sampling sites were all located on the southeast side of the Zhejiang province. The PHAHs under monitoring were 12 PBDE congeners, 23 PBB congeners, and 27 PCB congeners, as listed later in the result tables.

The recycling center consisted of four e-waste disassembly sites which collectively represented large sections of the towns



Fig. 1 – Sampling sites (●) in Zhejiang Province, China.

(villages) Tongshan, Panlang, Xiazheng, and Xinqiu. These towns or villages are located near the city of Wenling, which is on the southeast side of Zhejiang (Fig. 1). The town Yandang, located in a remote mountainous area 30 km SW of the recycling cluster, was used as a control site. Soil and hair samples were collected from these disassembly and control sites. Other environmental samples were cable coating, stuffing powder (for electronic component), and chipped circuit boards, and were collected from the disassembly sites only (since these e-waste items were not available in the control site). Hair samples were collected because human hair has been considered as a suitable non-destructive indicator for the study of environmental or occupational exposure to many chemical pollutants including PCBs and a number of pesticides (Schramm, 1997; US ATSDR, 2001; Harkins and Susten, 2003; Altshul et al., 2004). The present study had its focus on assessing the exposure potential of local residents to the 62 PHAHs that were deemed likely present in e-waste. In particular, this exploration represented the first of its kind in reporting extensively the recent levels of PBBs, PBDEs, and PCBs in the hair of local residents, in connection to environmental exposure. Information obtained from this type of exploration may also be useful for subsequent evaluation of the health risks at issue.

2. Materials and methods

2.1. Sample collection and storage

In April 2007, soil samples (each with 3 subsamples of ~1 kg, obtained directly under recycling activities, at the top 0–5 cm layer) were collected from each of the e-waste disassembly sites and from the control site. Also obtained from each disassembly site were samples (each weighing ~0.20 kg) of cable coating, stuffing powder, and chipped circuit boards. Hair samples (each of ~2–5 g) were collected from 48 local residents (including 44 villager workers engaged in primitive recycling operations from the disassembly sites, and 4 local residents from the control site) living in the five localities during their routine haircut, with each sample placed into a separate chemically-clean glass bottle (which, like those containers used to keep the soil and e-waste samples, was labeled with a unique code and the proper sampling date). No information was collected on hair color or treatments (e.g., dyeing or personal care products). All samples were transported to the analytical laboratory as soon as possible in ice boxes and continued to be stored in the dark at 4 °C until analysis.

2.2. Materials and chemicals

The following standards were obtained from the Cambridge Isotope Laboratory (USA): 12 native PBDE congeners; 7 $^{13}\text{C}_{12}$ -labeled PBDEs (PBDE15, 28, 47, 99, 153, 154, and 183); 23 PBB congeners; 27 PCB congeners; and surrogate standards pentachloro-nitrobenzene (PCNB), 2,4,5,6-tetrachloro-*m*-xylene (TMX), and PCB209. All solvents used (hexane, acetone, and methylene chloride) were of pesticide grade (Promochem, Germany). Silica gel (100–200 mesh) and florisil (60–100 mesh) were purchased separately from Promochem and ICN Biome-

dicals (Germany). Aluminum foil was rinsed with acetone and dried at ambient temperature prior to use. Sodium sulfate (granular, anhydrous) was pre-cleaned with methylene chloride and purified by heating at 450 °C for 8 h in a shallow metallic enamel tray. Cellulose extraction thimbles of 33 mm i.d. and 94 mm in length were from Schleicher & Schuell (Germany); these thimbles were pre-cleaned by Soxhlet extraction with *n*-hexane:acetone (3:1, v/v) for 4 h before use. Glassware was soaked, cleaned with chromic solution, rinsed thoroughly with distilled water and acetone, and finally heated in a baking oven (Heraeus, Germany) at temperatures programmed from 40 °C to 420 °C at a rate of 15 °C min⁻¹ for 16 h.

2.3. Sample preparation and clean-up

The soil and e-waste residue samples were all freeze-dried. The dried soil residues were directly ground into powder in a mortar, whereas the e-waste residues were pulverized by a stainless-steel machine and then sieved to pass a 100 mesh for subsequent analyses. Following the method modified by Altshul et al. (2004), the hair samples were individually covered with 20 mL Milli-Q water (18.2 M Ω , Millipore, Belgium), sonicated for 10 min, dried with paper towel, and then washed with shampoo twice before they were rinsed with Milli-Q water again and air-dried on absorbent paper. Afterwards, the hair samples from each volunteer were cut into pieces of 1 mm long each (with a pair of scissors). About 2–5 g of these hair pieces from each sample was introduced into a pre-cleaned thimble and Soxhlet extracted for 24 h using an *n*-hexane/acetone (3:1, v/v) solution. For this preparation process, TMX, PCNB, and PCB209 were added to each sample as surrogate congener standards. The extract from each sample was then concentrated to about 1 mL by rotary evaporation (550 mbar, 60 °C). The concentrated extracts were further cleaned individually by a multilayer silica gel column containing: 2 g of anhydrous sodium sulfate; 8 g of silver nitrate (AgNO₃) silica (10%, AgNO₃ w/w); 2 g of deactivated silica (3.3% organic-free reagent water w/w); 15 g of acidic silica (44% conc. sulphuric acid w/w); 1 g of deactivated silica (3.3% organic-free reagent water w/w); and 2 g of anhydrous sodium sulfate. The silica gel column was pre-eluted with 80 mL of hexane prior to adding to the extract. The first fraction eluted with *n*-hexane (100 mL) was used to concentrate the PCB congeners, with the second fraction (eluted with 10% methylene chloride in 80 mL *n*-hexane) intended for collection of the PBB and PBDE congeners (US EPA, 1996, 2003). The eluants were concentrated separately to about 1 mL, again by rotary evaporation. The solvent of each sample was evaporated to dryness by gentle nitrogen stream at 25 °C and redissolved in 200 μL hexane.

2.4. Chemical analysis

The chemical analysis was performed using an Agilent 5975 GC-MS system equipped with a capillary DB-5MS column (5% phenyl/95% methyl silicone, 30 m, 0.25 mm i.d., 0.25 μm film thickness, from J&W Scientific, Folsom, California, USA). The column oven temperature was programmed from 90 °C (initial time, 1 min) to 250 °C at a rate of 4 °C min⁻¹, then from 250 °C to 300 °C at a rate of 25 °C min⁻¹, and held for 5 min. The GC injector temperature was maintained at 260 °C, with the

Table 1 – Levels of PBBs (in ng g⁻¹ dw) measured in soil and e-waste samples collected from five localities in Zhejiang, China

Pollutants	Soil from the disassembly spot (n=6)				Soil from the control site (n=3)				E-waste (n=1)		
	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	Cable coating	Stuffing powder	Circuit boards chipping
PBB1	4.00	3.06	1.26–35.55	100	0.49	0.42	0.36–0.76	100	N.D.	1.02	1.71
PBB2	4.69	4.61	1.71–21.66	100	1.10	1.00	0.98–1.35	100	3.73	2.20	1.38
PBB3	N.A.	N.A.	N.A.	17	N.D.	N.D.	N.D.	0	3.59	N.D.	N.D.
PBB10	0.61	0.82	0.10–0.98	83	0.60	0.58	0.42–0.88	100	1.15	1.03	1.21
PBB4	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	1.11	N.D.	N.D.
PBB9	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	1.95	N.D.	N.D.
PBB7	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	1.70	N.D.	N.D.
PBB15	1.70	1.75	1.46–1.89	100	1.12	1.20	0.80–1.45	100	6.00	1.83	1.79
PBB30	0.57	1.25	0.10–1.52	67	1.70	1.54	1.20–2.68	100	1.70	1.61	1.49
PBB18	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBB29	1.67	1.65	1.42–1.93	100	1.59	1.22	1.04–3.17	100	1.94	2.38	1.87
PBB26	0.65	1.43	0.12–1.70	67	N.D.	N.D.	N.D.	0	1.75	N.D.	1.81
PBB31	0.67	1.48	0.12–1.75	67	1.51	1.62	1.04–2.05	100	1.80	2.53	1.87
PBB53	0.45	0.65	0.15–1.56	50	N.A.	N.A.	N.A.	33	N.D.	1.57	1.55
PBB38	1.89	1.93	1.51–2.36	100	1.25	1.22	0.89–1.82	100	2.23	1.98	2.17
PBB52	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBB49	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBB103	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBB80	1.96	1.98	1.75–2.21	100	1.17	1.02	0.86–1.81	100	2.13	N.D.	2.20
PBB101	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBB155	N.A.	N.A.	N.A.	17	N.A.	N.A.	N.A.	33	2.41	N.D.	N.D.
PBB153	1.69	2.06	0.32–3.15	83	0.94	0.80	0.62–1.70	100	2.04	2.42	2.18
PBBs	27.18	21.99	17.85–58.40	100	11.84	10.62	8.21–19.02	100	35.25	18.61	21.35
PBB209	2.70	2.15	0.80–54.68	50	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.

PBBs = polybrominated biphenyls; a value of half the limit of detection (LOD) was given for samples in which PBB residues were not detected; all statistical analyses were performed for congeners for which more than 50% of the samples were above the LOD; G.M.: geometric mean; N.A.: not available; N.D.: not detected; >LOD%: percent detected.

temperatures of the MS ion source and of the transfer line being kept at 230 °C and 300 °C, respectively. The carrier gas was helium at a constant flow rate of 1.5 mL min⁻¹. The mass spectrometer was operated in the electron impact (EI) ionization mode with an electron energy of 70 eV. Samples (1 µL) were injected in the splitless mode with a solvent delay set at 4 min. The molecular ions ([M]⁺ or [M+2]⁺) and the fragment ions

resulting from the loss of X₂ (i.e., [M–X₂+2]⁺ or [M–X₂+4]⁺, where X=chlorine or bromine) were selected as the precursor ions for mass spectrometric analysis. Quantitative analyses of PBB209 and PBDE209 were performed on the Agilent 5975 GC-MS equipped with a DB-5MS (5% phenyl/95% methyl silicone, 15 m, 0.25 mm i.d., 0.1 µm film thickness, from J&W Scientific, Folsom, California, USA), at temperatures programmed from

Table 2 – Levels of PBDEs (in ng g⁻¹ dw) measured in soil and e-waste samples collected from five localities in Zhejiang, China

Pollutants	Soil from the disassembly spot (n=6)				Soil from the control site (n=3)				E-waste (n=1)		
	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	Cable coating	Stuffing powder	Circuit boards chipping
PBDE3	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBDE15	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBDE17	1.73	2.05	0.10–14.25	83	N.D.	N.D.	N.D.	0	2.05	1.97	N.D.
PBDE28	2.41	2.53	1.83–2.90	100	1.03	0.90	0.66–1.84	100	2.34	2.68	2.4
PBDE47	6.22	5.86	2.62–13.48	100	2.15	2.42	1.60–2.55	100	2.56	5.03	3.53
PBDE66	N.A.	N.A.	N.A.	33	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBDE100	2.16	2.92	0.25–4.80	83	N.D.	N.D.	N.D.	0	N.D.	N.D.	2.75
PBDE99	1.45	2.60	0.25–7.30	67	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PBDE154	N.A.	N.A.	N.A.	33	N.D.	N.D.	N.D.	0	N.D.	N.D.	3.05
PBDE153	3.19	4.45	0.30–12.20	83	N.A.	N.A.	N.A.	33	N.D.	12.88	2.91
PBDE183	7.30	10.74	0.32–27.59	83	N.D.	N.D.	N.D.	0	0.17	7.16	3.65
ΣPBDEs	37.04	42.42	11.27–73.53	100	3.27	3.32	2.26–4.67	100	7.12	29.71	18.28
PBDE209	192.38	311.27	8.99–647.80	100	N.D.	N.D.	N.D.	0	N.D.	4.19×10 ³	3.15

PBDEs = polybrominated diphenyl ethers; a value of half the limit of detection (LOD) was given for samples in which PBDE residues were not detected; all statistical analyses were performed for congeners for which more than 50% of the samples were above the LOD; G.M.: geometric mean; N.A.: not available; N.D.: not detected; >LOD%: percent detected.

Table 3 – Levels of PCBs (in ng g⁻¹ dw) measured in soil and e-waste samples collected from five localities in Zhejiang, China^a

Pollutants	Soil from the disassembly spot (n=6)				Soil from the control site (n=3)				E-waste (n=1)		
	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	Cable coating	Stuffing powder	Circuit boards chipping
PCB8	1.37	1.87	0.50–2.74	100	1.30	1.24	1.02–1.73	100	41.57	2.91	3.41
PCB18	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PCB28	18.36	12.48	3.93–204.59	100	1.20	1.23	1.00–1.42	100	81.57	5.86	4.86
PCB52	15.41	17.53	1.46–68.90	100	0.57	0.45	0.41–0.99	100	24.72	2.42	1.73
PCB44	11.19	14.44	0.74–53.89	100	0.70	0.62	0.55–1.00	100	33.75	1.31	0.98
PCB66	8.45	11.61	1.32–37.40	100	1.03	1.09	0.82–1.21	100	60.92	0.98	3.31
PCB101	11.59	14.05	0.83–58.56	100	0.94	1.02	0.75–1.07	100	101.71	0.98	1.12
PCB153	1.99	1.54	0.96–5.35	100	0.83	0.82	0.80–0.87	100	2.11	0.97	0.99
PCB138	13.18	13.98	1.71–129.70	100	1.47	1.88	0.83–2.02	100	8.32	2.16	2.13
PCB187	1.78	1.63	0.66–6.86	100	N.D.	N.D.	N.D.	0	0.79	0.91	0.85
PCB128	5.68	5.70	0.94–22.78	100	0.57	0.52	0.46–0.79	100	62.96	1.08	0.94
PCB180	2.68	2.72	0.98–14.39	100	0.97	0.96	0.86–1.09	100	1.76	1.85	1.56
PCB170	3.29	3.72	0.86–11.43	100	0.78	0.79	0.74–0.81	100	13.16	1.33	1.27
PCB195	1.10	1.18	0.78–150	100	0.55	0.60	0.40–0.70	100	1.57	0.92	0.95
PCB206	0.96	0.93	0.77–1.19	100	0.57	0.62	0.40–0.75	100	1.43	1.15	0.94
PCB77	3.08	4.09	1.16–7.44	100	0.49	0.41	0.34–0.83	100	23.71	1.65	1.28
PCB81	3.11	3.40	1.11–7.33	100	0.54	0.45	0.42–0.83	100	23.45	1.58	1.22
PCB105	6.11	7.79	1.02–52.31	100	0.76	0.85	0.40–1.28	100	23.66	1.28	1.68
PCB114	2.42	2.87	0.75–4.46	100	0.61	0.62	0.50–0.74	100	49.99	1.05	1.05
PCB118	2.12	2.56	0.62–6.21	100	0.48	0.46	0.42–0.56	100	53.05	0.81	0.76
PCB123	3.34	2.84	0.72–23.11	100	0.52	0.45	0.44–0.70	100	38.81	0.93	0.88
PCB126	N.A.	N.A.	N.A.	33	N.D.	N.D.	N.D.	0	0.47	N.D.	N.D.
PCB156	N.A.	N.A.	N.A.	33	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PCB157	N.A.	N.A.	N.A.	33	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.
PCB167	2.08	1.71	0.57–7.80	100	0.50	0.47	0.44–0.61	100	0.93	0.83	0.71
PCB169	0.75	1.07	0.12–2.99	83	0.16	0.15	0.14–0.19	100	22.57	6.54	0.67
PCB189	2.00	2.42	0.84–3.54	100	0.49	0.45	0.32–0.83	100	7.02	1.09	1.17
ΣPCBs	152.87	146.79	27.77–738.96	100	16.20	16.26	12.56–20.81	100	680.02	40.57	34.42
ΣTEQs ^b	17.24 × 10 ⁻³	17.55 × 10 ⁻³	(3.06–101.04) × 10 ⁻³	100	2.20 × 10 ⁻³	2.10 × 10 ⁻³	(1.90–2.80) × 10 ⁻³	100	300.91 × 10 ⁻³	69.13 × 10 ⁻³	10.43 × 10 ⁻³

^aPCBs = polychlorinated biphenyls; a value of half the limit of detection (LOD) was given for samples in which PCB residues were not detected; all statistical analyses were performed for congeners for which more than 50% of the samples were above the LOD; G.M.: geometric mean; N.A.: not available; N.D.: not detected; >LOD%: percent detected; all localities, except Yandang (which was used as the control site), have a large site for e-waste disassembly. ^bTEQs = toxic equivalence quotients (or toxic equivalents), which each were calculated using the World Health Organization method and toxic equivalence factors (Van den Berg et al., 2006) in an effort to weight the toxicity as well as the potency of dioxin (2,3,7,8-TCDD)-like PCB compounds (i.e., those last 12 PCBs listed in this table) in relation to that of TCDD.

Table 4 – Statistical results of PBBs (in ng g⁻¹ dw) in hair collected from five localities of Zhejiang, China

Pollutant	Hair from Tongshan (n=8)				Hair from Panlang (n=11)				Hair from Xiazheng (n=9)				Hair from Xinqiu (n=8)				Hair from Yandang (n=4)			
	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %
PBB1	0.45	0.66	0.08–1.06	75	0.29	0.48	0.08–1.67	55	0.32	0.64	0.08–1.18	56	N.D.	N.D.	N.D.	0	0.23	0.34	0.08–0.67	50
PBB2	17.38	19.08	10.99–33.11	100	16.43	17.01	8.14–28.20	100	21.43	29.38	6.08–41.34	100	15.21	17.19	2.12–52.57	100	17.75	18.98	12.92–21.64	100
PBB3	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.A.	N.A.	N.A.	11	N.A.	N.A.	N.A.	20	N.D.	N.D.	N.D.	0
PBB10	0.31	0.38	0.10–0.77	75	0.33	0.43	0.10–1.76	73	0.65	0.74	0.08–2.80	89	2.23	2.08	1.46–3.50	100	0.32	0.46	0.08–0.63	75
PBB4	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBB9	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBB7	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBB15	0.88	0.82	0.53–1.62	100	0.86	0.91	0.13–3.14	100	1.60	1.34	0.83–3.60	100	3.78	3.83	2.62–5.38	100	0.97	0.97	0.78–1.24	100
PBB30	0.65	0.63	0.39–1.17	100	0.58	0.73	0.10–2.60	82	0.85	1.06	0.10–3.80	78	1.60	2.85	0.08–4.65	80	N.A.	N.A.	N.A.	25
PBB18	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBB29	0.77	0.76	0.49–1.42	100	0.68	0.87	0.12–4.48	82	1.65	1.40	0.73–3.74	100	4.49	4.50	2.68–7.54	100	0.91	0.94	0.68–1.17	100
PBB26	0.72	0.72	0.45–1.39	100	0.38	0.47	0.12–1.14	64	1.15	1.21	0.12–3.47	89	1.86	3.19	0.12–6.18	80	0.79	0.77	0.61–1.12	100
PBB31	0.74	0.74	0.47–1.45	100	0.54	0.82	0.12–4.31	73	1.18	1.24	0.12–3.63	89	4.06	4.02	2.49–6.41	100	0.82	0.80	0.63–1.15	100
PBB53	0.28	0.21	0.15–0.70	50	0.41	0.42	0.15–2.62	64	0.49	0.52	0.15–3.03	56	N.A.	N.A.	N.A.	20	N.D.	N.D.	N.D.	0
PBB38	0.87	0.85	0.57–1.58	100	1.05	1.01	0.54–3.55	100	1.28	1.40	0.15–4.40	89	2.35	4.43	0.15–5.97	80	0.98	0.97	0.74–1.33	100
PBB52	0.43	0.58	0.15–0.74	75	N.A.	N.A.	N.A.	36	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBB49	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBB103	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBB80	0.91	0.92	0.54–1.67	100	0.65	1.02	0.15–3.66	73	1.25	1.71	0.18–4.34	78	4.55	4.60	3.13–7.35	100	1.04	1.02	0.78–1.46	100
PBB101	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.A.	N.A.	N.A.	20	N.D.	N.D.	N.D.	0
PBB155	N.A.	N.A.	N.A.	13	N.A.	N.A.	N.A.	18	0.29	0.32	0.24–0.64	67	0.49	0.43	0.37–0.71	100	0.19	0.19	0.08–0.49	50
PBB153	1.01	0.96	0.58–2.07	100	1.19	1.09	0.58–3.74	100	1.41	1.58	0.32–4.74	100	2.86	4.70	0.32–6.68	80	1.08	1.04	0.80–1.60	100
PBBs	26.16	27.49	17.65–40.60	100	28.62	27.28	14.39–54.78	100	44.14	48.76	19.54–66.28	100	57.77	76.21	24.16–102.62	100	25.71	25.01	21.86–32.26	100
PBB209	N.A.	N.A.	N.A.	13	N.D.	N.D.	N.D.	0	N.A.	N.A.	N.A.	11	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0

PBBs = polybrominated biphenyls; a value of half the limit of detection (LOD) was given for samples in which PBB residues were not detected; all statistical analyses were performed for congeners for which more than 50% of the samples were above the LOD; G.M.: geometric mean; N.A.: not available; N.D.: not detected; >LOD%: percent detected; all localities, except Yandang (which was used as the control site), have a large site for e-waste disassembly.

90 °C (initial time, 1 min) to 250 °C at a rate of 10 °C min⁻¹, then from 250 °C to 300 °C at 15 °C min⁻¹, and finally held for 8 min. Mass spectrometer condition was performed by EI (70 eV) and selected ion monitoring of high abundance (*m/z* 943 and *m/z* 799 for PBB209 and PBDE209, respectively).

2.5. Quality assurance/quality control

For every batch of 10 samples, a solvent blank and a procedural blank were added to ensure that the samples and the analysis process were free of contamination. The detection limits (LOD) of the targeted compounds were defined as 3 times the signal to noise (*S/N*) ratio, ranged from 0.08 to 0.24 ng g⁻¹ dw for PBB congeners, from 0.08 to 0.32 ng g⁻¹ dw for PBDE congeners, from 0.02 to 0.12 ng g⁻¹ dw for PCB congeners, and from 0.80 to 1 ng g⁻¹ dw for PBB209 and PBDE209. Spike recoveries for ¹³C₁₂-labeled PBDEs (at 10 ng) ranged from 75.2 to 96.5%; and those for TMX, PCNB, and PCB209 ranged from 70.4 to 92.5%, 81.6 to 107.4%, and 90.8 to 112.6%, respectively. Triplicate analysis of six diluted standard solutions (1.0, 5.0, 10.0, 25.0, 50.0, and 100.0 ng mL⁻¹) was performed for each selected standard mixture. Multi-level calibration curves were constructed for the quantification; and good to excellent linearity (*r*²>0.99) was achieved. The results were not corrected for recovery.

2.6. Data analysis

A value of half LOD was given to the samples in which the contents of PBBs, PBDEs or PCBs were not detectable. Descriptive statistics (mean, range, etc.) were computed to characterize the concentrations of PBBs, PBDEs, and PCBs in the samples. All statistical analyses were performed for congeners for which more than 50% of the samples were above the LOD, using the Statistical Package for the Social Sciences (SPSS for Windows ver. 11.5) where applicable. The (statistical) term *mean* used throughout this paper referred to *geometric mean*. The levels of PBB209 and PBDE209, though measured and considered duly, were not included in calculating the total concentrations of PBBs and PBDEs. Non-parametric methods (Mann–Whitney *U*) were used to determine differences in PHAHs levels between disassembly sites and the control site, all statistical significance was set at Alpha=0.05.

3. Results

3.1. Levels of PBBs measured in the samples

The levels of the 23 PBB congeners measured in the e-waste, soil and hair samples are summarized in Tables 1 and 4. These data showed that among the three types of e-waste samples, the highest concentration (35.25 ng g⁻¹ dw) of PBBs was found in cable coating, with the low-brominated PBBs (including PBB1 and PBB2) accounting for 55% of the total PBBs observed. These low-brominated congeners were also found as the most predominant pollutants; they were detected in all of the e-waste samples. The PBB209 levels in all the e-waste samples were below LOD (<0.80 ng g⁻¹ dw).

Table 5 – Statistical results of PBDEs (in ng g⁻¹ dw) in hair collected from five localities of Zhejiang, China

Pollutant	Hair from Tongshan (n=8)				Hair from Panlang (n=11)				Hair from Xiazheng (n=9)				Hair from Xinqiu (n=8)				Hair from Yandang (n=4)			
	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %
PBDE3	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBDE15	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PBDE17	0.46	0.89	0.10–1.68	63	N.A.	N.A.	N.A.	18	N.A.	N.A.	N.A.	44	2.00	3.70	0.10–5.97	80	N.A.	N.A.	N.A.	25
PBDE28	1.12	1.16	0.58–1.81	100	1.00	1.03	0.10–4.03	91	1.95	1.85	0.77–4.40	100	5.32	5.19	3.52–7.59	100	0.81	0.84	0.53–1.14	100
PBDE47	0.74	1.00	0.20–1.96	75	1.12	1.20	0.20–4.72	91	2.18	1.95	0.87–5.00	100	5.49	5.24	3.54–9.65	100	1.23	1.17	1.07–1.57	100
PBDE66	N.A.	N.A.	N.A.	38	N.A.	N.A.	N.A.	9	N.A.	N.A.	N.A.	22	N.A.	N.A.	N.A.	20	N.A.	N.A.	N.A.	25
PBDE100	N.A.	N.A.	N.A.	13	N.A.	N.A.	N.A.	0	N.A.	N.A.	N.A.	33	N.A.	N.A.	N.A.	20	0.85	1.09	0.25–1.81	75
PBDE99	N.A.	N.A.	N.A.	38	N.A.	N.A.	N.A.	0	N.A.	N.A.	N.A.	33	N.D.	N.D.	N.D.	0	0.33	0.35	0.25–0.45	50
PBDE154	0.59	0.63	0.30–1.38	50	N.A.	N.A.	N.A.	18	N.A.	N.A.	N.A.	11	N.A.	N.A.	N.A.	40	N.D.	N.D.	N.D.	0
PBDE153	0.63	0.53	0.30–2.68	50	N.A.	N.A.	N.A.	46	1.23	0.98	0.30–7.51	89	3.02	4.84	0.30–12.04	80	0.83	1.10	0.30–1.39	75
PBDE183	0.59	0.91	0.32–6.50	50	0.97	0.32	0.32–5.98	64	1.64	2.00	0.32–8.99	89	5.21	5.06	1.62–24.28	100	N.D.	N.D.	N.D.	0
ΣPBDEs	7.41	7.63	4.42–13.64	100	4.73	7.03	0.72–19.55	100	11.10	8.24	6.06–27.32	100	29.64	30.96	14.90–59.52	100	4.49	4.82	3.12–5.68	100
PBDE209	10.82	15.46	1.00–32.47	88	5.42	5.34	1.00–62.18	73	3.10	1.50	1.00–73.10	56	N.A.	N.A.	N.A.	20	N.A.	N.A.	N.A.	25

PBDEs = polybrominated diphenyl ethers; a value of half the limit of detection (LOD) was given for samples in which PBDE residues were not detected; all statistical analyses were performed for congeners for which more than 50% of the samples were above the LOD; G.M.: geometric mean; N.A.: not available; N.D.: not detected; >LOD%: percent detected; all localities, except Yandang (which was used as the control site), have a large site for e-waste disassembly.

For soil samples, the PBB levels (mean=27.18 ng g⁻¹ dw, n=6) from the disassembly sites were significantly ($P<0.01$) greater than those (mean=11.84 ng g⁻¹ dw, n=3) from the control site. PBB209 was detected in 50% of the soil samples. For hair samples, the PBB levels (mean=57.77 ng g⁻¹ dw, n=8) from the disassembly site Xinqiu were significantly ($P<0.05$) higher than those from the other three disassembly sites (Tongshan: mean=26.16 ng g⁻¹ dw, n=8; Panlang: mean=28.62 ng g⁻¹ dw, n=11; and Xiazheng: mean=44.14 ng g⁻¹ dw, n=9). As expected, the control site Yandang had the lowest PBB levels (mean=25.71 ng g⁻¹ dw, n=4). PBB209 was detected in only 2 hair samples, with both approaching 1 ng g⁻¹ dw. PBB2 was the most predominant congener, being detected in 100% of the hair samples from all five sites (Table 4).

3.2. Levels of PBDEs measured in the samples

The levels of the 12 PBDE congeners measured in the environmental and hair samples are summarized in Tables 2 and 5, which shows that stuffing powder (for electronic component) had the highest PBDEs and PBDE209 concentrations (29.71 ng g⁻¹ dw and 4.19×10^3 ng g⁻¹ dw) among the three groups of e-waste samples collected. The data in this table also showed that PBDE153 and PBDE183 were the most predominant congeners, accounting for 43 and 24% (respectively) of the total PBDEs observed in stuffing powder. For soil samples from the disassembly sites, the mean level of PBDE209 (192.38 ng g⁻¹ dw, n=6) was approximately 5 times higher than that of the other 11 PBDE congeners combined (37.04 ng g⁻¹ dw, n=6). PBDE17, PBDE28, PBDE47, PBDE153, and PBDE183 were the most predominant congeners; they were detected in more than 83% of the six soil samples. PBDE209 were detected in 100% of the samples.

For hair samples, the mean PBDE level (29.64 ng g⁻¹ dw, n=8) from Xinqiu was highest compared with those from Tongshan (7.41 ng g⁻¹ dw, n=8), Panlang (4.73 ng g⁻¹ dw, n=11), Xiazheng (11.10 ng g⁻¹ dw, n=9), and Yandang (4.49 ng g⁻¹ dw, n=4). There was a very high frequency of detection for PBDE209 at Tongshan and Panlang, which dropped to 56% at Xiazheng and only 20% at Xinqiu. The means ranged from NA to 10.8. For Xinqiu, and for Yandang, from the >LOD% figures it appears that PBDE209 was detected in one hair sample from each site.

3.3. Levels of PCBs measured in the samples

As summarized in Table 3 (and Tables 1 and 2), among the three subfamilies of PHAHs (excluding PBDE209), PCBs had the highest concentrations in the soil samples collected from these e-waste disassembly sites, with a mean of 152.87 ng g⁻¹ dw (n=6). PCB28, PCB44, PCB52, PCB101, and PCB138 were the most predominant congeners; they were detected in all these soil samples. Cable coating had the highest levels of Σ PCBs and Σ TEQ_{PCBs}, at 680.02 and 300.91×10^{-3} ng g⁻¹ dw, respectively. As common practice, here the level Σ TEQ_{PCBs} referred to the sum of the toxic equivalents (or toxic equivalence quantities), which each were calculated using the World Health Organization method and toxic equivalence factors (Van den Berg et al., 2006) in an effort to weight the toxicity as well as the potency of dioxin (2,3,7,8-TCDD)-like PCB compounds (i.e.,

those last 12 PCBs listed in Table 3) in relation to that of TCDD. PCB101 was the most predominant congener, accounting for 15% of the total PCBs observed in cable coating.

Of the total 48 hair samples collected, only 40 were detected with PCBs. Xinqiu had the highest levels (mean=181.99 ng g⁻¹ dw, n=8), followed by Xiazheng (mean=68.36 ng g⁻¹ dw, n=9), Tongshan (mean=32.75 ng g⁻¹ dw, n=8), Panlang (mean=28.19 ng g⁻¹ dw, n=11), and lastly by the control site Yandang (13.30 ng g⁻¹ dw, n=4) ($P<0.05$). The most abundant PCB congeners found in the hair samples were: PCB28, PCB52, PCB66, and PCB138, all with 100% detection frequency (Table 6).

4. Discussion

Overall, the levels of PHAHs in the three subfamilies (i.e., the PBBs, PBDEs, and PCBs) were all considerably higher ($P<0.05$) in hair samples collected from the disassembly sites than from the control site Yandang. The highest levels were found in samples from Xinqiu. Among the three subfamilies, PCB had the highest levels in hair samples, except for those samples collected from Tongshan where the levels of PBBs and PCBs in hair were comparable (Tables 4 and 6).

The PHAHs in the three subfamilies were all detectable in the e-waste samples. The levels of PBBs, PBDEs, and PCBs were all significantly higher ($P<0.05$) in the soil and the hair samples from the disassembly sites than from Yandang. These data collectively supported the notion that the PHAHs under study might have been released from the e-waste into the local environments through leakage, evaporation, runoff, and leaching, and eventually into (or onto) the bodies of local residents through bioaccumulation.

4.1. PBBs in hair and their potential sources

The production and the use of hexabromobiphenyl have been discontinued in most countries shortly following the agricultural contamination episode that occurred in the United States in 1974 (US ATSDR, 2004). However, as stated earlier, it is likely that this PBB congener is still being used in electrical and electronic substances in some developing countries (Danish EPA, 1999), where the manufacture or assembly of most electrical and electronic products actually takes place. In addition, large quantities of e-waste are reported (BAN et al., 2002) to have been shipped to developing countries, including China, to be salvaged for usable parts. Such usage and imports, whether legal or illegal, may explain how the local environments under study could have been so heavily polluted with PBBs. Therefore, the concerns over imports of electronic waste to China should not be overlooked. PBBs that were manufactured for commercial use typically consisted of the high-brominated compounds hexa-, octa-, nona-, and decabromobiphenyls (WHO, 1994a), which could be released from electrical and electronic products with relative ease since by design they were only physically mixed into the products and not chemically bound to them. Based on a use-life expectancy of 5–10 years for most electrical and electronic products, it is anticipated that many of the PBB-containing products now have already been disposed of (US ATSDR, 2004). High-brominated PBBs thus are expected to be detected in the e-waste

Table 6 – Statistical results of PCBs (in ng g⁻¹ dw) in hair collected from five localities of Zhejiang, China^a

Pollutant	Hair from Tongshan (n=8)				Hair from Panlang (n=11)			
	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %
PCB8	0.90	1.66	0.02–3.88	88	1.48	1.58	0.38–2.59	100
PCB18	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PCB28	9.63	10.66	4.11–15.31	100	4.47	5.25	0.65–11.21	100
PCB52	2.97	2.46	0.97–12.6	100	1.33	1.23	0.72–3.72	100
PCB44	N.A.	N.A.	N.A.	13	N.A.	N.A.	N.A.	19
PCB66	3.58	3.09	1.11–8.97	100	1.71	2.45	0.17–9.27	100
PCB101	2.38	2.36	1.26–4.52	100	1.85	1.65	0.66–3.71	100
PCB153	0.67	0.64	0.33–1.91	100	0.61	0.83	0.08–1.40	91
PCB138	2.38	1.88	1.15–8.14	100	2.09	1.74	0.49–7.80	100
PCB187	0.30	0.31	0.10–0.57	88	0.49	0.43	0.08–2.01	91
PCB128	0.37	0.35	0.06–2.11	88	0.40	0.29	0.08–1.48	91
PCB180	0.36	0.40	0.11–1.15	100	0.51	0.50	0.10–1.93	91
PCB170	0.70	0.63	0.34–1.61	100	0.75	0.63	0.25–3.29	100
PCB195	0.65	0.70	0.34–1.45	100	0.49	0.49	0.18–1.62	100
PCB206	0.42	0.40	0.27–0.77	100	0.50	0.47	0.25–1.72	100
PCB77	0.19	0.15	0.06–2.21	50	1.14	0.74	0.28–5.26	100
PCB81	0.20	0.17	0.06–2.12	50	1.03	0.69	0.27–5.15	100
PCB105	0.28	0.16	0.07–4.12	63	0.69	0.92	0.07–5.66	73
PCB114	0.15	0.13	0.07–0.38	50	0.39	0.39	0.08–7.18	82
PCB118	N.A.	N.A.	N.A.	25	0.60	0.36	0.08–7.01	82
PCB123	N.A.	N.A.	N.A.	25	0.60	0.42	0.08–7.59	82
PCB126	N.D.	N.D.	N.D.	0	N.A.	N.A.	N.A.	18
PCB156	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PCB157	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
PCB167	0.43	0.51	0.09–1.64	88	0.41	0.52	0.08–1.28	91
PCB169	N.A.	N.A.	N.A.	13	0.18	0.18	0.08–0.68	73
PCB189	0.58	0.72	0.06–2.22	88	0.60	0.57	0.12–1.99	82
ΣPCBs	32.75	35.45	16.12–57.10	100	28.19	28.54	12.30–62.19	100
ΣTEQs ^b	0.33 × 10 ⁻³	0.37 × 10 ⁻³	(0.01–2.12) × 10 ⁻³	100	3.45 × 10 ⁻³	4.20 × 10 ⁻³	(0.15–88.71) × 10 ⁻³	100

^aPCBs = polychlorinated biphenyls; a value of half the limit of detection (LOD) was given for samples in which PCB residues were not detected; all statistical analyses were performed for congeners for which more than 50% of the samples were above the LOD; G.M.: geometric mean; N.A.: not available; N.D.: not detected; >LOD%: percent detected; all localities, except Yandang (which was used as the control site), have a large site for e-waste disassembly. ^bTEQs = toxic equivalence quotients (or toxic equivalents), which each were calculated using the World Health Organization method and toxic equivalence factors (Van den Berg et al., 2006) in an effort to weight the toxicity as well as the potency of dioxin (2,3,7,8-TCDD)-like PCB compounds (i.e., those last 12 PCBs listed in this table) in relation to that of TCDD.

and the local environments under study. However, the data in Table 1 show that PBB209 was not detected in any of the e-waste residue samples even though this congener was detected in 50% of the soil samples. Such findings suggest that the PBB209 found in the soil samples could come from sources other than the e-waste available in the vicinity. Another possibility is that this highest-brominated congener could have been (almost) completely released into the local environment by the time the e-waste products were ready to be salvaged. Therefore, more in-depth investigations are needed for determining the possible sources of soil contamination with PBB209 at the four disassembly sites. PBB209 was detectable in only 2 of the hair samples (Table 4), which implies that what is present in the soil is not particularly bioavailable.

On the other hand, low-brominated PBBs (including PPB1 and PPB2) were seen to have accounted for as much as 55% of the total PBBs observed in the cable coating sample (with the highest level being 35.25 ng g⁻¹ dw). This finding is consistent with the dominant level of low-brominated PBBs observed in the soil samples (Table 1). Human recycling operations (e.g. melting of cable coating at high temperature) and chemical or biological degradation could have been responsible for such a

dominance (US ATSDR, 2004; POPRC, 2007a). The data further showed that PBB levels were higher in hair samples collected from villager workers at the disassembly sites (Xiazheng and Xinqiu) than from those residing near the control site Yandang (Table 4). These findings are not surprising in that, as mentioned earlier, the soils at the disassembly sites were also seen to have been polluted by PBBs. The contamination was likely due to the high stability nature of these compounds, which tend to bioaccumulate in organic-rich media, such as soils, and lipid-rich biotic tissues. This type of pollutants thus actually can be easily bioaccumulated in the environment and then biomagnified in the food chain, and eventually can be taken into or onto the human body via breathing, eating, drinking, and/or skin contact (WHO, 1994a).

4.2. PBDEs in hair and their potential sources

As shown in Table 2, the highest levels of PBDEs were found in the stuffing powder sample. The measured level (4.19 × 10³ ng g⁻¹ dw) of PBDE209 actually was well over 100 times higher than that (29.71 ng g⁻¹ dw) of the other 11 PBDE congeners combined. Such a finding is not surprising at all. According to

Hair from Xiazheng (n=9)				Hair from Xinqiu (n=8)				Hair from Yandang (n=4)			
G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %	G.M.	Median	Range	>LOD, %
1.67	0.02	0.36–8.44	100	4.35	4.07	1.36–11.63	100	0.36	0.92	0.02–1.06	75
N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	0
8.46	5.85	1.32–69.04	100	25.75	18.76	7.35–247.09	100	2.18	2.35	1.54–2.70	100
4.68	5.73	0.99–13.40	100	12.34	9.35	4.03–53.98	100	0.97	1.51	0.20–2.18	100
3.40	3.05	0.65–18.15	100	10.40	9.00	4.67–27.91	100	N.D.	N.D.	N.D.	0
4.50	5.07	1.20–16.14	100	15.25	13.78	4.62–74.65	100	0.57	0.59	0.46–0.64	100
3.33	2.98	0.79–13.52	100	9.89	9.07	2.83–68.87	100	0.79	0.69	0.47–1.79	100
1.17	1.05	0.50–3.07	100	1.95	1.79	1.26–3.20	100	0.31	0.39	0.13–0.44	100
7.16	9.90	0.94–28.47	100	19.73	12.41	8.65–82.65	100	1.56	1.46	0.87–3.26	100
1.32	1.57	0.45–5.50	100	2.25	1.69	1.17–10.07	100	0.50	0.38	0.35–1.24	100
1.95	1.83	0.84–4.78	100	4.53	3.67	1.55–16.80	100	0.26	0.30	0.11–0.49	100
1.45	1.76	0.52–6.86	100	3.73	2.77	2.46–9.24	100	0.18	0.16	0.10–0.47	50
2.11	2.60	0.44–9.64	100	5.49	5.42	2.41–16.02	100	0.74	0.60	0.50–1.64	100
0.84	0.75	0.51–2.00	100	2.11	1.96	1.48–2.87	100	0.48	0.59	0.21–0.72	100
0.87	0.76	0.43–1.92	100	1.96	1.88	1.41–2.65	100	0.46	0.47	0.36–0.56	100
3.98	3.72	1.23–10.66	100	10.63	11.42	5.46–17.59	100	0.50	0.40	0.21–1.91	100
2.49	1.78	1.21–7.47	100	4.06	3.90	1.94–8.59	100	0.30	0.24	0.08–1.87	75
3.60	5.46	0.69–11.69	100	11.28	10.22	3.55–52.89	100	0.15	0.15	0.07–0.33	75
0.78	0.77	0.08–2.60	89	3.01	3.13	1.52–5.53	100	0.19	0.14	0.08–0.92	75
0.54	0.68	0.07–2.25	78	2.03	1.71	1.23–3.76	100	0.14	0.16	0.08–0.28	50
0.74	0.78	0.08–3.61	89	3.12	1.96	1.42–18.89	100	0.12	0.12	0.08–0.19	50
N.A.	N.A.	N.A.	44	N.A.	N.A.	N.A.	20	N.D.	N.D.	N.D.	0
N.A.	N.A.	N.A.	22	2.17	3.15	0.08–11.07	80	N.D.	N.D.	N.D.	0
N.A.	N.A.	N.A.	22	1.93	2.72	0.08–9.41	80	N.D.	N.D.	N.D.	0
0.84	0.64	0.31–2.20	100	1.65	1.73	1.09–2.26	100	0.32	0.38	0.15–0.53	100
0.20	0.34	0.08–0.46	56	0.34	0.78	0.08–1.19	60	0.26	0.33	0.08–0.58	75
1.45	1.01	0.57–14.20	100	2.53	2.29	2.04–3.59	100	0.20	0.16	0.12–0.57	50
68.36	82.39	18.54–224.10	100	181.99	131.87	78.06–736.00	100	13.30	13.04	10.60–17.79	100
8.40×10^{-3}	6.46×10^{-3}	$(0.85-42.37 \times 10^{-3})$	100	19.3×10^{-3}	21.57×10^{-3}	$(5.32-74.31) \times 10^{-3}$	100	1.9×10^{-3}	3.6×10^{-3}	$(0.20-6.40) \times 10^{-3}$	100

the World Health Organization (WHO, 1994b, 1997), the annual global consumption of PBDEs as flame retardants (and for other purposes as well) is 40,000 tonnes, of which deca-BDE

(i.e., PBDE209) accounts for as much as 70%. Furthermore, many PBDE-containing plastics and polyurethane foams were once widely used in electrical or electronic products that are

Table 7 – Levels of PBDEs, PBBs, and PCBs (in ng g⁻¹ dw) in human hair measured in various localities in China and in other countries

Countries (or districts)	Year	N	PBDEs	PBBs	PCBs	References
<i>International</i>						
Greece	1996	35	–	–	5.2 (ND–17.6) ^a	Covaci et al. (2002)
Romania	2000	2	–	–	10.2 (10–10.4) ^a	
Belgium	2000	10	–	–	13.7 (ND–44.7) ^a	Altshulet al. (2004)
USA	2004	10	–	–	47.5 ^b	
<i>China</i>						
Tongshan	2007	8	7.4 (4.4–13.6)	26.2 (17.7–40.6)	32.8 (16.1–57.1)	The present study
Panlang	2007	11	4.7 (0.7–19.6)	28.6 (14.4–54.8)	28.2 (12.3–62.2)	
Xiazheng	2007	9	11.1 (6.1–27.3)	44.1 (19.5–66.3)	68.4 (18.5–224.1)	
Xinqiu	2007	8	29.6 (14.9–59.5)	57.8 (24.2–102.6)	182.0 (78.1–736.0)	
Yandang	2007	4	4.5 (3.12–5.68)	25.7 (21.9–32.3)	13.3 (10.6–17.8)	

^a Sum of PCB 99, 118, 138, 149, 153, 170, and 180.

^b Sum of PCB 6, 8, 16, 18, 26, 28, 31, 33, 37, 41, 44, 49, 52, 60, 66, 70, 74, 77, 84, 87, 95, 97, 99, 101, 105, 110, 118, 135, 136, 138, 141, 146, 149, 151, 153, 156, 157, 167, 170, 171, 174, 177, 180, 183, 187, 189, 196, 199, and 203 (49 congeners); Calculated according to 1.8% lipid in hair (Altshul et al., 2004).

now referred to as “end-of-life” e-waste (POPRC, 2007b). These facts all support the observation that PBDE209 was the predominant congener measured in stuffing powder. High levels (mean = 192.38 ng g⁻¹ dw, n = 6) of PBDE209 were also found in all of the soil samples collected from the four disassembly sites (Table 2). PBDE209 can be degraded easily through exposure to light (e.g., UV radiation, direct sunlight) and through biological activity in the environment, with a short half-life in days (Hagmar et al., 2000; Stapleton et al., 2004). Therefore, it is possible that PBDE209 was sporadically being released from the e-waste into the soil in the vicinity. In their study, Sjödin et al. (1999) made a similar observation finding that the airborne levels of PBDE209 were higher around an e-waste disassembly plant (12–200 ng m⁻³) than around their control site (0.08 ng m⁻³).

PBDEs contents (7.41–29.64 ng g⁻¹ dw) in the hair samples from these e-waste disassembly sites were about 2–7 times higher than those from the control site (4.49 ng g⁻¹ dw) except for at Panlang site (Table 5), suggesting that the local residents too had been heavily exposed to these pollutants at the disassembly sites. PBDE209 was detected in more than 50% of the hair samples collected from three (Tongshan, Panlang, and Xiazheng) of the four e-waste disassembly sites under study. Similar results were obtained by other investigators; for example, Thuresson et al. (2005) observed higher blood levels of the congener in workers dismantling electronics or handling flame-retarded rubber. These findings tend to support the notion that PBDE209 through occupational or environmental exposure could eventually be bioaccumulated in or on to the human body. Currently very limited information is available regarding the use of PBDEs, especially that of the *deca*-BDE congener, in China. Therefore, more investigations into the use and impacts of PBDEs in China are needed in order to further substantiate the above notion.

4.3. PCBs in hair and their potential sources

The highest level of ΣPCBs was found in cable coating, at 680.02 ng g⁻¹ dw (Table 3). Accordingly to UNEP (UNEP, 2003), PCBs once were added to polyvinyl chloride to improve the latter's use as an insulating material for high-voltage cables. These chemicals were also included in certain low-voltage cables as flame retardants. Cables of this sort, which are an important component of many older electrical and electronic devices that could still be existing, could be contaminated by PCBs in the heat transfer fluids that got spilled off the electrical transformers or capacitors, a speculation that now may be supported in part by the high levels of PCBs detected in the cable coating samples.

PCBs (and other PHAHs) actually can be released from e-waste into the soil in the vicinity either through leakage directly, or through volatilization into the atmosphere first (WHO, 1993). As stated earlier, higher levels of PCBs were detected in soil samples from the disassembly sites than from the control site (Table 3). Such a finding lends further support of the notion that e-waste is an important source for contamination of a local environment with PCBs.

The data in Table 6 further show that hair samples from the disassembly sites had higher levels of PCBs than those from the control site. These data can be used to support the speculation that residents spent most of their time near the disassembly

sites had higher exposure to PCBs than those around the control site, especially when these compounds are known to be highly bioaccumulative and persistent in the environment (WHO, 1993; Ayotte et al., 2003). Among the three PHAH subfamilies, PCBs were found as the most predominant in hair samples collected from the disassembly sites, except for those from Panlang. Similar findings were observed in the soil and e-waste samples. Taken together, these observations point to the direction that hair analysis could be a valid screening tool for assessing human exposure potential to PHAHs present in e-waste.

4.4. International comparison

To further appreciate the level of contamination in hair from the four study localities, the three PHAHs subfamilies levels monitored in the present study were conducted to compare with those reported recently for districts located in other countries. It is to be regretted that not much documentation has been made concerning the use of PHAH levels in hair as a valid exposure index. To this date, there are only two papers which reported the levels of PCBs; no paper has been found concerning PBBs and PBDEs levels in human hair. As shown in Table 7, the levels of PCB congeners in hair samples from these disassembly sites were obviously higher than those reported by Covaci et al. (2002). Table 7 also shows that the PCB levels in the hair samples from Panlang and Tongshan (28.2 ng g⁻¹ and 32.8 ng g⁻¹) seems to be somewhat lower than those reported by Altshul et al. (2004) (47.5 ng g⁻¹), which might be due to more PCB congeners (49 congeners) were detected by Altshul et al. than those (27 congeners) in the present study. By and large, these findings suggested that residents living around the disassembly site have been exposed to higher levels of PCBs than those places listed in Table 7.

4.5. Health implications

There were no noticeable health defects found in the local residents from whom hair samples were collected in the sampling process. Nonetheless, the present exploration does not necessarily imply that the exposures to PHAHs at the four disassembly sites, especially at Xinqiu, were biologically insignificant. Although the toxic effects of PHAHs may not be evident even from high level exposure, the local residents might have already been suffering from (or subjected to) certain subclinical effects from exposure to these compounds. Adverse health effects (such as carcinogenicity, developmental defects, immunotoxicity, neurotoxicity, and reproductive toxicity) induced by PHAHs in the three study subfamilies have been reported in humans (Safe, 1994; Rogan and Ragan, 2003) and other species (US ATSDR, 2004; UNEP, 2006; POPRC, 2007a,b). Therefore, further research is needed into the long-term health impacts of chronic exposure to PHAHs for those Chinese residents who spend much of their time around an e-waste disassembly site.

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