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Polybrominated diphenyl ethers and bromophenols in paired serum, hair, and urine samples of e-waste dismantlers: Insights into hair as an indicator of endogenous exposure

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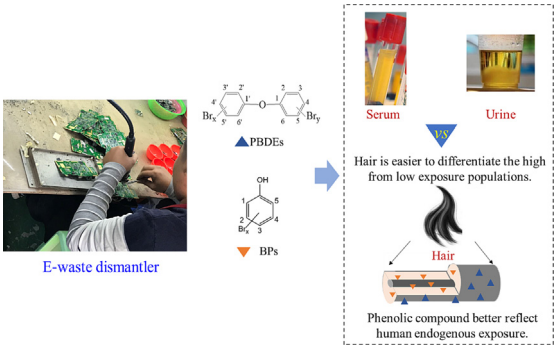
HIGHLIGHTS

- PBDEs and BPs were widely detected in paired samples from workers at e-waste site.
- Hair analysis was easier to differentiate the high from low exposure populations.
- Hair analysis of PBDEs was easily disturbed by exogenous pollutants.
- Hair of phenolic compound or metabolite could better reflect endogenous exposure.
- High body burden of 2,4,6-TBP represents a cause for concern.

GRAPHICAL ABSTRACT



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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are important pollutants during dismantling activities of electronic waste (e-waste) in China due to its large production and usage. Bromophenols (BPs), which are a kind of flame retardants and diphenyl ether bond cleavage metabolites of PBDEs, are often neglected in the assessment of human exposure to e-waste. Herein, 22 PBDEs and 19 BPs were determined in paired serum, hair, and urine samples collected from workers and residents of a typical e-waste dismantling site in southern China. Both PBDE and BP congeners were more frequently detected in hair than serum and urine samples. The medians of ΣPBDEs and ΣBPs were 350 and 547 ng/g dw in hair internal (hair-In) of occupational population, respectively, which were significantly higher than non-occupational population. However, a non-significant difference was found in levels of ΣPBDEs and ΣBPs in serum and urine between occupational and non-occupational populations, suggesting that hair analysis could easily differentiate between the exposure intensities of PBDEs and BPs to populations than serum and urine analyses. Moreover, levels of BPs in hair-In were 1–2 orders of magnitude higher than those in hair external (hair-Ex), while a non-

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significant difference was found in the levels of PBDEs. This result indicated that BPs might have originated from endogenous contribution. Notably, as the predominant congeners, the level of 2,4,6-tribromophenol (2,4,6-TBP) in hair-In was 3–8 times higher than that of BDE-209, while level of 2,4,6-TBP in hair-Ex was 1–3 times lower than that of BDE-209. Furthermore, *in vivo* experiments performed on Sprague–Dawley rats following a 28-day oral treatment with BDE-209 and 2,4,6-TBP verified that endogenous accumulation of 2,4,6-TBP in hair could be attributed to the metabolism of BDE-209 and exposure to 2,4,6-TBP. In conclusion, compared with PBDEs, biomonitoring phenolic compounds or metabolites with hair could better reflect human endogenous exposure.

1. Introduction

With the rapid upgradation of electronic and electric products, the increase in global electronic waste (e-waste) is increasing (Zhang et al., 2012). Polybrominated diphenyl ethers (PBDEs) are a type of additive flame retardants, which are extensively applied in electronic and electric products. Although the use of PBDEs has been forbidden or restricted in the European Union (EU) and the United States (USA) for more than a decade, decabromodiphenyl ether (BDE-209) is still produced in large quantities in China (Ji et al., 2017).

Human exposure to PBDEs from the dismantling of primitive e-waste has been widely reported in multiple human matrices, including blood, serum, hair, breast milk, and placenta samples. Indeed, adult residents, child residents, and neonates in e-waste dismantling regions have been found to have higher serum and blood PBDE levels than those in other regions (Han et al., 2011; Wu et al., 2010; Xu et al., 2014; Zhao et al., 2010; Zheng et al., 2014). Based on analysis of placenta and breast milk samples, the PBDE body burdens of pregnant and lactating women connected to e-waste sites have also been shown to be remarkably higher than those from the reference sites (Leung et al., 2010; Li et al., 2017; Zheng et al., 2014). In the period of primitive dismantling, family workshops with old-fashioned tools and means were the principal reason for high PBDE exposure observed in the non-occupational population (An et al., 2011; Wu et al., 2010). Moreover, BDE-209 has been found to be the dominant PBDE congener in human samples originating from e-waste sites (Bi et al., 2007; Li et al., 2017; Wu et al., 2010; Zhao et al., 2010; Zheng et al., 2014). The highest level of BDE-209 (not detected–3100 ng/g lipid weight [lw]) in a human serum sample from an e-waste dismantling site was reported in 2007 (Bi et al., 2007). Evidence has shown that PBDE exposure has thyroid-disrupting and hepatotoxic effects on populations living in or around a dismantling e-waste or brominated flame-retardant production site (Zhao et al., 2021; Zheng et al., 2017).

Animal studies have proven that hydroxylated PBDEs (OH-PBDEs) and bromophenols (BPs) are two phenolic metabolites of PBDEs (Qiu et al., 2007; Sandholm et al., 2003). Moreover, the PBDE phenolic metabolites in human samples show regional variations in their composition due to the type of commercial PBDE mixtures used in different regions. Indeed, 5-OH-BDE-47, 5′-OH-BDE-99, and 2,4-dibromophenol (2,4-DBP) were the dominant OH-PBDEs and BPs in human blood samples from pregnant women in the United States, where the less brominated PBDEs are the dominant PBDE congeners in human samples (Qiu et al., 2009). Furthermore, OH-octa-BDE, OH-nona-BDE, and 2,4,6-Tribromophenol (2,4,6-TBP) were identified in human blood samples of e-waste dismantling workers in China and India, where BDE-209 was the most abundant PBDE congener in human samples (Eguchi et al., 2012; Ma et al., 2022; Yu et al., 2010). Notably, the levels of predominant BP congeners were comparable to, or 1–2 orders of magnitudes higher than those of OH-PBDEs in human samples (Eguchi et al., 2012; Lin et al., 2020a; Qiu et al., 2009). Some studies have shown that the phenolic metabolites of PBDEs display even severer biological effects than the parent PBDEs, particularly by exhibiting stronger competition potency with the thyroid hormone (thyroxine on transthyretin binding) after PBDE metabolic conversion (Meerts et al., 2000; Meerts et al., 2001). Therefore, further study of PBDEs in the presence of BPs in human tissues is needed.

Though blood and serum have been widely used for assessing human exposure to PBDEs, the short half-lives of highly brominated congeners can cause significant fluctuation in the endogenous levels, resulting in an unreliable evaluation (Morck et al., 2003; Thuresson et al., 2006). As a result, the hair burdens of PBDEs were put forward due to various advantages such as non-invasive collection and the possibility of retrospectively determining long-term exposure. Indeed, previous studies have indicated that hair is a valuable matrix for assessing human exposure to PBDEs (Liang et al., 2016; Liu et al., 2016; Mi et al., 2017). Significant relationships between the concentrations of PBDEs in human hair and the internal tissues have also been reported in some previous studies (D'Have et al., 2005; Liu et al., 2016; Zheng et al., 2014). However, the distinction between the endogenous and exogenous sources of compounds in hair has long been debated, which introduces uncertainty for using hair as an endogenous exposure bioindicator. Moreover, limited studies have focused on the occurrence of PBDE metabolites in human hair.

In this study, paired human serum, hair, and urine samples were collected from occupational and non-occupational populations in a typical e-waste dismantling site in southern China. The concentrations and patterns of 22 PBDEs and 19 BPs were analyzed in the collected samples, and an animal study was conducted to confirm the endogenous source of PBDEs and BPs in hair. The purpose of this study was to reveal the reliability of using hair as a sample for monitoring endogenous exposed compounds.

2. Materials and methods

All chemicals and reagents used in this work are provided in Text S1 in the Supporting Information (SI).

2.1. Human study design and sample collection

Seventy-five paired serum, hair, and urine samples were collected from participants living in an e-waste dismantling area in southern China, and included 27 e-waste (EW) workers who were directly engaged in e-waste dismantling activities at the e-waste dismantling industrial park for >2 years, 28 non-EW workers who were engaged in other activities at the e-waste dismantling industrial park, and 20 adult residents (≥18 years old) living in the surrounding area (around 5 km from the industrial park). Nineteen paired hair and urine samples were also collected in the same residential area from child residents (≤14 years old). Moreover, all the participants had not dyed or permed their hair for nearly a year. The general demographic characteristics of the participants are provided in Table S1. All samples were collected between November 2017 and December 2018 after the e-waste dismantling industrial park had started operations. Venous blood samples were drawn from each subject with a 10-mL vacutainer anticoagulant-free serum tube by a medical professional in the local hospital. Before transferring to an 8-mL amber glass vial, the serum was isolated using centrifugation at 3000 rpm for 10 min within 3 h of collection. Hair samples (1–2 g) were cut within 1 cm from the scalp at the posterior vertex using stainless steel scissors that were precleaning using ethyl alcohol. Hair strands were wrapped in aluminum foil and sealed in a Ziploc bag. The morning urine samples were collected in polyethylene bottles, and the creatinine level of each urine sample was measured immediately. All of the serum, hair, and urine samples were stored at −20 °C until further analysis.

The human study was approved by the Human Ethics Committee of Guangdong University of Technology, China. Consent was obtained from all the participants after they were informed of the purpose of the study.

2.2. Animal study design and sample collection

A batch of 8-week-old adult male Sprague-Dawley (SD) rats (SPF grade, obtained from Southern Medical University Animal Centre, Guangzhou, China), with an average weight of 200 ± 20 g, were raised in the SPF animal laboratory under a 12/12-h light/dark cycle with access to food and water *ad libitum*. After 1 week of acclimation, the rats were randomly divided into five groups (n = 3 rats per group), with the exposure doses of 2, 20, and 200 mg/kg/d of BDE-209, 20 mg/kg/d of 2,4,6-TBP, and the control. The BDE-209 and 2,4,6-TBP were prepared separately from corn oil and stirred to their final concentrations. The four groups of rats were administered the corresponding dose of the compound using gavage daily for 28 days, while the control group was administered corn oil using gavage daily for 28 days. On the first day of exposure, hair was cut from over the scapulae of each rat to ensure that the hair used for the analysis was regrown during the administration period. After 28 days of administration, euthanasia was conducted, with a dose of 120 mg/kg i.p. of sodium pentobarbital administered to each experimental rat. Blood was collected in a 5-mL vacutainer anticoagulant-free serum tube by cardiac puncture, and serum was isolated using centrifugation at 3000 rpm for 10 min. Regrown hair was collected from the previously shaven area. The rat samples were stored according to the procedure adapted for the human samples.

The animal experiments were approved by The Institutional Animal Care and Use Committee, Southern Medical University (L2019213), China prior to the beginning of study.

2.3. Sample preparation and analysis

The serum samples were extracted according to a previously reported methods (Hovander et al., 2000; Qiu et al., 2009) with slight modifications. Briefly speaking, each serum sample (including human and rats serum samples, 2–5 mL) was transferred to a clean Teflon tube and spiked with known amounts of surrogate standards. Serum samples were denatured using 1 mL hydrochloric acid (6 M) and 6 mL 2-propanol, and after each addition, vortex-mixed. Samples were extracted with 6 mL hexane/methyl tert-butyl ether mixture (1:1, *v*/v) three times using vortex-mixing for at least 2 min each time. The upper organic layer was collected after centrifugation (4000 rpm) for 10 min. The three extracts were combined and washed with 1 % of potassium chloride solution. Trace moisture in the extract was removed using anhydrous sodium sulfate. Then, the organic extract was evaporated and the total lipid weight was determined gravimetrically. Furthermore, the extracts were reconstituted with 1 mL hexane/dichloromethane mixture (1:1, v/v) for removing lipid using gel permeation chromatography (GPC). The fraction of GPC of target analytes was evaporated and redissolved in 1 mL hexane. Then, the extract was loaded onto a 500 mg silica column, which was previously conditioned with 3 mL ethyl acetate, 3 mL dichloromethane and 6 mL hexane. The first fraction that contained PBDEs was eluted with 10 mL 3 % ethyl acetate in hexane, and finally, concentrated and stored in 30 μL of isooctane. The second fraction that contained BPs was eluted with 8 mL 50 % ethyl acetate in hexane, and finally, concentrated and stored in 200 μL of methanol.

Details of the extraction and cleanup of hair and urine samples have been reported in our previous studies (Lin et al., 2020a; Lin et al., 2019). Briefly speaking, the biomonitoring of hair external (hair-Ex) was conducted by analyzing the chemicals on the surface of washed hair. The biomonitoring of hair internal (hair-In) was conducted by analyzing the chemicals in the digested clean hair. Our previous study demonstrated that washing thrice with acetone could effectively remove the external PBDEs and phenolic compounds in hair, whereas the internal compounds can be preserved adequately (Lin et al., 2019). Each hair-Ex and hair-In sample was spiked with surrogate standards before extraction. Hair-In samples were digested with sodium hydroxide (1 M). The targeted compounds in the residual liquid were subjected to liquid-liquid extraction with a hexane/methyl tert-butyl ether mixture (1:1, *v*/v) under alkaline and re-acidification conditions. Each extract of the hair-In sample or washing solution of the hair-Ex sample was concentrated to dryness and reconstituted with 1 mL hexane/dichloromethane mixture (1:1, v/v) for clean-up using GPC. Then, the polar and non-polar compounds were separated with a 1 g silica column by eluting with 5 % ethyl acetate in hexane for PBDEs and 50 % ethyl acetate in hexane for BPs. The fraction of PBDEs was evaporated to dryness and finally, reconstituted to 50 μL with isooctane. The fraction of BPs was also evaporated to dryness and finally, reconstituted to 200 μL with methanol.

Urine samples were extracted with Oasis® HLB SPE cartridges after enzymolysis overnight using β-glucuronidase/arylsulfatase enzyme under the pH of 5.5. SPE cartridges were conditioned with 6 mL of methanol:dichloromethane (1:1, v/v), 6 mL of MeOH, 6 mL of water, and 8 mL of 25 mmol/L KH_2PO_4 buffer. Then, the samples were loaded onto the cartridges and washed with KH_2PO_4 buffer (25 mmol/L; 3 mL) and purified water (3 mL). Finally, the cartridges were dried using a vacuum pump, and the target analytes were eluted with 8 mL of mixed solvent of methanol:dichloromethane (1:1, v/v). The eluates were concentrated to being nearly dry, and the residues were reconstituted to 200 μL with methanol.

For all samples, the instrument analysis, quality assurance (QA), and quality control (QC) are described in Texts S2–S4.

2.4. Statistical analysis

Statistical differences among the populations, as well as among various samples, were assessed using the Mann–Whitney *U* test. A Partial Least Squares Discriminant Analysis (PLS-DA) based on log-transformed data was applied to distinguish the endogenous analytes from exogenous analytes in hair. During the statistical analysis, the concentrations that were lower than the limit of detection (LOD), were assigned a value of zero. Furthermore, PLS-DA was accomplished using SIMCA-P. Other statistical analyses were accomplished using SPSS. A p-value < 0.05 was regarded as being statistically significant.

3. Results and discussion

3.1. PBDEs in human serum and hair samples

As shown by the results presented in Table 1, the detection frequencies of most of the less brominated PBDEs were lower than those of highly brominated PBDEs in serum samples. However, the detection frequencies of the less brominated PBDEs in hair-In and hair-Ex samples were higher than those in the serum samples (Tables 2 and S2). In contrast, for PBDEs that were detected in <100 % of serum and hair samples, their detection frequencies were higher for EW workers than for other populations.

The total concentrations of PBDEs (ΣPBDEs) in serum samples lied within the range of 107–1546 ng/g lw for EW workers, 105–608 ng/g lw for non-EW workers, and 31.7–223 ng/g lw for adult residents (Table 1). Statistically speaking, there was a non-significant difference among the concentrations in the serum samples of EW workers (median value of ΣPBDEs: 190 ng/g lw) and non-EW workers (median value: 218 ng/g lw) ($p > 0.05$). However, significantly lower concentrations were observed in serum samples of adult residents (median value of ΣPBDEs: 69.7 ng/g lw) ($p < 0.01$). Moreover, BDE-209 was the most dominant PBDE congener in the serum samples, and accounted for 35 %–45 % of the ΣPBDEs (Fig. 1), with the median values of 78.0 ng/g lw, 95.7 ng/g lw and 20.9 ng/g lw for EW workers, non-EW workers and adult residents, respectively (Table 1). Two prior studies on PBDEs in serum samples had only focused on EW workers, who exhibited higher PBDE levels compared to the EW workers in the present study (Bi et al., 2007; Zheng et al., 2014). Moreover, the highest level of serum BDE-209 of EW workers (554 ng/g lw) in this study (Table 1) was 5 times lower than that of the previously reported highest level (3100 ng/g lw) (Bi et al., 2007). This finding suggests that, compared with the traditional primitive mode of e-waste dismantling activities, the current intensive mode effectively reduces the level of PBDE exposure to occupational population. Even so, due to the relatively short half-life of BDE-209 (Mi et al., 2017; Thuresson et al., 2006), the high contribution of BDE-209 observed in the serum samples of the present study suggests

Table 1
Concentrations of PBDEs in human serum samples (ng/g lw).

	EW worker				Non-EW worker				Adult resident				*p* value[c]		
	Median	Mean	Range	*DF*[a] (%)	Median	Mean	Range	*DF* (%)	Median	Mean	Range	*DF* (%)	EW *vs* non-EW[d]	EW *vs* A.R[e]	Non-EW *vs* A.R[f]
N	(27)				(28)				(20)						
BDE-17	n.d.	0.59	n.d.[b]–9.30	48	n.d.	0.38	n.d.–1.72	39	n.d.	0.25	n.d.–1.31	50	8.09E − 01	7.46E − 01	8.18E − 01
BDE-28	2.83	10.6	0.19–68.6	100	2.93	4.95	1.54–22.2	100	1.73	1.79	n.d.–4.58	85	8.01E − 01	5.50E − 03	2.42E − 03
BDE-71	0.22	3.02	n.d.–25.9	56	0.37	8.80	n.d.–56.3	50	n.d.	4.24	n.d.–33.9	45	5.45E − 01	5.07E − 01	3.67E − 01
BDE-47	5.53	13.6	n.d.–87.5	96	2.44	5.00	n.d.–30.3	96	0.48	0.87	n.d.–4.54	65	9.06E − 02	6.89E − 06	5.97E − 05
BDE-66	n.d.	1.63	n.d.–28.3	41	n.d.	0.44	n.d.–4.27	25	n.d.	n.d.	n.d.	0	2.50E − 01	–	–
BDE-100	1.21	1.53	n.d.–7.49	85	0.34	0.64	n.d.–3.00	64	n.d.	0.08	n.d.–0.39	50	1.09E − 02	1.17E − 05	9.78E − 03
BDE-99	1.83	4.50	n.d.–52.6	85	0.35	0.98	n.d.–6.86	50	0.28	0.36	n.d.–1.59	55	3.57E − 03	1.08E − 04	2.98E − 01
BDE-85	n.d.	0.22	n.d.–2.07	44	n.d.	0.30	n.d.–1.36	29	n.d.	0.01	n.d.–0.08	20	6.39E − 01	2.50E − 02	2.71E − 01
BDE-154	0.28	0.74	n.d.–4.13	63	n.d.	0.29	n.d.–1.11	43	n.d.	0.21	n.d.–1.97	20	1.44E − 01	4.29E − 03	1.22E − 01
BDE-153	31.0	44.5	0.95–237	100	24.8	40.9	0.71–215	100	4.49	10.4	0.62–40.9	100	8.27E − 01	7.89E − 04	2.03E − 02
BDE-138	0.30	0.58	n.d.–3.88	74	n.d.	0.18	n.d.–1.26	21	n.d.	0.01	n.d.–0.27	5	1.04E − 03	6.90E − 06	1.02E − 01
BDE-183	4.80	12.4	0.56–98.7	100	3.95	7.19	n.d.–42.7	93	0.12	0.86	0.10–3.64	100	1.57E − 01	1.71E − 07	1.82E − 04
BDE-190	1.59	2.58	n.d.–18.6	89	0.43	1.43	n.d.–11.7	50	0.10	0.32	n.d.–1.10	50	2.52E − 02	2.93E − 06	1.34E − 01
BDE-202	3.33	5.26	0.46–31.3	100	4.48	4.88	0.94–12.6	100	6.77	6.27	1.11–12.3	100	2.92E − 01	1.60E − 01	3.36E − 01
BDE-201	5.41	7.90	2.27–46.8	100	6.81	7.30	3.56–15.2	100	7.06	6.17	2.08–9.58	100	1.53E − 01	5.47E − 01	4.26E − 01
BDE-197	16.3	32.8	2.61–240	100	10.5	19.0	3.50–107	100	6.42	7.13	2.21–17.3	100	1.73E − 01	2.99E − 05	1.28E − 02
BDE-203	5.26	7.52	2.63–50.7	100	5.17	6.55	2.33–35.6	100	3.67	3.64	1.32–6.15	100	9.46E − 01	4.91E − 04	6.15E − 03
BDE-196	3.35	5.36	0.70–37.2	100	1.77	2.63	n.d.–17.7	82	1.73	1.76	n.d.–3.99	85	1.33E − 02	1.81E − 03	6.37E − 01
BDE-208	5.41	10.5	3.59–95.9	100	6.31	8.36	3.96–29.2	100	3.37	3.89	1.91–7.86	100	4.59E − 01	1.40E − 04	3.16E − 05
BDE-207	12.8	26.2	6.31–238	100	9.92	14.4	4.86–35.5	100	4.53	5.24	2.64–10.4	100	1.21E − 01	2.42E − 07	1.13E − 05
BDE-206	7.98	10.0	3.58–40.3	100	12.7	12.7	4.31–23.0	100	4.64	8.37	n.d.–24.9	95	1.05E − 02	1.27E − 01	8.42E − 03
BDE-209	78.0	104	17.7–554	100	95.7	97.7	31.0–166	100	20.9	45.0	6.51–144	100	1.30E − 01	4.82E − 03	3.22E − 04
ΣPBDEs	190	301	107–1546		218	245	105–608		69.7	100	31.7–223		5.56E − 01	6.88E − 05	1.13E − 05

[a] Detection frequency.
[b] Not detected.
[c] Obtained by Mann–Whitney *U* test between the two groups.
[d] EW worker *vs* non-EW worker.
[e] EW worker *vs* adult resident.
[f] Non-EW worker *vs* adult resident.

that populations living in the e-waste dismantling area were continuously exposed to high levels of BDE-209.

The distribution of ΣPBDE levels of hair-In samples was found to be lying in the following descending order: EW workers (11.5–7109 ng/g dw, median value: 350 ng/g dw) ≫ non-EW workers (4.49–1016 ng/g dw, median value: 40.7 ng/g dw) > adult residents (0.85–280 ng/g dw, median value: 31.5 ng/g dw) > child residents (2.33–204 ng/g dw, median value: 16.7 ng/g dw) (Table 2). Similarly, the ΣPBDE levels of hair-Ex samples presented the highest concentration in the EW workers, followed by non-EW workers, adult residents, and child residents (Table S2). Significant differences were obtained for the ΣPBDE concentrations in both the hair-In and hair-Ex samples between the EW workers and other populations

Table 2
Concentrations of PBDEs in human hair-In samples (ng/g dw).

	EW worker				Non-EW worker				Adult resident				Child resident			
	Median	Mean	Range	*DF*[a] (%)	Median	Mean	Range	*DF* (%)	Median	Mean	Range	*DF* (%)	Median	Mean	Range	*DF* (%)
N	(27)				(28)				(20)				(19)			
BDE-17	0.93	1.85	0.20–13.2	100	0.39	0.74	0.05–5.02	100	0.09	0.09	0.01–0.24	100	0.12	0.20	0.04–0.87	100
BDE-28	7.86	10.7	1.17–62.2	100	2.22	4.57	0.28–37.5	100	0.46	0.70	0.04–2.78	100	0.84	1.33	0.39–6.10	100
BDE-71	0.83	1.31	0.04–9.32	100	0.11	0.37	0.02–3.08	100	0.05	0.06	n.d.–0.20	100	0.07	0.15	0.03–0.90	100
BDE-47	11.8	27.9	1.19–296	100	2.65	8.51	0.35–73.4	100	1.12	1.06	0.03–2.16	100	1.63	3.41	0.57–26.1	100
BDE-66	3.01	7.98	0.33–95.0	100	0.68	2.45	0.10–19.9	100	0.28	0.29	0.01–0.74	100	0.42	0.99	0.16–7.83	100
BDE-100	0.80	2.06	0.04–21.8	100	0.12	0.44	0.02–3.77	100	0.07	0.10	n.d.–0.34	95	0.11	0.25	n.d.–1.54	95
BDE-99	7.18	21.7	0.45–279	100	1.02	4.16	0.16–30.6	100	0.45	0.46	0.01–1.10	100	0.49	1.28	0.18–8.25	100
BDE-85	0.40	1.00	0.03–12.0	100	0.05	0.20	0.01–1.23	100	0.02	0.03	n.d.–0.16	80	0.04	0.09	0.02–0.34	100
BDE-154	0.79	1.52	0.04–14.1	100	0.06	0.28	0.01–2.59	100	0.05	0.09	n.d.–0.35	100	0.06	0.17	0.02–1.09	100
BDE-153	2.07	3.89	0.16–38.4	100	0.27	0.70	0.02–4.93	100	0.17	0.31	0.01–1.89	100	0.14	0.29	0.03–1.01	100
BDE-138	0.28	0.45	n.d.[b]–4.10	96	0.02	0.08	n.d.–0.52	64	n.d.	0.01	n.d.–0.07	25	0.00	0.02	n.d.–0.11	32
BDE-183	1.94	3.72	0.06–25.1	100	0.13	0.52	0.03–4.44	100	0.12	0.31	0.01–2.39	100	0.12	0.31	0.03–1.34	100
BDE-190	0.30	0.53	n.d.–3.13	96	0.04	0.10	n.d.–0.83	68	0.02	0.04	n.d.–0.18	60	0.03	0.05	n.d.–0.25	63
BDE-202	0.47	0.60	n.d.–2.72	96	0.04	0.16	n.d.–1.74	64	0.03	0.06	n.d.–0.25	85	0.04	0.09	0.01–0.40	100
BDE-201	1.12	1.32	0.05–6.32	100	0.07	0.31	0.02–3.13	100	0.07	0.14	n.d.–0.58	95	0.07	0.15	0.02–0.71	100
BDE-197	1.28	2.16	0.07–12.9	100	0.11	0.38	0.04–2.60	100	0.10	0.23	0.03–1.01	100	0.10	0.23	0.03–0.90	100
BDE-203	3.53	6.17	0.15–39.1	100	0.23	1.18	0.09–11.0	100	0.19	0.44	0.08–1.83	100	0.22	0.49	0.07–2.47	100
BDE-196	3.25	5.66	0.12–25.9	100	0.16	0.88	0.04–7.53	100	0.16	0.39	0.03–1.49	100	0.12	0.37	0.04–1.86	100
BDE-208	4.55	11.9	0.12–104	100	0.28	2.12	0.04–23.6	100	0.24	0.84	n.d.–5.50	95	0.22	0.76	0.02–3.79	100
BDE-207	6.29	16.3	0.15–144	100	0.35	2.71	0.07–29.9	100	0.33	1.15	n.d.–6.79	100	0.30	1.02	0.03–5.26	100
BDE-206	9.25	33.2	0.37–297	100	0.67	4.30	n.d.–44.1	82	0.63	2.22	n.d.–15.6	85	0.33	1.37	n.d.–9.97	74
BDE-209	267	664	6.61–6427	100	22.0	86.9	2.50–723	100	23.8	50.2	0.30–242	100	11.3	34.1	0.54–167	100
ΣPBDEs	350	826	11.5–7109		40.7	122	4.49–1016		31.5	59.2	0.85–280		16.7	47.1	2.33–204	

[a] Detection frequency.
[b] Not detected.

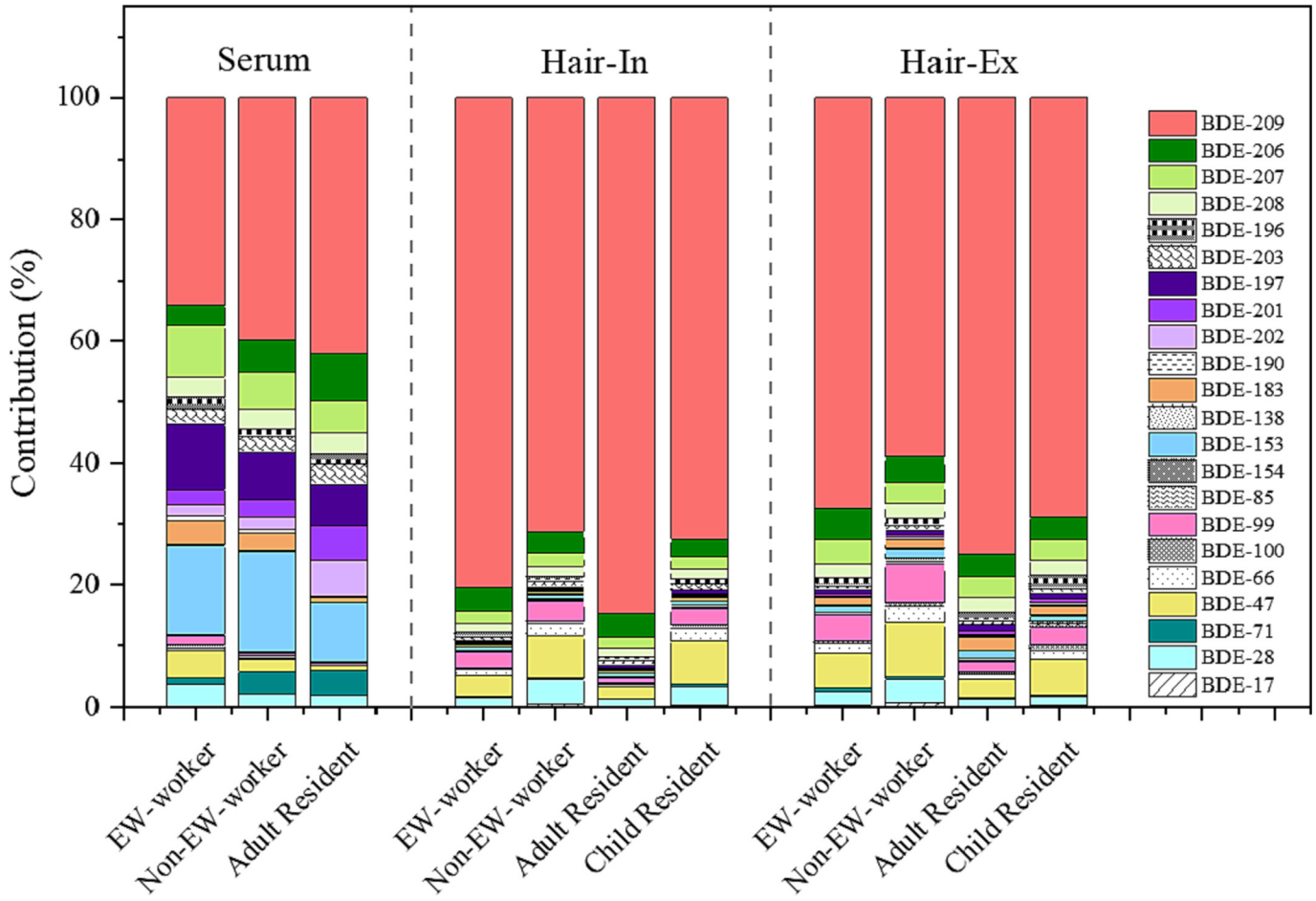

Fig. 1. PBDE congener profiles in human serum, hair-In, and hair-Ex samples.

($p < 0.05$). However, a non-significant difference was observed between every two groups of non-EW workers, adult residents, and child residents, suggesting a more profound effect of PBDEs on workers who were directly engaged in the EW dismantling activities. Furthermore, BDE-209 was the most dominant PBDE congener in both the hair-In and hair-Ex samples, with values lying within the ranges of 71 %–85 % and 59 %–75 % of the ΣPBDEs, respectively. However, the distribution patterns of PBDEs in hair samples differed from those in the serum samples, with a remarkably higher contribution of BDE-47 and BDE-99, but lower contributions from BDE-153, octa-BDEs, and nona-BDEs.

Furthermore, the concentrations of PBDEs in the hair-In samples of this study were compared with those (in hair) reported in previous studies. The concentrations of hair-In samples from EW workers (11.5–7109 ng/g dw) in the present study were comparable to those in the hair samples from the occupationally exposed workers (18.1–9400 ng/g dw) in the Luqiao area, which is another EW recycling area in east China (Wen et al., 2008). Additionally, the PBDE levels in the hair samples from the occupationally exposed workers in two other EW recycling areas in China (Wenling (Liang et al., 2016): 70.8–868 ng/g dw; Longtang (Zheng et al., 2014): 33–1284 ng/g dw) were lower than those reported in the present study. This discrepancy may be attributed to the differences in the types of e-wastes.

3.2. BPs in human serum, urine, and hair samples

As shown by the results presented in Table 3, the detection frequencies of BP congeners were highly variable in different matrices. Among the 19 BP congeners, only 4-monobromophenol (4-MBP), 2,4-DBP, 2,4,5-TBP, 2,4,6-TBP, 2,3,4,6-tetrabromophenol (2,3,4,6-TeBP), 2,3,5,6-TeBP, and pentabromophenol (PBP) were detected in the serum samples. Additionally, 2,4,6-TBP and 2,3,4,6-TeBP were the most frequently detected (>80 %) congeners in the serum samples. For urine samples, only 4-MBP, 3,4-DBP, 3,5-DBP, 2,4-DBP, 2,4,5-TBP, 2,4,6-TBP, and 2,3,4,6-TeBP were detected. Moreover, 2,4-DBP and 2,4,6-TBP were the most frequently detected (>80 %) congeners in the urine samples. Different detection frequencies of BP congeners were observed between the hair-In and the hair-Ex samples. Nine of the 19 BPs were detected in the hair-In samples, while 5 of the 19 BPs were detected in the hair-Ex samples. Furthermore, 4-MBP, 2,4-DBP, and 2,4,6-TBP were detected in all the hair-In samples except for 2,4-DBP in the child residents. Compared to biological fluids, the BP congeners were more frequently detected in the hair-In samples.

The concentrations of total BPs (ΣBPs) in the serum samples lied within the ranges of 10.3–486 ng/g lw (median: 126 ng/g lw) in EW workers, 38.0–320 ng/g lw (median: 181 ng/g lw) in non-EW workers, and not detected–381 ng/g lw (median: 155 ng/g lw) in adult residents (Table 3). For urine samples, the highest ΣBPs concentration was found in child residents (1.25–23.8 μg/g creatinine, median: 2.44 μg/g creatinine), followed by EW workers (1.01–16.4 μg/g creatinine, median: 2.81 μg/g creatinine). The concentrations of ΣBPs in urine samples of non-EW workers (0.44–7.38 μg/g creatinine, median: 1.92 μg/g creatinine) and adult residents (0.60–8.21 μg/g creatinine, median: 1.68 μg/g creatinine) were comparable. Statistically speaking, a non-significant difference was observed in the ΣBPs levels of serum and urine between the EW workers and the residents ($p > 0.05$).

The levels of ΣBPs in hair-In and hair-Ex samples were found to lie in the following descending order: EW workers (hair-In: 58.4–42,191 ng/g dw, median: 547 ng/g dw; hair-Ex: 2.94–3296 ng/g dw, median: 87.4 ng/g dw) > non-EW workers (hair-In: 82.6–6099 ng/g dw, median: 455 ng/g

Table 3
Concentrations of BPs in serum, urine and hair. (Only the detectable BP congeners were shown).

	EW worker				Non-EW worker				Adult resident				Child resident			
	Median	Mean	Range	*DF*[a] (%)	Median	Mean	Range	*DF* (%)	Median	Mean	Range	*DF* (%)	Median	Mean	Range	*DF* (%)
Serum (ng/g lw)																
N	(27)				(28)				(20)				(0)			
4-MBP	1.56	4.64	n.d.[b]–64.0	67	n.d.	0.69	n.d.–3.72	36	1.61	1.92	n.d.–6.75	65				
2,4-DBP	n.d.	7.93	n.d.–29.9	50	n.d.	2.15	n.d.–22.8	21	n.d.	7.49	n.d.–47.4	48				
2,4,5-TBP	n.d.	0.66	n.d.–13.1	31	n.d.	0.06	n.d.–1.11	7	n.d.	0.02	n.d.–0.46	14				
2,4,6-TBP	101	118	10.3–376	100	178	175	33.8–300	100	126	146	n.d.–381	96				
2,3,4,6-TeBP	2.58	2.73	n.d.–7.26	90	2.50	2.55	n.d.–7.87	82	1.65	1.85	n.d.–4.35	88				
2,3,5,6-TeBP	0.64	0.91	n.d.–4.23	78	0.25	0.57	n.d.–4.27	54	0.11	0.20	n.d.–1.01	60				
PBP	n.d.	3.38	n.d.–34.8	58	n.d.	0.78	n.d.–5.30	32	n.d.	0.25	n.d.–3.09	35				
ΣBPs	126	138	10.3–486		181	181	38.0–320		155	158	n.d.–381					
Urine (μg/g creatinine)																
N	(27)				(28)				(20)				(19)			
4-MBP	0.36	1.16	0.13–8.77	100	0.24	0.26	0.06–0.54	100	0.26	0.29	0.12–0.75	100	0.40	0.73	n.d.–5.37	89
2,4-DBP	0.15	0.48	n.d.–2.20	56	0.09	0.24	n.d.–1.80	54	n.d.	0.02	n.d.–0.22	10	n.d.	1.36	n.d.–17.0	16
3,4-DBP	n.d.	0.004	n.d.–0.05	11	n.d.	0.003	n.d.–0.08	4	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
3,5-DBP	n.d.	0.006	n.d.–0.05	26	n.d.	0.006	n.d.–0.05	29	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
2,4,5-TBP	0.43	0.53	n.d.–1.68	96	0.32	0.33	n.d.–1.08	89	n.d.	0.20	n.d.–1.22	35	n.d.	0.41	n.d.–1.77	47
2,4,6-TBP	1.50	2.12	0.35–7.44	100	1.23	1.69	0.29–5.94	100	1.08	1.99	0.35–6.49	100	1.73	1.85	0.47–5.26	100
2,3,4,6-TeBP	0.02	0.03	n.d.–0.28	59	n.d.	0.01	n.d.–0.03	43	n.d.	0.007	n.d.–0.08	15	n.d.	0.02	n.d.–0.15	21
ΣBPs	2.81	4.19	1.01–16.4		1.92	2.53	0.44–7.38		1.68	2.52	0.60–8.21		2.44	4.37	1.25–23.8	
Hair-In (ng/g dw)																
N	(27)				(28)				(20)				(19)			
4-MBP	18.4	38.6	2.33–214	100	12.2	21.5	2.98–73.6	100	4.62	6.02	1.82–12.0	100	3.86	4.54	1.61–12.2	100
3,4-DBP	0.71	1.95	n.d.–16.9	78	0.37	0.72	n.d.–4.23	71	n.d.	0.20	n.d.–1.57	40	0.22	0.29	n.d.–0.91	58
3,5-DBP	1.26	2.24	n.d.–21.0	93	0.47	0.68	n.d.–3.01	89	0.23	0.37	n.d.–1.72	65	0.27	0.50	n.d.–2.26	68
2,4-DBP	36.7	80.6	9.87–870	100	26.7	37.7	4.99–133	100	9.22	15.2	3.82–56.3	100	8.02	10.0	n.d.–27.1	89
2,4,5-TBP	n.d.	2.06	n.d.–48.0	44	n.d.	0.64	n.d.–6.94	46	n.d.	0.12	n.d.–0.81	30	n.d.	0.13	n.d.–0.91	21
2,4,6-TBP	490	2124	46.2–41139	100	410	673	67.4–5906	100	206	310	54.3–1493	100	151	165	38.0–395	100
2,3,4,6-TeBP	n.d.	0.55	n.d.–4.54	30	n.d.	0.67	n.d.–3.00	43	0.79	0.81	n.d.–2.78	60	n.d.	0.40	n.d.–2.68	32
2,3,5,6-TeBP	n.d.	0.02	n.d.–0.37	7	n.d.	0.11	n.d.–1.50	18	n.d.	0.04	n.d.–0.61	15	n.d.	n.d.	n.d.	0
PBP	n.d.	0.11	n.d.–1.26	11	n.d.	0.04	n.d.–1.03	4	n.d.	0.04	n.d.–0.73	15	n.d.	n.d.	n.d.	0
ΣBPs	547	2250	58.4–42191	7	455	735	82.6–6099		225	333	67.5–1562		176	181	45.2–414	
Hair-Ex (ng/g dw)																
N	(27)				(28)				(20)				(19)			
4-MBP	3.46	8.25	n.d.–50.1	93	2.85	4.62	n.d.–34.1	96	1.15	1.97	n.d.–12.1	90	0.20	0.25	n.d.–1.02	58
3,4-DBP	n.d.	0.17	n.d.–1.32	33	n.d.	0.03	n.d.–0.79	7	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
3,5-DBP	0.21	0.30	n.d.–1.13	46	n.d.	0.08	n.d.–0.80	18	n.d.	0.04	n.d.–0.35	30	n.d.	n.d.	n.d.	0
2,4-DBP	2.11	6.59	n.d.–36.5	67	2.60	4.33	n.d.–24.3	75	n.d.	0.95	n.d.–4.88	45	n.d.	0.08	n.d.–1.52	5
2,4,6-TBP	82.9	220	2.94–3244	100	37.3	80.4	7.31–543	100	32.6	62.4	8.94–613	100	9.41	13.1	1.28–55.5	100
ΣBPs	87.4	235	2.94–3296		45.2	89.5	7.39–552		34.3	65.4	9.22–630		9.53	13.4	1.28–55.7	

[a] Detection frequency.
[b] Not detected.

dw; hair-Ex: 7.39–552 ng/g dw, median: 45.2 ng/g dw) > adult residents (hair-In: 67.5–1562 ng/g dw, median: 225 ng/g dw; hair-Ex: 9.22–630 ng/g dw, median: 34.3 ng/g dw) > child residents (hair-In: 45.2–414 ng/g dw, median: 176 ng/g dw; hair-Ex: 1.28–55.7 ng/g dw, median: 9.53 ng/g dw). Significant differences were found in the concentrations of ΣBPs in the hair samples (both hair-Ex and hair-In) between the EW workers and other populations ($p < 0.05$) (Table 3). These results demonstrate that, compared to serum and urine samples, hair biomonitoring of BPs can be used to easily distinguish the occupational and non-occupational exposure populations.

As shown in Fig. 2, 2,4,6-TBP was found to be the most dominant BP congener in all the matrices, and accounted for 85 %–96 % in serum samples, 51 %–80 % in urine samples, 91 %–94 % in hair-In samples, and 90 %–98 % in hair-Ex samples, with no significant differences among the studied populations. Notably, the levels of 2,4,6-TBP in hair-In samples were 3–8 times higher than those of BDE-209 ($p < 0.01$), while the levels of 2,4,6-TBP in hair-Ex samples were 1–3 times lower than those of BDE-209 ($p < 0.01$). Therefore, the endogenous exposure of 2,4,6-TBP should be of particular concern. Comparing other BP congeners among various matrices, a higher contribution of TeBPs was found in the serum, presenting a declining trend with the decreasing exposure potency of e-waste dismantling activities, and with the following descending order: EW workers (2.5 %) > non-EW workers (1.7 %) > adult residents (1.3 %). Relatively higher proportions of 2,4-DBP and 2,4,5-TBP were observed in the urine samples of workers at the e-waste dismantling park. Though the contributions of 3,4-DBP and 3,5-DBP to the total BPs were tiny in hair samples, their detection frequencies were >70 % in the hair-In samples of both the EW and non-EW workers. These trace compounds presented a matrix-specific accumulation in the human body. However, the analysis of these trace compounds requires more sophisticated pretreatment and instrumentation that it is difficult to popularize.

Only two prior studies have reported the levels of BPs in the serum samples from e-waste recycling workers in India and North Vietnam (Eguchi et al., 2012; Eguchi et al., 2015), both of which were lower than those of the present study. Moreover, only a handful of data are available on BPs in human hair and urine samples from e-waste dismantling areas. The present study found a non-significant difference in the ΣBPs levels of serum and urine between the occupational and non-occupational exposure populations ($p > 0.05$). In contrast, significant disparities were observed in the hair samples ($p < 0.05$). After the exposure, most non-persistent chemicals are transferred from serum to urine within a few hours, and their concentrations may become undetectable or decrease after the discontinuation of exposure (Hernandez et al., 2019). Moreover, the metabolized efficiency of cytochrome P450 enzyme varies in populations of different ages (Anderson, 2002), which may lead to overestimating or underestimating the compound level in serum and urine samples for spot

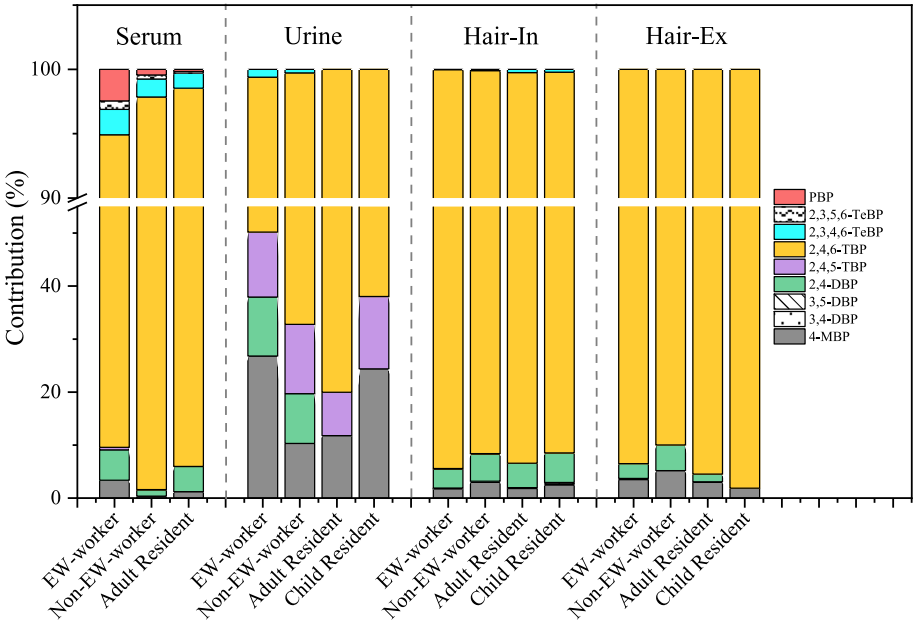

Fig. 2. BP congener profiles in human serum, urine, hair-In, and hair-Ex samples.

sampling. Therefore, serum and urine mainly provide information on short-term exposure and may present a high level of variability (Fays et al., 2021; Li et al., 2010). However, hair can chronologically capture chemicals, from weeks to months, and can therefore provide information about the long-term exposure. This wide temporal detection window highly increases the chances of detecting trace compounds with short half-lives. Therefore, the levels of BPs in hair in the present study could differentiate between high and low exposure populations. A study based on the rat model also demonstrated that hair analysis was superior to serum and urine analyses for reliably differentiating various individuals according to their level of exposures (Appenzeller et al., 2017).

3.3. Implication of the compounds in hair-In and hair-Ex

Statistically speaking, a non-significant difference was found in the levels of ΣPBDEs between hair-In and hair-Ex samples of EW workers, adult residents, and child residents ($p > 0.05$) (Table 2). In detail, only a few PBDE congeners (for example BDE-71, BDE-203, BDE-206 and BDE-209 for EW workers; BDE-28 and BDE-209 for adult residents; BDE-17, BDE-71, BDE-47, BDE-66, BDE-99, BDE-153, BDE-138, BDE-202, BDE-203 and BDE-209 for child residents) exhibited a non-significant difference in levels of hair-In and hair-Ex samples ($p > 0.05$). The levels of other PBDE congeners in hair-In samples were significantly lower than those in hair-Ex samples ($p < 0.05$). For non-EW workers, all the PBDE congeners in hair-In samples were significantly lower than those in hair-Ex samples. However, the levels of ΣBPs in hair-In samples were 1–2 orders of magnitude higher than those in hair-Ex samples (Table 3). All BPs congeners in hair-In samples were significantly higher than those in hair-Ex samples ($p < 0.05$).

Furthermore, as observed from the PLS-DA model, the score plot with two components successfully separated the hair-In samples from hair-Ex samples (Fig. S1a). According to the loading plot (Fig. S1b), all BPs were closely located in the upper right panel, with high positive values for both Components 1 and 2, which corresponded to the location of hair-In samples in the score plot. All parent PBDEs were clustered in the lower left panel, with negative values for Component 1 and lower values for Component 2, which corresponded to the location of hair-Ex samples in the score plot. The variable important in projection (VIP) values of the targeted compounds was found to lie in the following descending order: 2,4,6-TBP > 2,4-DBP > 3,5-DBP > 4-MBP > 3,4-DBP > 1 > all PBDE congeners (Fig. S1c).

These results may indicate that PBDEs in hair were subject to great exogenous exposure interference. In contrast, BPs were mainly derived from the endogenous contribution of hair samples. However, similar composition profiles of PBDEs and BPs between hair-In and hair-Ex seemed to suggest the consistent sources of these compounds in hair-In and hair-Ex samples (Figs. 1 and 2). This contradiction might be due to following reasons. First, the hydrophobicity of PBDEs is favorable for binding with hair sebum. Some endogenous PBDEs of hair could be extracted with hair sebum during the washing process of the sample preparation and becomes a part of hair-Ex contaminants, whereas some exogenous PBDEs of hair could permeate and incorporate into hair to become a part of hair-In contaminants. Therefore, concentrations and profiles of PBDEs in hair-In and hair-Ex were in equilibrium and similar to each other. Second, the endogenous BPs of hair were not easy to drain with hair sebum due to the hydrophilicity of BPs, while the external BPs could easily be removed during daily shampooing. Even so, a small amount of endogenous BPs could still be extracted during the washing process of the sample, which led to similar composition profiles of BPs in hair-In and hair-Ex samples, though much higher concentrations of BPs were observed in the hair-In samples than those in hair-Ex samples. Our previous study on polycyclic aromatic hydrocarbons (PAHs) and their hydroxylated metabolites (OH-PAHs) in hair samples found that the concentrations of OH-PAHs in hair-In were extremely higher than those in hair-Ex (Lin et al., 2020b). Therefore, hair biomonitoring of phenolic compounds or metabolites might readily represent the endogenous source of these compounds. However, only a handful of studies have explored the endogenous accumulation of PBDEs and BPs in hair so far.

3.4. Animal study

As the predominant compounds of PBDEs and BPs, both the BDE-209 and 2,4,6-TBP were administered in the animal study to determine whether these compounds, and their metabolites could be endogenously incorporated into hair. The distribution of these compounds was also evaluated in rat serum.

The total ion chromatograms of the full scan of PBDE standards, rat serum, rat hair, and blank samples analyzed using gas chromatography-electron capture negative chemical ionization-mass spectrometry are shown in Fig. S2. In rat samples, BDE-209 and its debromination metabolites were identified by comparing to the retention time and mass spectra of known PBDE standards. The peaks of the rat serum sample matched

well with those of the standards of BDE-202, BDE-201, BDE-197, BDE-203, BDE-196, BDE-208, BDE-207, BDE-206, and BDE-209, indicating that these octa- and nona-BDEs in rat serum were the debromination metabolites of BDE-209. Both BDE-209 and its debromination metabolites could accumulate in serum samples. Some previous rat model studies found that the metabolites of BDE-209 were responsible for the distribution of highly brominated BDE congeners in serum samples (Mi et al., 2017; Zhang et al., 2011). However, after exposure to BDE-209, only BDE-209 and a small amount of BDE-208, BDE-207, and BDE-206 could accumulate in rat hair, while no other less brominated PBDE metabolites were found in rat serum and hair samples. These results suggest that the octa- and nona-BDEs could not easily endogenously incorporate into hair. This result confirms that octa- and nona-BDEs in human serum samples primarily originated from the endogenous metabolism of BDE-209, while octa- and nona-BDEs in human hair samples may be highly interfered by exogenous environmental pollution.

Fig. S3 shows the distribution of diphenyl ether bond cleavage metabolites of BDE-209 in rat serum and hair samples. The *m/z* values of MBP (170.9451), DBP (250.8536), TBP (328.7641), TeBP (408.6726), and PBP (486.5831) congeners of standard, rat serum, rat hair, and blank samples were extracted. As MBP and DBP congeners were not found in any rat serum and hair sample, only the extracted ion chromatograms of TBP, TeBP, and PBP congeners are shown in Fig. S3. The results show that 2,4,6-TBP, 2,3,4,5-TeBP, 2,3,4,6-TeBP, 2,3,5,6-TeBP, and PBP were mainly the diphenyl ether bond cleavage metabolites in rat serum, whereas only 2,4,6-TBP and 2,3,4,6-TeBP were found in rat hair samples. These results were similar as the distribution of 2,4,6-TBP and TeBPs were found only in human serum and hair samples in this study. Due to the negative detection of TeBPs and PBP in the hair-Ex samples, the levels of TeBP and PBP were likely attributed to the endogenous source *via* the metabolism of BDE-209. However, when the rats were repeatedly exposed to 2,4,6-TBP, 2,4,6-TBP was also distributed in the serum and hair without any BP metabolite (data not shown, but similar to that presented in Fig. S3 a1–a5).

It has been reported that 2,4,6-TBP has broad anthropogenic and natural sources, including flame retardants (Covaci et al., 2011), decomposition products of BFRs *via* abiotic transformation (Bendig and Vetter, 2013), wood preservatives (Nichkova et al., 2008), and natural products from marine organisms (Chung et al., 2003). Furthermore, biotransformation of BDE-100, BDE-154, and 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) could also contribute to high levels of 2,4,6-TBP in humans (Qiu et al., 2009; Zheng et al., 2022). However, in this study, the levels of BDE-100 and BDE-154 in hair samples were 2–3 magnitudes lower than those of BDE-209 (Table S2), while TTBP-TAZ was not detected in hair samples. Similarly, the levels of BDE-100, BDE-154, and TTBP-TAZ were >2 orders of magnitude lower than those of BDE-209 in dust samples from the e-waste dismantling workshop (unpublished data). Therefore, the contributions of BDE-100, BDE-154, and TTBP-TAZ to the endogenous exposure of 2,4,6-TBP could easily be neglected. In the context of present study, BDE-209 metabolites and 2,4,6-TBP exposure were likely to be the sources of high level of 2,4,6-TBP that was detected in the hair-In samples. Notably, the level of 2,4,6-TBP was significantly higher than that of BDE-209 in the hair-In samples (Tables S4 and S5). Moreover, some experimental data demonstrate the ability of 2,4,6-TBP to disrupt thyroid hormone homeostasis (Lee et al., 2016; Meerts et al., 2000). Therefore, the endogenous exposure of 2,4,6-TBP warrants further attention. Further research is needed to investigate the relationship between the concentration of 2,4,6-TBP in hair and its subsequent health effects.

4. Conclusions

In the current study, the occurrence of PBDEs and BPs in human paired serum, hair, and urine samples were directly compared with each other from an e-waste dismantling area. According to the detection frequencies and significant differences in the levels of compounds, the hair analysis could more easily differentiate among high-to-low PBDEs and BPs exposure populations than the serum and urine analyses. Moreover, based on the comparison of compounds in hair-In and hair-Ex samples, BPs rather than the PBDEs were mainly derived from the endogenous contribution of hair samples. As the predominant congeners, the level of 2,4,6-TBP in hair-In was much higher than BDE-209, which was attributed to the BDE-209 metabolites and 2,4,6-TBP exposure. In short, hair biomonitoring of phenolic compounds or metabolites could readily represent the endogenous exposure to these compounds.

Statement

This work has received approval for research ethics from Guangdong University of Technology and a proof/certificate of approval is available upon request.

CRediT authorship contribution statement

Meiqing Lin: Data curation, Formal analysis, Methodology, Writing – review & editing. **Shengtao Ma:** Conceptualization, Methodology, Validation, Writing – review & editing. **Jian Tang:** Data curation, Formal analysis. **Yingxin Yu:** Methodology, Validation. **Guiying Li:** Validation, Writing – review & editing. **Ruifang Fan:** Methodology, Validation. **Guoxia Zhang:** Methodology, Validation. **Bixian Mai:** Supervision. **Taicheng An:** Conceptualization, Writing – review & editing, Supervision.

Data availability

No data was used for the research described in the article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.161980.

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