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Contamination of Brominated Flame Retardants (BFRs) in Human Hair from E-waste Recycling Site in Vietnam

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Abstract—In this study, polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and polychlorinated biphenyls (PCBs) were determined in human scalp hair from Vietnam. Levels of PBDEs and HBCDs were significantly higher in hair of e-waste recycling workers in Bui Dau (e-waste recycling site), an e-waste recycling site than those in general residents in Bui Dau, Dong Mai (lead battery recycling site) and Hanoi (urban control site). Additionally, comparable levels of PBDEs in some samples of non-recyclers in Bui Dau to hair of e-waste recycling workers were detected. This suggests that residents in Bui Dau were highly exposed to PBDEs and HBCDs from e-waste recycling operations. Deca-BDE (BDE-209) was the dominant congener in human hair among 26 PBDE congeners quantified in this study. These profiles in human hair observed in this study were relatively similar to those in indoor dust that deca-BDE was the dominant congener, while were entirely different from those in human tissues such as breast milk and adipose tissue. This suggests that PBDEs detected in human hair may be attributed to indoor dust. Thus biomonitoring using human hair is important to understand the status of contamination and to assess the exposure of human to those chemicals through indoor dust.

Keywords: brominated flame retardants (BFRs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), human hair, Vietnam, e-waste

INTRODUCTION

Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) have been widely used in electronic and electrical products such as computers, printers and television sets. These chemicals are lipophilic and persistent in the environment and accumulate in biota including human. Recent studies showed that these chemicals are capable

of disrupting the endocrine system and could affect neurodevelopment (Hallgren and Darnerud, 2002; He *et al.*, 2009). Obsolete electrical and electronic products (e-waste) containing BFRs are becoming a major environmental concern in recent years, particularly in Asian developing countries such as China, India, and Vietnam. The recycling techniques of e-waste are often crude in these countries, and it is of concern that toxic chemicals are released into the environment during the recycling processes.

Human scalp hair has been used as a bioindicator of exposure to metals and some persistent organic pollutants (POPs) such as organochlorine pesticides (Covaci *et al.*, 2002; Zhang *et al.*, 2007), PCBs and dioxins (Nakao *et al.*, 2002) because it is easily accessible and non-invasive to sample.

In consideration of these contexts, the present study was carried out to determine the levels of PBDEs, PCBs and HBCDs in human scalp hair from Vietnam. In addition, regional variation and exposure pathway for BFRs in hair were also investigated to reveal the pollution sources and human exposure to these contaminants.

MATERIALS AND METHODS

Sample collection

Human scalp hair samples ($n = 70$) were collected from Dong Mai, Bui Dau, and Hanoi in Vietnam in 2007–2008 (Fig. 1). We collected hair samples from e-waste recyclers ($n = 14$) and non-recyclers ($n = 14$) from Bui Dau, an e-waste recycling site. Samples were also collected from Dong Mai ($n = 28$), a battery recycling site, and Hanoi ($n = 14$), as an urban control site.

Chemical analysis

Analysis of PBDEs, HBCDs and PCBs was performed according to the method described elsewhere (Malarvannan *et al.*, 2010; Eguchi *et al.*, 2011). Human hair samples were rinsed by shampoo (0.3% polyoxyethylene lauryl ether), distilled water and Milli-Q water. After drying, hair samples were cut into pieces of ~2 mm. Hair samples was spiked with internal standards of PBDEs ($^{13}C_{12}$-labeled BDE-3, -15, -28, -47, -99, -100, 153, -154, -183, -197, -207 and -209), HBCDs ($^{13}C_{12}$-labeled α-, β- and γ-HBCD) and PCBs ($^{13}C_{12}$-labeled CB-28, -52, -95 -101, -105, -118, -138, -153, -156, -157, -167, -170, -178, -180, -189, -194, -202, -206, -208 and -209) as surrogates, and incubated overnight at 40°C with 20 mL of hydrochloric acid (4 M) and 20 mL of hexane/dichloromethane (4:1, v/v). Extraction of analytes from the incubation medium was done by a liquid–liquid extraction (LLE) procedure with 2×4 mL of hexane/dichloromethane (4:1, v/v). The extract was then subjected to gel permeation chromatography (GPC) column for lipid removal and eluted with mixture of 50% hexane/dichloromethane (1:1). The GPC fraction containing the target compounds was concentrated and passed through a column packed with 4 g of activated silica gel (Wakogel® DX, Wako Pure Chemicals, Japan) for further cleanup and

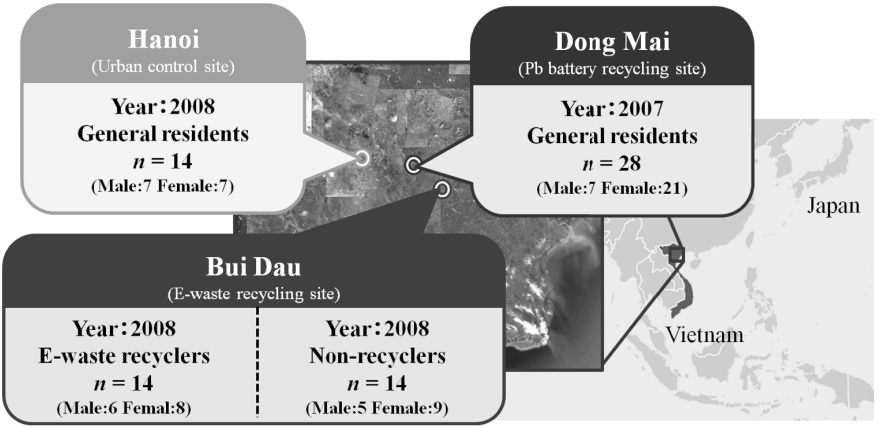

Fig. 1. Sampling locations of human hair.

fractionation. The fraction containing PBDEs and PCBs was eluted by 80 mL of 5% dichloromethane in hexane (v/v), while the fraction containing HBCDs was eluted by 100 mL of 25% dichloromethane in hexane (v/v). The PBDE and PCB fraction was concentrated to 0.5 mL. $^{13}C_{12}$-BDE-139, -126 and -205 was added to the PBDE and PCB fraction as syringe spike and concentrated prior to GC-MS analysis. 42 congeners of PBDEs and 62 congeners of PCBs were quantified in this study.

The HBCD fraction was evaporated, transferred into methanol and spiked with 10 ng of d_{18}-labeled α-, β- and γ-HBCD as syringe spike prior to the liquid chromatography combined with tandem mass spectrometry (LC-MS/MS) analysis. The concentration of PBDEs, HBCDs and PCBs were expressed in ng/g hair basis unless otherwise specified. Detection limits (DLs) were <0.20 ng/g hair for deca-BDE (BDE-209), <0.10 ng/g hair for octa-BDE (BDE-194, -196, -197, -201, -203, -204 and -205) and nona-BDE (BDE-206, -207 and -208) and <0.05 ng/g hair for other PBDEs and every HBCD isomers. DL for each PCB congeners was <0.01 ng/g hair.

RESULTS AND DISCUSSION

Concentrations of BFRs and PCBs in human hair from Vietnam

PBDEs and PCBs were detected in most of the hair samples, whereas HBCDs were detected in only 15 hair samples (Fig. 2). These results suggest that Vietnamese population is widely exposed to PBDEs and PCBs. Levels of PBDEs, HBCDs and PCBs in human hair showed no difference between genders. This result was consistent with the previous report (Schramm, 2008) on PBDEs in human hair. Levels of PBDEs in human hair were significantly higher than those of PCBs and HBCDs in all the locations ($p < 0.001$).

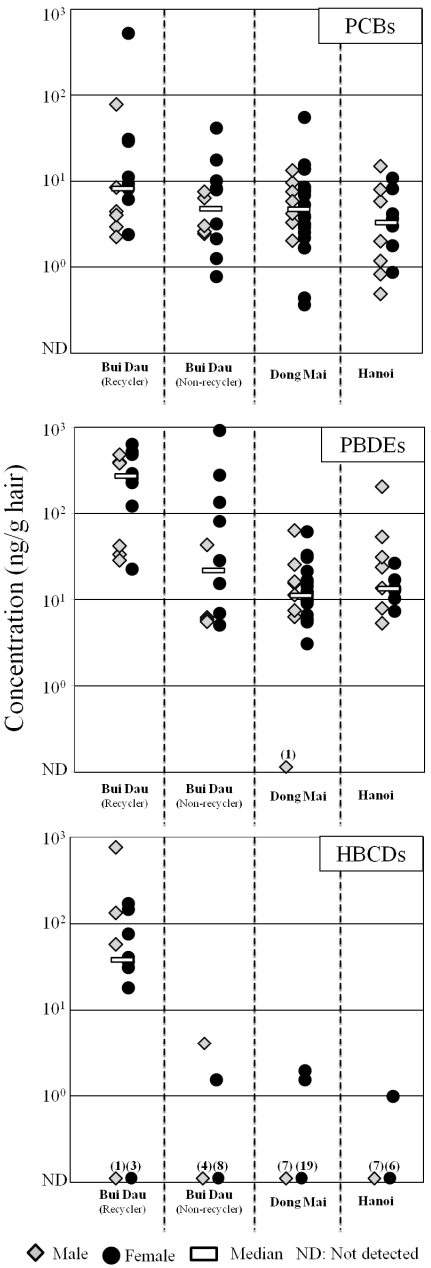

Fig. 2. Concentrations of PCBs, PBDEs and HBCDs in human hair from Bui Dau (e-waste recycling workers), Bui Dau (general residents), Dong Mai and Hanoi, Vietnam.

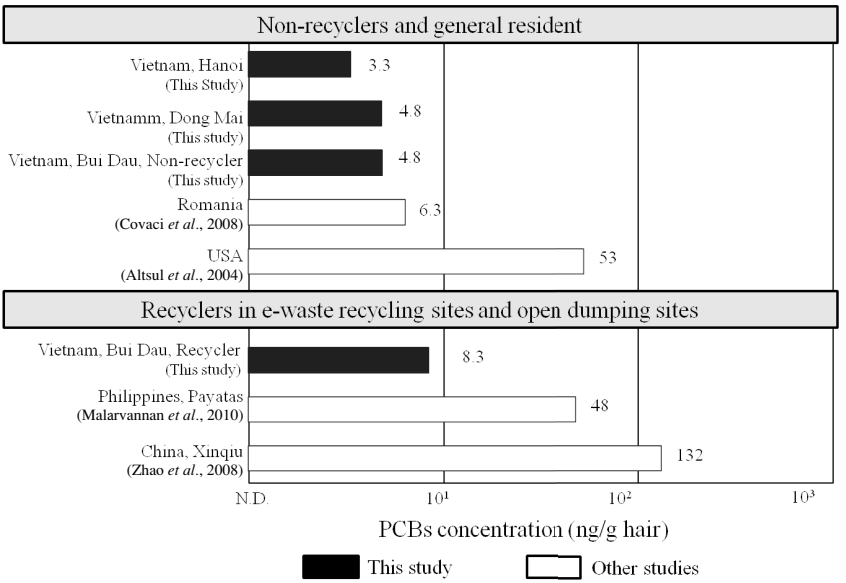

Fig. 3. Comparison of PCBs concentrations in human hair with other countries: The values are means in each group.

Levels of PBDEs (median: 276 ng/g hair) and HBCDs (median: 3.9 ng/g hair) in e-waste recycling workers from Bui Dau were significantly higher than those in the other groups, while levels of PCBs in hair samples were not significantly different among all groups (median: 3.3–8.3 ng/g hair). These results reflect the contamination caused by the e-waste recycling activities in Bui Dau. Furthermore, levels of PBDEs in some hair samples of general residents from Bui Dau were comparable to those of e-waste recyclers. These findings imply that residents in Bui Dau are highly exposed to PBDEs, which might have been derived from e-waste recycling oprerations.

Geographical comparison of PCBs and PBDEs

Concentrations of PCBs and PBDEs in human hair were compared with other studies. Generally, levels of PCBs in this study (4.8–8.3 ng/g hair) were lower than those of the general population and recyclers from other countries (6.3–53 ng/g hair) (Altshul *et al*., 2004; Covaci *et al*., 2008; Zhao *et al*., 2008; Malarvannan *et al*., 2010) (Fig. 3). Concentrations of PBDEs in general population from Vietnam (11–22 ng/g hair) were relatively higher than those in Spanish residents (7.9 ng/g hair) (Tadeo *et al*., 2009) (Fig. 4). In addition, concentrations in e-waste recycling workers from Bui Dau were higher than those in residents in recycling site from China (22 ng/g hair) (Zhao *et al*., 2008) and Philippines (73 ng/g hair)

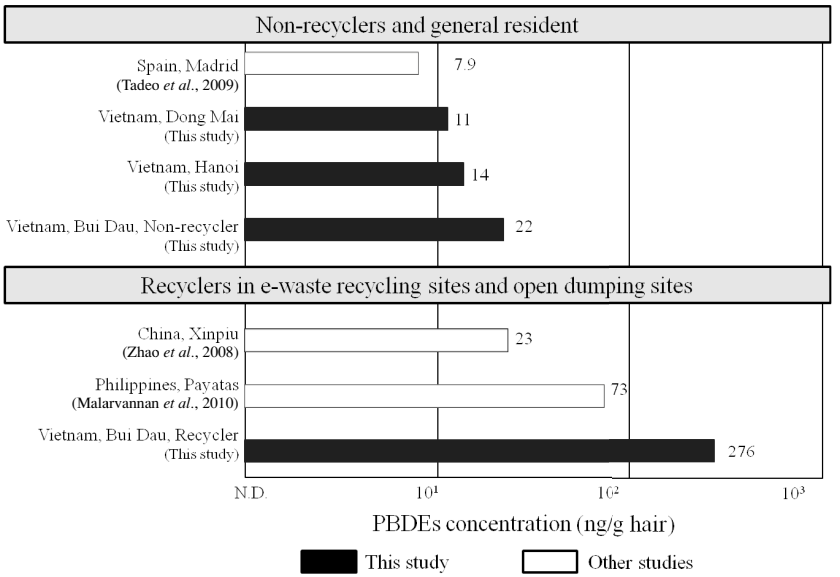

Fig. 4. Comparison of PBDEs concentrations in human hair with other countries: The values are means in each group.

(Malarvannan *et al.*, 2010). Contamination by PBDEs in Bui Dau (23–639 ng/g hair) was the highest among the monitoring surveys using human hair. Although the exposure source of PCBs was reported mainly diet (Covaci *et al.*, 2002), PBDEs in human hair may be originated from e-waste recycling activities. Therefore, effect of BFRs contamination on the health of the e-waste recyclers and other residents in Bui Dau should be further investigated.

PBDE congener profiles in various samples

Congener profiles of PBDEs in this study were significantly different from those in previous reports which analyzed internal tissues such as breast milk, adipose, and serum (Fig. 5) (Sjodin *et al.*, 1999; Kunisue *et al.*, 2007; Tue *et al.*, 2010). This may be due to the difference in exposure routes of PBDEs. The sources of PBDEs contamination for internal tissues are thought to be diet including fish, meat and dairy products, whereas those for hair, an external tissue, could be adsorption of indoor dust and aerosol. Since PBDEs profiles in hair (this study) were similar to indoor dust (Tue *et al.*, 2009), human hair could be used as a screening media for human exposure to PBDEs through indoor dust or aerosol. Further studies are needed to evaluate human health risk of BFRs and to initiate epidemiological researches in Vietnam.

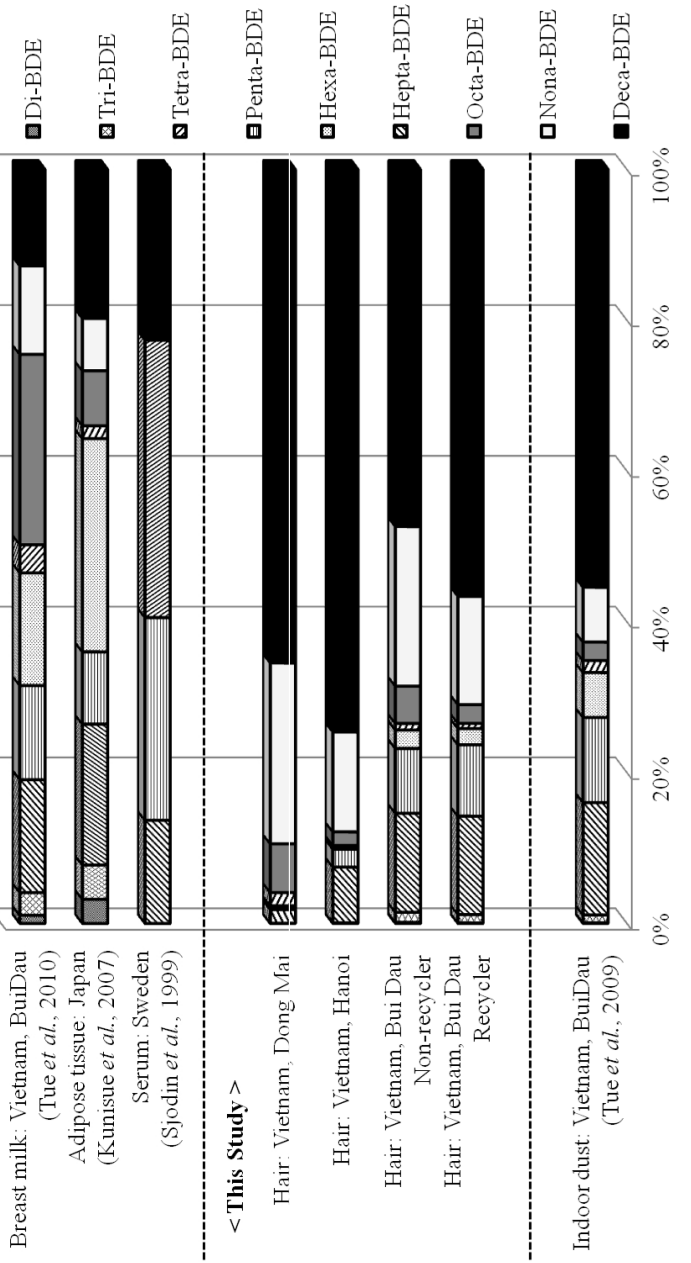

Fig. 5. Averaged congener profiles of PBDE in human hair, breast milk, adipose tissue, serum and indoor dust.

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