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Characterization of Brominated Flame Retardants in House Dust and Their Role as Non-Dietary Source for Human in Indonesia

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Abstract—The present study determined the levels of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) and compared them with the levels of polychlorinated biphenyls (PCBs) in house dust and other environmental media from Indonesia, aiming at characterization of these compounds in house dust and the role of house dust as a human non-dietary exposure. PBDEs and HBCDs were detected in all the samples of indoor dust, indicating their ubiquitous contamination with varying concentrations depending on the indoor environment characteristics; work places > homes, living room > others, and rooms with computers > rooms without computers. Concentrations of PBDEs in house dust (range: 20–1500 ng/g dust, mean 200 ng/g dust and median 120 ng/g dust) were higher than HBCDs (range: 1.5–75 ng/g dust, mean 24 ng/g dust and median 12 ng/g dust), which is concomitant with the difference in the historical usage of these two BFRs. PCBs levels were the lowest (ranged 1.5–78 ng/g dust, mean 14 ng/g dust, median 10 ng/g dust). Levels of PBDEs and HBCDs in house dust from Indonesia were among the lowest when compared globally. BDE-209 was almost the only congener present in the dust of this study, implying the predominant use of deca-BDE formulation in household products, similar to other Asian and European countries reported by several literatures, but different with those in North America where Penta-BDE mixtures constitute larger proportion. Estimation of total daily intake of BFRs indicate that, unlike PCBs, dust ingestion contributes significantly to human exposure to PBDEs and HBCDs.

Keywords: PBDEs, HBCDs, PCBs, house dust, exposure source pathway, daily intake

INTRODUCTION

Brominated flame retardants (BFRs) have become compounds of interest due to their similarities in chemical structures, properties and toxic potencies to some

persistent organochlorines (OCs), such as polychlorinated biphenyls (PCBs) and dioxins which are well-known endocrine disrupters. Among BFRs, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), have been widely detected in the environment and animal tissues/organs and their concentrations seem to be increasing (Sjodin *et al.*, 2003) and thus these compounds are of concern for their possible effects on human health. Although the primary route of human exposure is still unclear, humans are most probably exposed to BFRs via food intake, as is the case for OCs. However, due to usage of BFRs in household consumer products, direct exposure via inhalation and ingestion of particulate-bound BFRs in indoor environments may also contribute to human exposure (Sjodin *et al.*, 2003). In this regard, house dust is often used as a marker of indoor exposure due to its importance as a sink and repository for semivolatile organic compounds and particle-bound matter. Recently, the role of dust as potential human non-dietary exposure source to BFRs has been an attractive area of study due to their frequent presence at high levels in house dust (Stapleton *et al.*, 2005; Suzuki *et al.*, 2006; Wu *et al.*, 2007; Bets, 2008). The present study determined concentrations of PBDEs and HBCDs; the two most commonly use BFRs, in comparison with PCBs in house dust and other environmental media from Indonesia, aiming at characterization of BFRs in house dust and understanding the role of house dust as a human non-dietary exposure source by comparing their intake values through various exposure pathways for adults and toddlers.

MATERIALS AND METHODS

Twenty five house dusts were randomly collected from home in Bogor during August 2007–June 2008. House dusts ($n = 25$) were collected from several rooms including living room ($n = 10$), bedroom ($n = 6$), pooled samples from several rooms ($n = 5$) and others ($n = 4$; kitchen, study room and store room). In addition, dusts were also collected from work places ($n = 4$) such as bank office ($n = 1$), electronic repair shop ($n = 2$) and rental play station ($n = 1$) for comparison. Samples were kept in pre-cleaned containers, transported to Japan and stored at environmental specimen bank for global monitoring (*es*-BANK) of Ehime University, Japan at –20°C until chemical analysis.

Analyses of BFRs and PCBs were carried out according to the method described elsewhere (Minh *et al.*, 2007), with slight modifications. Fourteen PBDE congeners (BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-206, BDE-207, BDE-209), HBCDs (α-, β- and γ-HBCD) and 62 PCB isomers were analyzed in representative samples. Briefly, the samples were spiked with internal standards ($^{13}C_{12}$-labeled BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-153, BDE-154, BDE-183, BDE-209, PCBs and, extracted by liquid-liquid extraction and then subjected to gel permeation chromatography (GPC). The GPC extract was further purified and fractioned by silica chromatography. $^{13}C_{12}$-labeled BDE-139 and deuterized HBCD (HBCD-d_{18}: α-, β- and γ-HBCD-d_{18}) were added as an internal standard

to the final solution prior to analysis. Quantifications of PBDEs and PCBs were carried out with gas chromatography with a mass spectrometry detector (GC-MS) in the negative chemical ionization mode, and with liquid chromatography with tandem mass spectrometry detector (LC-MS-MS) using electrospray ionization for the isomeric composition of HBCDs.

For estimation of daily intake of contaminants through dust ingestion by adults and toddlers, we used the exposure factors following the US-EPA approach (Lorber, 2008). Furthermore, available data of BFRs and PCBs in various environmental/exposure media and their intake estimation were also used in this study (Wurl *et al*., 2006; Sudaryanto *et al*., 2008).

Statistical analysis was performed using Mann-Whitney *U*-test to compare concentrations of PBDEs between groups. Spearman rank correlation was used to examine the strength of associations between parameters. All statistical analyses were performed using SPSS program version 12.0.1 for Windows. A probability value $p < 0.05$ was considered as statistically significant.

RESULTS AND DISCUSSION

Characterization of BFRs in indoor dust

PBDEs and HBCDs were detected in indoor dust, indicating ubiquitous contamination by BFRs with concentrations varying depending on the indoor environment characteristics; work places >> homes, living room > others, and computer available room > computer not available room (Fig. 1). Concentration of PBDEs in dust from work places is higher than those of home for all the markers of commercial formulation. Our study is different with a study in UK where office dust was less contaminated with PBDEs than in house dust, particularly for Penta-BDE (Harrad *et al*., 2008), but is in the line with a study in Japan where office dust was more contaminated with PBDEs than household dust (Suzuki *et al*., 2006). With regard to house dust, residue levels of PBDEs (ranged 20–1500 ng/g dust, mean 200 ng/g dust and median 120 ng/g dust) were higher than those of HBCDs (ranged 1.5–75 ng/g dust, mean 24 ng/g dust and median 12

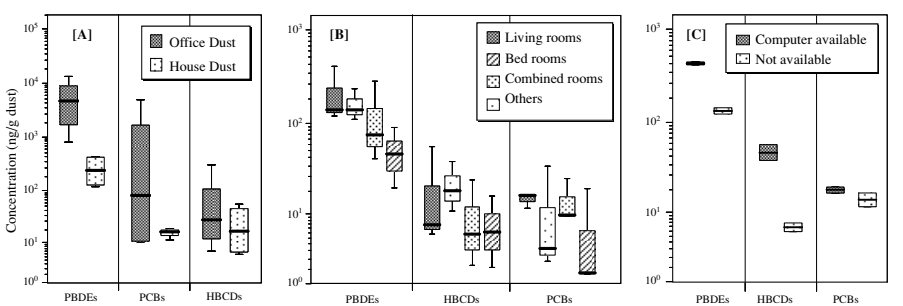

Fig. 1. Concentration of PBDEs, HBCDs and PCBs in indoor dust from Indonesia (ng/g dust).

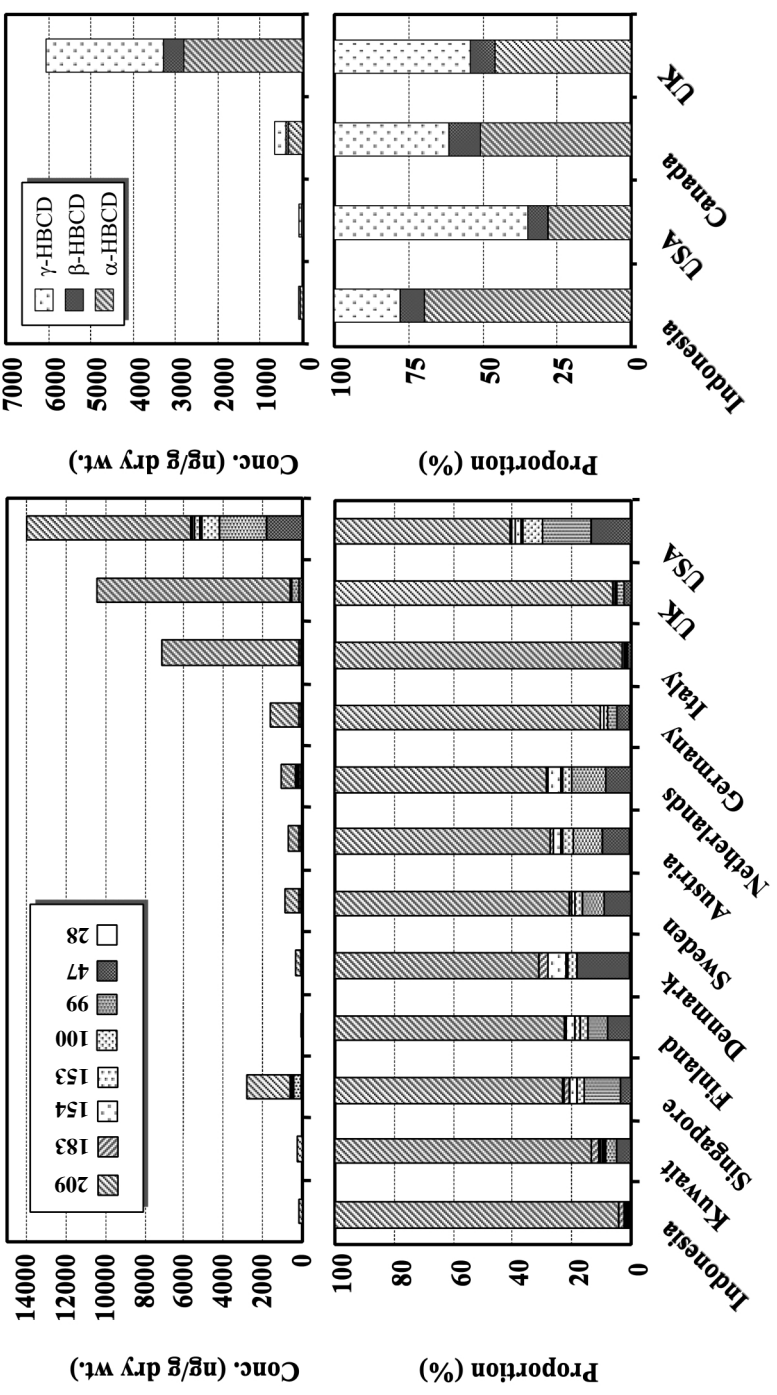

Fig. 2. Levels and BFR profiles in house dust in comparison with other countries worldwide.

Table 1. Spearman's rank correlations among PBDE congeners.

	BDE-15	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-196	BDE-197	BDE-206	BDE-207	BDE-209
BDE-15	1	0.74**	0.36	0.40*	0.44*	0.64**	0.61**	0.48**	0.37*	0.39*	0.40*	0.40*	0.35
BDE-28		1	0.68**	0.69**	0.64**	0.66**	0.61**	0.60**	0.59**	0.54**	0.58**	0.56**	0.54**
BDE-47			1	0.90**	0.72**	0.55**	0.47**	0.59**	0.59**	0.56**	0.44*	0.44*	0.40*
BDE-99				1	0.78**	0.66**	0.60**	0.73**	0.60**	0.64**	0.51**	0.51**	0.46*
BDE-100					1	0.75**	0.72**	0.61**	0.49**	0.56**	0.43*	0.38*	0.45*
BDE-153						1	0.93**	0.88**	0.64**	0.80**	0.64**	0.64**	0.66**
BDE-154							1	0.80**	0.52**	0.71**	0.50**	0.53**	0.52**
BDE-183								1	0.69**	0.90**	0.64**	0.68**	0.63**
BDE-196									1	0.90**	0.90**	0.93**	0.84**
BDE-197										1	0.82**	0.86**	0.80**
BDE-206											1	0.96**	0.93**
BDE-207												1	0.90**

Values indicate coefficient correlation, *$p < 0.05$, **$p < 0.01$.

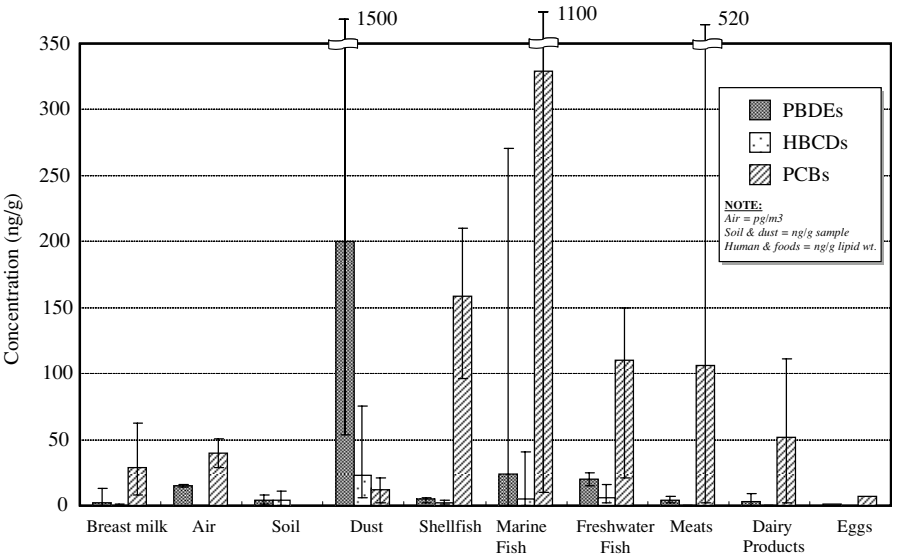

Fig. 3. Levels of BFRs and PCBs in various environmental media and human breast milk (data were cited from Wurl *et al*., 2006; Sudaryanto *et al*., 2008).

ng/g dust), which may result from the different historical usage between these two BFRs. Whereas, PCBs levels were the lowest (ranged 1.5–78 ng/g dust, mean 14 ng/g dust, median 10 ng/g dust). Among the house microenvironment, PBDEs levels were significantly higher in living room area and were lowest in bedroom than others (Fig. 1B). Allen *et al*. study also found significantly higher concentrations of PBDEs in living room compared to those in dust from bedroom (Allen *et al*., 2008). These results suggest that room characteristics play important role in the distribution of PBDEs in household dust. Higher concentration of BFRs in dust from living room area than others may be associated with their usage in household products (electric and electronic appliances, polymer materials and others) in this specific area. In fact, living room with computer available has higher concentration of BFRs in their dust as compared to living rooms with not available computer (Fig. 1C).

Figure 2 shows worldwide comparison of BFRs levels and its composition in house dust. Levels of PBDEs and HBCDs in house dust from Indonesia were among the lowest when compared globally (Santillo and Johnston, 2003; Sharp and Lunder, 2004; Stapleton *et al*., 2005; Gevao *et al*., 2006; Tan *et al*., 2007; Harrad *et al*., 2008). BDE-209 was almost the only congener present in the dust of this study (Fig. 2), implying the predominant use of deca-BDE formulation in household products of the surveyed houses, similar to reports in other Asian and European countries (Santillo and Johnston, 2003; Gevao *et al*., 2006; Tan *et al*., 2007; Harrad *et al*., 2008), but different with reports in North America where

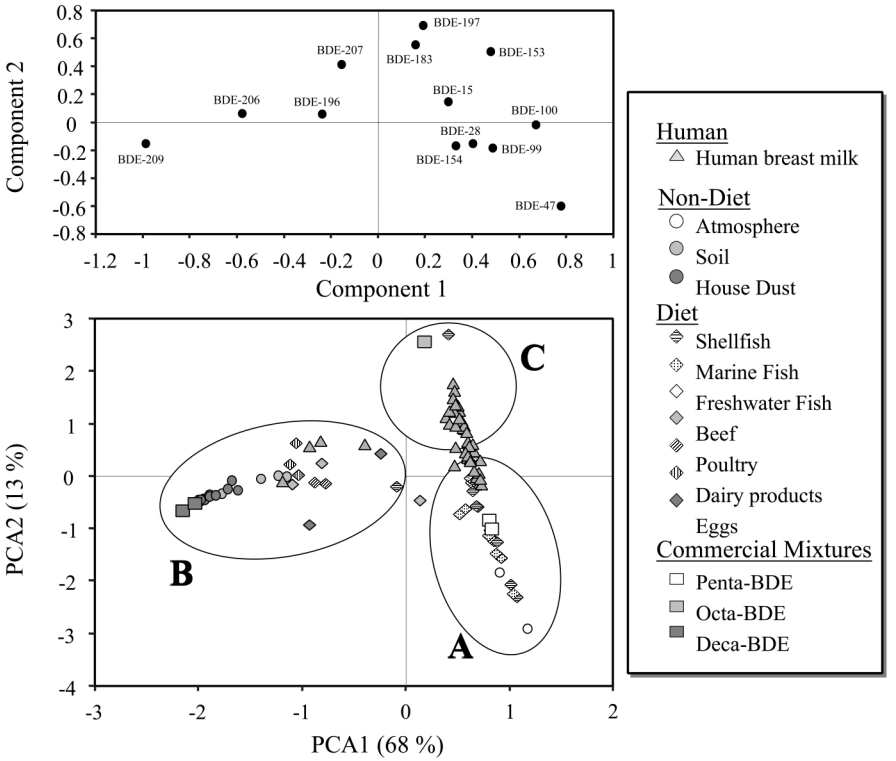

Fig. 4. PCA analysis of PBDE congener profiles in humans, environmental media, food products and commercial formulations.

Penta-BDE mixtures constitute larger proportion (Sharp and Lunder, 2004; Stapleton *et al*., 2005). On the other hand, the large proportion of α-HBCD could be due to thermal isomerization during technical production.

Association among contaminants shows significant positive correlation between concentrations of PBDEs and HBCDs only ($r = 0.77$, $p < 0.05$), which indicates similar sources of these two BFRs in home environment (household products), but not for PCBs (industrial purposes). Furthermore, there were significant positive correlations among PBDE congeners (Table 1), which may also suggest the formation of lower brominated congeners from higher brominated congeners in indoor environment, probably due to photolytic debromination. It has been shown in experimental study that the photolytic debrominated products of BDE-209 in house dust includes a range of lower congeners such as BDE-206, -207, -208, -196, -197, -201, -202/-203 (Stapleton and Dodder, 2008).

Significance of house dust as a source of human non-dietary exposure to BFRs

Beside house dust, BFRs and PCBs were also detected in human breast milk

Table 2. Average total daily intake (ng/day) and contribution by each exposure pathway.

Pathways	PBDEs	HBCDs	PCBs
Adult			
Soil/dust ingestion	8.3	1.1	0.6
Soil/dust dermal contact	0.49	0.066	0.003
Inhalation	0.2	na	0.53
Shellfish	0.34	0.16	na
Marine fish	19	2.1	410
Freshwater fish	20	6.2	110
Beef	0.58	0.0077	16
Poultry	2.2	0.059	1.5
Dairy products	0.35	0.01	7.1
Eggs	0.66	0.086	5.2
Total	52	9.8	550
Toddlers			
Soil/dust ingestion	19	2.3	1.1
Soil/dust dermal contact	0.09	0.012	0.003
Inhalation	0.11	na	0.3
Lactation	28	4.1	370
Total	47	6.4	370

and various other environmental exposure media from Indonesia (Fig. 3), suggesting wide environmental contamination and human exposure to these compounds in Indonesia. PCBs, which have longer history and larger amount of usage than BFRs, were found at higher concentrations than PBDEs and HBCDs in all the samples, except for house dust. Higher concentrations of BFRs than PCBs in house dust indicate that home environment can be one of the important human exposure sources to PBDEs and HBCDs. Similar to house dusts, other environmental exposure media also contained higher levels of PBDEs than HBCDs.

Principle component analysis (PCA) done to assess similarities of PBDE congener patterns in humans with those in diet, non-dietary sources and available commercial formulations (Fig. 4) indicate that food is a source of human exposure to these compounds (cluster A). However, the similarities of PBDE congener profiles in some donors with house dust profiles (cluster B) imply that non-dietary exposure pathways may also be an important route of exposure. Profiles of human samples in cluster C, which were characterized by higher brominated congeners (BDE-197, -183, -153) and did not resemble the profiles in the environmental media, indicate exposure to deca-BDE (main congener in house dust) that has been environmentally/biologically degraded (such as debromination) resulting in the observed profile.

Table 2 shows the estimated intakes of PBDEs, HBCDs and PCBs by adults and toddlers, considering various exposure pathways. For the general population, the intake via dust ingestion was estimated based on concentrations of those

contaminants in house dust only and excluded the dust from work places. The total intake of BFRs was lower than that of PCBs and agreed well with the body burdens estimated from breast milk concentrations (Fig. 3). Compared to PCBs (<0.20%), the contribution of non-dietary intake of BFRs by adults was much larger (17% for PBDEs and 12% for HBCDs). For toddlers, the contribution of dust ingestion to total intake of BFRs was much greater than for adults (41% for PBDEs and 36% for HBCDs). These results suggest that unlike PCBs, dust ingestion contributes significantly to total intake of BFRs.

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