BROMINATED FLAME RETARDANTS IN HOUSE DUST FROM THE PHILIPPINES: LEVELS, PROFILES AND FATE

Malarvannan Govindan[1], Isobe Tomohiko[1], Sudaryanto Agus[1], Takahashi Shin[1], Prudente Maricar[2] and Tanabe Shinsuke[1]

[1]Center for Marine Environmental Studies, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan
[2]Science Education Department, De La Salle University, Manila, Philippines

Abstract

House dust samples (*n*=20) from Payatas a waste dump site, and Malate a reference site in the Philippines were collected in 2008 and analyzed for two brominated flame retardants (BFRs), viz., polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs). Concentrations of PBDEs found in house dust (mean: 665 ng/g dust) were significantly higher than HBCDs (mean: 22 ng/g dust), which is concomitant with the difference in the historical usage of these two BFRs. Overall mean concentrations of PBDEs found in our study were higher than those in Indonesia, Finland, Kuwait and Denmark, but several orders of magnitude lower than those in Canada, US and UK. On an average the major congeners detected in house dust samples were BDE -209 followed by -99, -47, and -183. Among HBCDs, α- and γ- HBCD were the predominant isomers in both locations. The extent of contamination varied between homes because of the different set of circumstances in every microenvironment. House dust may be regarded as the most important exposure route of PBDEs and HBCDs for children. This study was the first of its kind to be conducted in the Philippines to measure concentrations of BFRs in house dust.

Introduction

We are all surrounded by chemicals in everyday life, in everything we handle, eat, drink and breathe. The quality and characteristics of the environments people are exposed to can have important implications on their well-being. Because of their environmental stability, persistence and high production volume, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are among the most abundant brominated flame retardants (BFRs) detected in the environment and in wildlife and humans[1]. Global market demand in 2001 showed that Asia consumed large quantity of the total commercial PBDEs (24,650 tons, 37%) ranking second after America (33,100 tons, 49%), whereas Europe was the lowest (8360 tons, 12%)[2]. HBCDs are used as an alternative for PBDEs in some applications[3] and consist mainly of three diastereomeric pairs of enantiomers; α-, β-, and γ- HBCD, with the γ-isomer being the major constituent (>70%). By 2001 world market demand for HBCDs was 16,700 metric tons, of which 23% were sold in Asia[2]. Thus, there is an urgent need to identify sources of exposure to PBDEs and HBCDs in Asian countries, quantify emission and document their potential environmental fate in the region.

The Philippines is one of the archipelagic countries in the Southeast Asian region, with a population of 85 million. Because of the lack of advanced facilities, large amount of municipal wastes are directly dumped at dumping sites without proper management, causing probably several adverse environmental consequences and increased human health risk to local communities. House dust acts as a sink and repository for semivolatile organic compounds. The analyses of compounds in house dust therefore can give a reliable indication of the extent of indoor contamination[4]. Non-dietary exposure to chemicals via inhalation and dust ingestion may therefore constitute an important exposure pathway for humans. Although estimates of dust ingestion vary widely, there is consensus that children, especially those who crawl, ingest more dust than adults. The present study was therefore carried out to determine concentrations of BFRs such as PBDEs and HBCDs in house dust samples in two locations in the Philippines, viz., one near a waste dumpsite, Payatas, and a reference site, Malate. This study was the first of its kind to be conducted in the Philippines to measure concentrations of BFRs in house dust. The primary objective of this study was to assess the extent of indoor exposure to chemicals from dust ingestion. Specific objectives include (i) to provide information about indoor contamination in the Philippines for BFRs and (ii) to compare the relative significance of human non-dietary exposure via dust ingestion for children and adults.

Materials and Methods

Sample collection

House dust samples (*n*=20) were collected at two different locations; Payatas a waste dump site and Malate a reference site in the Philippines during 2008 (Figure 1). Samples were collected using nylon sample socks mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie, sealed in a plastic bag and shipped to the laboratory in Japan under frozen condition and stored at −20°C in the Environmental Specimen Bank (*es*-Bank) of Ehime University[5] until analysis. We randomly selected the house. Seven samples are from the reference site at Malate city and thirteen samples are from the dumping site at Payatas. Plastic materials were avoided throughout the collection procedures. Residence characteristics including dust sample source, floor area, number of computers/televisions, furniture’s and type of flooring were documented at the time of sample collection.

Chemical analysis

Analysis of PBDEs and HBCDs was performed according to the method described elsewhere[6], with slight modifications. Briefly, 5 g of house dust sample was extracted using high speed solvent extractor (SE-100; Dia Instruments co., Ltd., Japan) with a mixture of acetone and hexane (1:1), and again eluted with toluene and combined both the mixtures. An aliquot of the extract, after spiking 5 ng of internal standards for PBDEs ($^{13}C_{12}$ – labeled BDE-3, -15, -28, -47, -99, -100, -153, - 154, -183, -197, -207 and -209) and 10 ng of internal standards for HBCDs ($^{13}C_{12}$-labeled α-, β- and γ-HBCD) as surrogates, and then treated with sulfuric acid and followed by multi layer column with various acids and concentrated and after the extract was loaded to a gel permeation chromatography (GPC) column. The GPC fraction containing BFRs were concentrated and subjected to an activated silica gel column (Wakogel DX) for further clean-up and fractionation. Identification and quantification of PBDEs was done using gas chromatography combined with mass spectrometry (GC-MS), while HBCD isomers were identified and quantified using liquid chromatography combined with tandem mass spectrometry (LC-MS-MS) in a multiple reaction monitoring (MRM) mode. Procedural blanks were analyzed simultaneously with samples to check for interference or contamination from solvents and glassware. The concentration of PBDEs and HBCDs were expressed in ng/g dust basis unless otherwise specified.

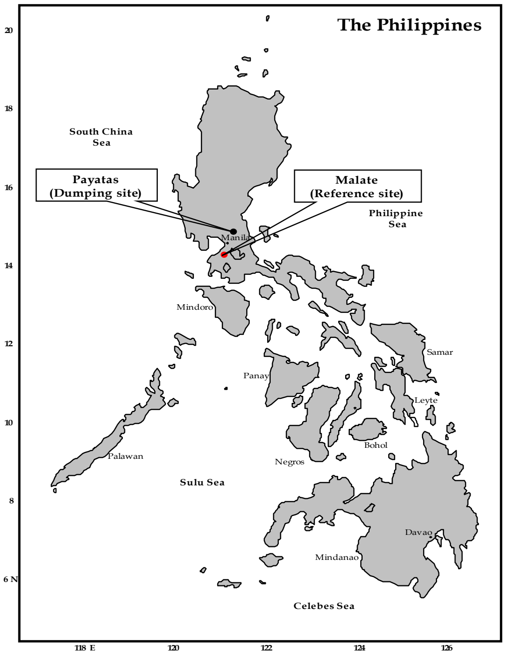

Figure 1. Map showing the sampling locations.

Statistical analysis

Statistical analyses were performed using Stat View program version 5 (SAS Inc., 1998). The Mann–Whitney *U*-test was used to compare each group, and Spearman rank correlation was used to examine the strength of associations between parameters. A probabilistic value of $p<0.05$ was considered significant.

Results and Discussion

Residue levels and contamination status of BFRs

In the present study, BFRs were detected in variable quantities in all the house dust samples collected from Payatas and Malate, suggesting that the residents living in two locations in the Philippines have been widely exposed to these contaminants. Thirteen PBDE congeners from di- to deca-BDE were identified. BDE-3 was not found above the detection limit of 0.05 ng/g dust in all the samples. The concentrations of the sum of the 13 congeners (∑PBDEs) found in house dust samples varied widely, from 6.6 to 5407 ng/g dust, with an overall mean of 665 ng/dust (Table 1). Overall mean concentrations of PBDEs found in our study were higher than those in Indonesia, Finland, Kuwait and Denmark[7, 8], but several orders of magnitude lower than those in Canada, US and UK[9, 10]. Interestingly, it seems that PBDEs may become a major environmental concern in the Philippines as they were found higher in the present study and also in human breast milk[11], when compared to other Asian countries. Elevated PBDEs concentrations in US house dust may be attributed to the widespread use of commercial penta- and deca-BDE on the North American continent, where the average consumption of penta-BDE is over four times that that of Asia[2]. Different locations of the world may be expected to have various PBDE profiles in both the environment and human tissue due to differences in use of technical mixtures of PBDEs.

In the case of HBCDs, this is the first comprehensive study on house dust from Asia. The concentrations of the sum of the 3 isomers (∑HBCDs) found in house dust samples varied widely, from 0.64 to 99 ng/g dust, with an overall mean of 22 ng/dust (Table 1). Levels of HBCDs in house dust from the Philippines were among the lowest when compared globally[12]. The observed levels of the PBDE congeners and HBCD isomers from the two different locations (Payatas and Malate) were not statistically significant and probably due to the corresponding background residue levels in the environment. In this study, we were unable to explain our concentration data on the basis of the questions posed in the questionnaire. This is, in part, due to the sample size and differences in makes, models and year of manufacture of the electronic items in the various homes. The lack of correlation may also be linked to insufficient knowledge about the use of BFRs in the items found in the homes.

Table 1. Concentrations of PBDEs and HBCDs (ng/g dust) in house dust from the Philippines.

	Dumping site (Payatas)			Reference site (Malate)			All samples		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
Number of samples	13			7			20		
Compounds									
PBDEs									
BDE-15	0.10	0.070	0.030 - 0.26	0.059	0.055	0.040 - 0.087	0.085	0.060	0.030 - 0.25
BDE-28	0.42	0.27	0.078 - 1.1	0.45	0.40	0.11 - 1.0	0.43	0.27	0.078 - 1.1
BDE-47	14	4.1	0.83 - 91	15	2.5	0.74 - 59	14	3.8	0.74 - 90
BDE-99	46	6.3	1.1 - 411	17	3.6	0.79 - 64	36	5.5	0.80 - 411
BDE-100	4.3	0.83	0.19 - 32	3.3	0.56	0.22 - 13	3.9	0.77	0.19 - 32
BDE-153	14	2.1	0.26 - 94	2.8	2.2	0.53 - 7.1	10	2.1	0.26 - 93
BDE-154	4.1	0.47	0.11 - 26	1.8	1.3	0.085 - 5.4	3.3	0.47	0.084 - 26
BDE-183	43	1.4	0.36 - 522	3.7	3.6	0.087 - 6.6	31	3.0	0.4 - 522
BDE-196	11	0.70	0.21 - 123	7.7	2.6	0.73 - 36	9.6	1.5	0.21 - 122
BDE-197	19	0.72	0.22 - 231	3.8	1.8	0.55 - 14	14	1.4	0.21 - 230
BDE-206	14	2.6	1.0 - 110	385	17	0.33 - 2601	143	10	0.32 - 2600
BDE-207	21	2.2	0.91 - 210	238	13	7.3 - 1370	89	7.4	0.91 - 1370
BDE-209	262	57	16 - 1983	423	350	4.6 - 1376	318	143	4.5 - 1983
Sum PBDEs (mono to hepta)	124	18	2.7 - 679	40	13	1.7 - 152	95	17	1.7 - 679
Sum PBDEs (mono to deca)	451	102	29 - 3336	1063	423	6.6 - 5407	665	214	6.6 - 5407
HBCDs									
α-HBCD	6.1	2.0	0.62 - 28	14	13	0.22 - 26	8.7	4.4	0.21 - 28
β-HBCD	1.4	0.63	0.13 - 5.5	3.8	4.0	0.059 - 9.2	2.2	0.93	0.05 - 9.1
γ-HBCD	5.1	2.6	0.26 - 28	22	17	0.36 - 66	11	3.4	0.26 - 66
Sum HBCDs	13	6.5	1.3 - 44	39	43	0.64 - 99	22	7.8	0.64 - 99

Congener profiles of BFRs

Among the PBDE homologues analyzed, BDE -209, -99, -47, and -183 (Table 1) had the highest abundance at both the sites. This profile is to be expected as less volatile BDE-209 is more firmly bound to particles, while others are likely to remain in gas phase. Deca-BDE mixture is the most widely used commercial mixture, and comprises 97% BDE-209[13]. This mixture is mainly used in plastic casings for computers and electronic equipments. Studies on PBDEs in house dust are limited, but increasing worldwide. The dust data, dominated by BDE-209, suggests that deca is a dominant technical formulation present in the homes investigated. The reason for extremely high values in this study is most likely due to dust samples being collected via carpet & soft surfaces, and Deca-BDE is widely used as an additive to carpet textiles. However, if we discard BDE-209 and express the congener contribution as the percentage the remaining congeners (-47, -99, -100, -153, -154, and -183) it becomes apparent that the penta-formulation is also ubiquitous in the homes investigated. The penta-formulation is primarily used to flame retard polyurethane foam used in household furniture. Differences in concentrations between countries may suggest differences in use patterns of flame retardants and fire regulations; whereas differences between homes in the same country could be related to differences in sources in the domestic environment. These differences between countries are also reflected in reported concentration of PBDEs in humans in different regions of the world[14].

There are only a few reports regarding stereoisomer-specific concentrations of HBCDs in house dust in the world. In this study, the stable isomer, α- and γ- HBCD was predominant in both locations (Table 1). The relative abundance of β-HBCD was similar in both locations. The observed levels of the isomers from the two different locations were not statistically significant, may be due to the corresponding background residue levels in the environment. In contrast, the even greater relative abundance of α-HBCD in dust from the same microenvironments is difficult to explain, but is consistent with the existence of processes that induce a post depositional shift from γ-HBCD to α-HBCD in this matrix. It might also be a result of direct leaching from HBCD-treated products within the sampled microenvironments (where the above-mentioned γ- to α-HBCD transformation has occurred during treatment)[12]. The faster degradation rate of γ-HBCD compared to α-HBCD reported previously by Davis et al.[15] may also contribute to the observed HBCDs profiles in dust. Further work is required to confirm this finding and to elucidate its cause, although these data suggest that usage patterns for HBCDs in reference and dumping sites are not significantly different.

Implication for non-dietary exposure

Humans are exposed to pollutants via inhalation, dermal uptake, and diet and non-diet ingestion. Non-dietary exposure occurs principally via inhalation and ingestion of dust. The second scenario is particularly relevant for children. Using dust ingestion estimates of 100 mg/day for children and 50 mg/day for adults[16]. The total intake of PBDEs by children (66%) was higher than adults (33%), but the trend was reverse in the case of HBCDs. In most of the studies, in intake estimation of the total PBDEs was based on few target congeners from terra – hexa BDEs, but to some extent up to octa and deca BDE. However, due to lack of detailed information on PBDEs and HBCDs in foodstuffs of the Philippines and dermal absorption parameters which may also influence body intake, the actual daily intake cannot be accurately determined. Although the total daily intake of BFRs by toddlers was comparable to adults, the contribution from dust ingestion to the total intake was much greater than that for adults. This study provides a snapshot of chemical contamination in homes in the Philippines and suggests that exposure to dust is a significant route of human non-dietary exposure to chemicals. The ubiquitous distribution of these chemicals as noted in this study highlights the fact that we are continuously exposed to low doses of chemicals in the indoor environment.

Acknowledgments

This study was supported by the Global Environmental Research Fund (RF-064) and the Waste Management Research Grant (K1821 and K1953) from the Ministry of the Environment and by Grants-in-Aid for Scientific Research (S) (No. 20221003) and (B) (No. 18310046), Young Scientists (B) (project 19780239) and "Global COE Program" from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT) and Japan Society for the Promotion of Science (JSPS).

References

1. Alaee M., Arias P. and Sjodin A., Bergman A. *Environ. Int* 2003; 29: 683–689.
2. BSEF 2008. Available from: http://www.bsef.com/.
3. Sellstrom U., Kierkegaard A., de Wit C. and Jansson B. *Environ. Toxicol. Chem* 1998; 17: 1065–1072.
4. Roinestad K.S., Louis J.B. and Rosen J.D. *J. AOAC Int* 1993; 76: 1121–1126.
5. Tanabe S. *J. Environ. Monit* 2006; 8: 782–790.
6. Miyake Y., Kato M. and Urano K. *J. Chromatogr. A* 2007; 1139: 63-69.
7. Sudaryanto A., Eguchi A., Isobe T., Eka I. S., Slamet R.A., Ilyas M., Budi W. I., Takahashi S. and Tanabe S. *Organohalogen Comp* 2008;70: 2236- 2239.
8. Gevao B., Al-Bahloul M., Al-Ghadban A. N., Al-Omair A., Ali L., Zafar J. and Helaleh M. *Chemosphere* 2006; 64: 603-608
9. Harrad S., Ibarra C., Diamond M., Melymuk L., Robson M., Douwes J., Roosens L., Dirtu A. C and Covaci A. *Environ. Int* 2008; 34: 232–238.
10. Stapleton H.M., Dodder N.G., Offenberg J.H., Schantz M. and Wise S.A. *Environ. Sci. Technol* 2005; 39: 925–931.
11. Malarvannan G., Kunisue T., Isobe T., Sudaryanto A., Takahashi S., Prudente M., Subramanian A. and Tanabe S. *Environ Pollut* 2009; 157: 1924-1932.
12. Abdallah M. A. and Harrad S. *Environ. Int* 2009; In press.
13. Schecter A., Papke O., Joseph J. E. and Tung K. C. *J. Toxicol. Environ. Health* 2005; 68: 501–513.
14. Betts K.S. *Environ. Sci.Technol* 2003; 37:164–165.
15. Davis J., Gonsior S., Markham D., Friederich U., Hunziker R. and Ariano J. *Environ. Sci. Technol* 2006; 40: 5395–5401.
16. Butte W. and Heinzow B. *Rev. Environ. Contam. Toxicol* 2002; 175: 1–46.