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Contamination Status of Polychlorinated Biphenyls and Brominated Flame Retardants in Environmental and Biota Samples from India

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Abstract—The present study aimed to estimate the current contamination status of organohalogen compounds (OHCs), including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in human milk ($n = 55$), fish ($n = 100$) and dust samples ($n = 35$) collected from different locations in India as limited information is available. High levels of PCBs were found in human milk from the municipal waste dumping site in India suggesting greater risk for infants living near these sites. Different congener and isomer profiles among contaminants between dumping site and general populations indicate the presence of region-specific sources and pathways. Relatively high levels of PCBs and PBDEs were present in farm-raised fish than wild fish, but the dietary intake values were far lower than the guideline values indicating less risk through fish consumption. Significantly higher levels of OHCs were found in dust samples from e-waste recycling locations, suggesting that the crude e-waste recycling/dismantling activities are the major emission sources of these contaminants. The hazard quotients (HQs) values of PCBs were above one for the infants and toddlers living near the municipal dumping and e-waste recycling areas indicating high risk, which warrants regular monitoring and regulations to reduce the pollution levels.

Keywords: polychlorinated biphenyls, polybrominated diphenyl ethers, hexabromocyclododecanes, India

INTRODUCTION

Organohalogen compounds (OHCs), including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) have been widely used for various purposes due to their broad range of applications. PCBs were extensively used as dielectric and coolant fluids in transformers and capacitors, lubricants, placticizers, paints, etc. PBDEs and HBCDs are a class of additive brominated flame retardants (BFRs), which have been widely used in electronics, plastics, furniture and textiles to inhibit or slow down the extend of fire. OHCs have been found in all kinds of environmental and biotic samples because of their persistent and bioaccumulative properties (Hites, 2004; Shaw and Kannan, 2009). Humans are exposed to PCBs mainly through the consumption of contaminated food, particularly from fish consumption. However, both the dietary and non-dietary (ingestion of dust) routes are the major exposure pathways for BFRs. Exposure to these compounds is recognized as an important environmental risk factor for humans and animals because of the following effects: cancer; nervous system damages; reproductive and immune system impairments; and hormonal imbalance (Darnerud *et al.*, 2001; Safe, 2004). As a result, many industrialized countries imposed regulations and bans on the production, use and discharge of these compounds but developing countries including India are yet to initiate such actions due to the availability of limited baseline data. In recent years, the rapid increase in economy, industrialization and population have led to the degradation of the quality of the environment and human health in India. Previous studies reported elevated levels of classical persistent organic pollutants (POPs) in various environmental and biotic samples from India (Kumari *et al.*, 2008; Devanathan *et al.*, 2009; Someya *et al.*, 2010). In recent years, scientists also focusing on the emerging contaminants including 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenylethane (DBDPE) in developed countries for evaluation of their potential threat to environmental and biota health (Nakari and Huhtala, 2010). Therefore, the present study was carried out to understand the current contamination status of organohalogens in human breast milk, fish and dust samples collected from several locations in India with special focus on municipal dumping and e-waste recycling sites.

MATERIALS AND METHODS

Sample collection

Human breast milk samples ($n = 55$) were collected from different locations including metropolitan cities such as Chennai ($n = 10$), Kolkata ($n = 7$) and Bangalore ($n = 10$), suburban (Chidambaram; $n = 10$), fishing village (Parangipettai; $n = 10$) and municipal dumping site (Kolkata; $n = 8$) in India during 2009. Fish ($n = 100$) and indoor dust ($n = 35$) samples were also collected along with the milk samples. All the samples were shipped to Ehime University, Japan, on dry ice and stored in the environmental specimen bank (*es*-BANK) for global monitoring at –20°C until chemical analysis.

Chemical analysis

Approximately, 5 g each of freeze-dried fish and milk samples and 0.5 g of dust samples were extracted with a high speed solvent extractor using 50% acetone in hexane. Fat content in the biota samples was determined gravimetrically from an aliquot of the extract. The remaining extract was subjected to gel permeation chromatography (GPC). The fraction from GPC containing OHCs was concentrated and passed through 4 g of activated silica gel column. The first fraction having PCBs and PBDEs were quantified using a gas chromatograph equipped with a mass spectrometry (GC-MS). The second fraction containing HBCDs was quantified using a liquid chromatograph coupled with a tandem mass spectrometer (LCMS/MS), based on the method published elsewhere (Asante *et al.*, 2011). Sixty-two PCB congeners, forty-two congeners of PBDEs (from mono to deca) and three HBCD isomers (α-, β-, γ-HBCD) were quantified.

RESULTS AND DISCUSSION

Contamination status of PCBs and BFRs in human breast milk

Among the target compounds, PCBs were the highest in all the human milk samples (mean: 36 ng/g lipid wt.), followed by PBDEs (mean: 1.5 ng/g lipid wt.) and HBCDs (0.38 ng/g lipid wt.) from the general population of India. Among the locations, human milk samples from the municipal dumping site in Kolkata had significantly ($p < 0.05$) higher concentrations of PCBs and PBDEs (mean: 1700 and 5.7 ng/g lipid wt., respectively) than the other locations in India (PCBs: 3.2 to 160 and PBDEs: 0.10 to 15 ng/g lipid wt., respectively) which clearly indicates the presence of prominent sources of these contaminants in municipal dumping site. The present levels of PCBs in human milk from mothers living near the dumping site of India (1700 ng/g lipid wt.) are at the highest end of recent reports. High levels of POPs in human milk and fish samples from municipal dumping sites in and around the major cities of India were reported previously (Kunisue *et al.*, 2004; Someya *et al.*, 2010). Indian cities dispose of their wastes in an unscientific manner, without any segregation, in open dumps located in the outskirts, without concern for environmental degradation or impact on human health. This may lead to high concentrations of persistent chemicals in the bodies of human living in and near such locations. In India, the amount of municipal solid waste (MSW) is expected to increase significantly in the near future as the country is striving hard to attain an industrialized nation status by the year 2020 (Kumar *et al.*, 2009). This may lead to additional threats on the environmental quality and human health in near future. Congener pattern of PCBs was dominated by CB-153 followed by CB-138 and CB-118 from the general population in India, whereas the dumping site showed a different congener pattern with penta-CB (CB-118) being the dominant followed by CB-138 and CB-153 (data not shown). PBDE profiles varied widely among locations, BDE-47 was the dominant congener in human milk from Bangalore, Kolkata urban and Kolkata dumping site but BDE-209 dominated the profile in other locations such as Chennai, Chidambaram and Parangipettai. Many studies have reported that dietary intake was the dominant exposure pathway for lower brominated congeners (Fromme *et al.*, 2009) and dust ingestion for higher brominated congeners (Jones-Otazo *et al.*,

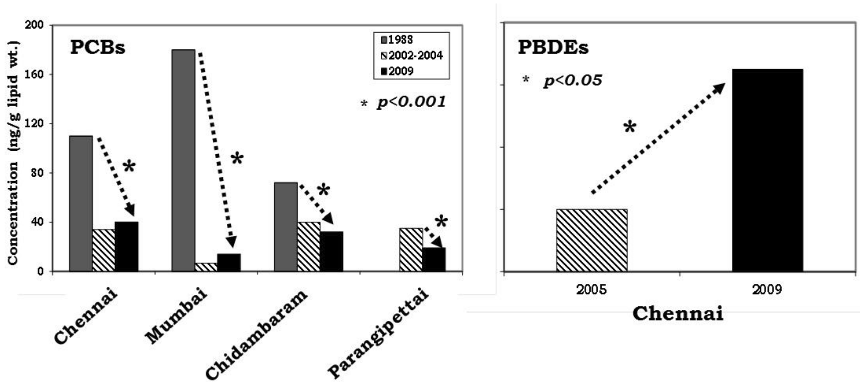

Fig. 1. Temporal variation of PCBs and PBDEs in human milk from several locations in India.

2005). Therefore, intake of contaminated food may be the cause for high levels of lower brominated congeners and dust ingestion may be contributing to higher brominated congeners. However, there is not much information on PBDE contamination in India, thus further studies are needed on food stuffs, dust and air samples to assess the major exposure pathways for Indians. Among HBCDs, the stable isomer α-HBCD was the predominant, contributing from 93% to 98% to the total HBCDs, with very low contribution by γ-HBCDs and the β-isomer being below the limit of quantification in human milk from Chennai and Kolkata. However, the isomer pattern was slightly different in human milk from dumping site donors with relatively high contribution of both α-HBCD (59%) and γ-HBCDs (41%), which may be due to recent specific exposure to the technical mixture containing products. As HBCD commercial mixture contains mainly the γ-HBCD (ranging from 75% to 89%), while the α- and β-HBCD isomers are present in lower amounts (10–13% and 1–12%, respectively).

In temporal variation, levels of PCBs in human breast milk collected from Chennai, Chidambaram, and Parangipettai (110, 180 and 72 ng/g lipid wt., respectively) in the southern part of India in 1988 (Tanabe *et al.*, 1990) declined sharply to 30, 8.2 and 17 ng/g lipid wt., respectively, in the present study (Fig. 1). Studies have reported declining trends of organochlorine pesticides and PCBs in human milk and sediments samples from India which clearly indicates phasing out of these compounds (Devanathan *et al.*, 2009; Sahu *et al.*, 2009).

Levels of PCBs and BFRs in fish

Concentrations of OHCs varied widely among locations and species. Levels of PCBs in fish samples (mean: 440 ng/g lipid wt.) were significantly ($p < 0.05$) higher than those of PBDEs and HBCDs (17 and 3.0 ng/g lipid wt.). High levels of PCBs and PBDEs were found in freshwater farmed fish than wild fish (data not shown). Feed may also contribute to higher levels of contaminants in farmed fish.

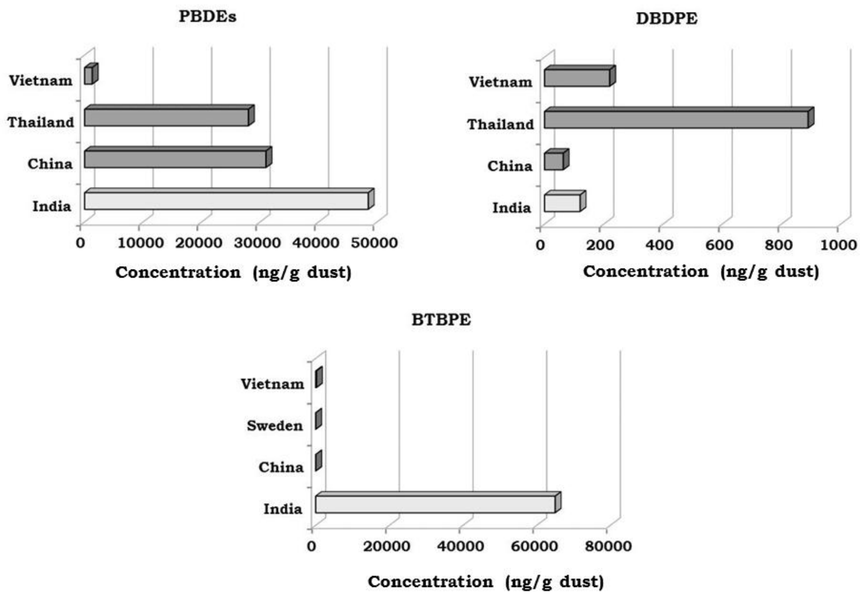

Fig. 2. Comparison of BFR levels in dust samples from e-waste recycling locations in different countries.

Easton *et al.* (2002) found high levels of contaminants in farmed salmon and suggested are likely a consequence of the elevated levels of contamination in the commercial salmon feed. Among the locations, significantly ($p < 0.05$) higher levels of PCBs (mean: 640 ng/g lipid wt.) were found in Mumbai samples compared to Chennai and Sivakasi (mean: 310 and 110 ng/g lipid wt., respectively). India has emerged as a leading nation involved in ship breaking activities (Reddy *et al.*, 2006), and the improper management of ship-breaking activities may act as an important source of PCBs contamination in Mumbai. The congener pattern of PCBs was in accordance with other studies and in the order of: hexa > hepta > penta-chlorinated biphenyls. Among the PBDE congeners, BDE-47 was the predominant congener in fish from the present study, which is consistent with the general pattern found in biota samples. HBCDs were detected only in few samples at low levels as in many Asian developing countries.

Organohalogen contaminants in dust samples

The concentrations and contamination patterns of PCBs and BFRs varied widely in dust samples from different indoor environments in India. Significantly higher ($p < 0.05$) levels of PCBs, PBDEs, BTBPE and DBDPE (median: 7100, 48000, 65000 and 120 ng/g dust) were found in dust samples from e-waste recycling locations than commercial (median: 23, 460, 220, and 67 ng/g dust) and residential buildings (median: 13, 1000, 48 and 15 ng/g dust) suggesting that a

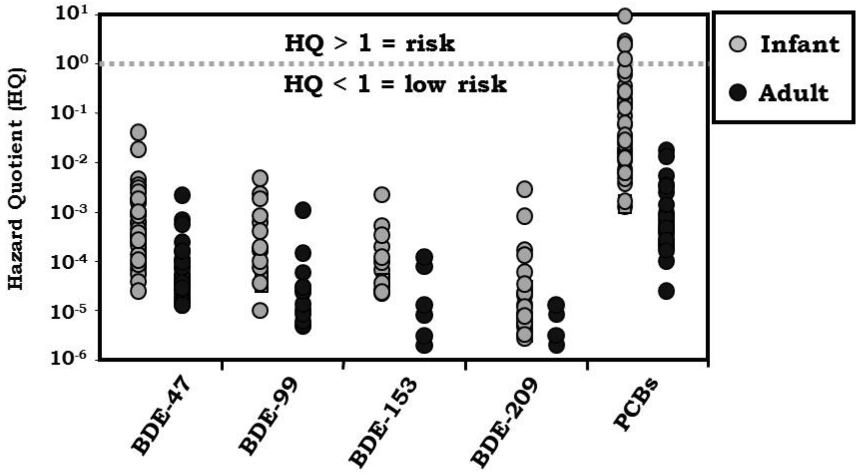

Fig. 3. Health risk assessment of PBDEs and PCBs in infants and adults through human milk and fish consumption.

major emission source of PCBs and BFRs is the crude e-waste recycling/ dismantling activities in India. However, HBCD levels were relatively lower in dust from e-waste recycling buildings (median: 8 ng/g) than in commercial and residential premises (median: 3 and 30 ng/g) indicating the wide use of HBCD-containing products such as textiles and other household materials rather than electronics in India. The median levels of PBDEs and BTBPE in dust samples from e-waste recycling locations in India were higher than in other countries such as China, Thailand, Sweden and Vietnam (Fig. 2) suggesting that large amounts of e-waste have been recycled by crude methods that could release considerable amount of toxic compounds into the environment exposing the workers to elevated levels in India. The PBDEs profile was dominated by BDE-209 in dust from e-waste (63%), commercial (85%) and residential (67%) sites which is not surprising because of the wide consumption of deca-commercial mixtures in Asian countries including India (Gevao *et al.*, 2006; Tan *et al.*, 2007).

Health risk assessment through hazard quotient

The health risks for infants, toddlers and adults associated with organohalogens in were assessed using hazard quotient (HQ), which is the ratio between the estimated daily intakes (DIs) of chemicals and corresponding reference dose (RfD). As shown in Fig. 3, the HQ values were below 1 for PBDEs indicating low risk. However, the HQ values were exceeded one for PCBs indicating high risk for infants, particularly living near the municipal dumping site. Daily intakes of BFRs and PCBs via dust ingestion were much higher for toddlers than adults, particularly for the population exposed to e-waste recycling

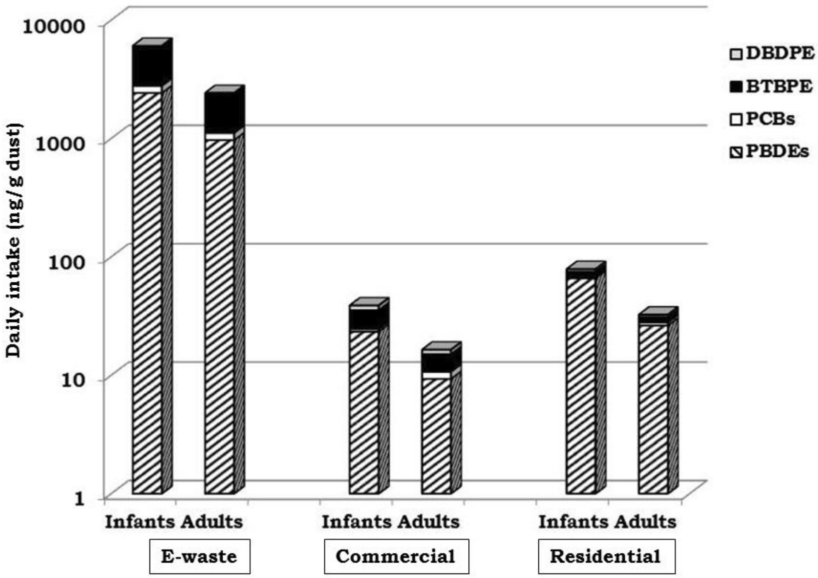

Fig. 4. Daily intakes of PCBs and BFRs for toddlers and adults in different areas by dust ingestion.

activities is of great concern (Fig. 4). Therefore, further studies are urgently needed to find the additional exposure sources and pathways in municipal dumping and e-waste recycling sites, in order to reduce the exposure levels.

CONCLUSION

Significantly high levels of organohalogens were found in human milk from municipal waste dumping sites indicating that the open dumping sites could act as potential sources for contamination. Differences in congener and isomer profiles of organohalogens between dumping site and the general population suggest the presence of region-specific sources and pathways. The dietary intake values were far lower than the guideline values indicating less risk through fish consumption. Elevated levels of OHCs were found in dust samples from e-waste recycling locations, suggesting that the crude e-waste recycling/dismantling activities are the major emission sources of these contaminants. In time-based study, the present PCB levels clearly decreased from the previous reports indicating that the restrictions imposed on the usage of PCBs in India seemed to have yielded positive impact. However, the hazard Quotient (HQ), values for PCBs shows exceeding one to infants and toddlers living near the municipal dumping sites and e-waste recycling sites indicate high risk and caution. Long term health impacts of POPs on humans living in and around these dumping sites and workers in informal sectors of e-waste recycling activities are probably a major concern for future research in India.

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REFERENCES

Asante, K. A., S. Adu-Kumi, K. Nakahiro, S. Takahashi, T. Isobe, A. Sudaryanto, G. Devanathan, E. Clarke, O. D. Ansa-Asare, S. Dapaah-Siakwan and S. Tanabe (2011): Human exposure to PCBs, PBDEs and HBCDs in Ghana: Temporal variation, sources of exposure and estimation of daily intakes by infants. *Environ. Int.*, **37**, 921–928.

Darnerud, P. O., G. S. Eriksen, T. Johannesson, P. B. Larsen and M. Viluksela (2001): Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environ. Health Perspect.*, **109** Suppl. 1, 49–68.

Devanathan, G., A. Subramanian, M. Someya, A. Sudaryanto, T. Isobe, S. Takahashi, P. Chakraborty and S. Tanabe (2009): Persistent organochlorines in human breast milk from major metropolitan cities in India. *Environ. Pollut.*, **157**, 148–154.

Easton, M. D., D. Luszniak and G. E. Von der (2002): Preliminary examination of contaminant loadings in farmed salmon, wild salmon and commercial salmon feed. *Chemosphere*, **46**, 1053–1074.

Fromme, H., W. Korner, N. Shahin, A. Wanner, M. Albrecht, S. Boehmer, H. Parlar, R. Mayer, B. Liebl and G. Bolte (2009): Human exposure to polybrominated diphenyl ethers (PBDE), as evidenced by data from a duplicate diet study, indoor air, house dust, and biomonitoring in Germany. *Environ. Int.*, **35**, 1125–1135.

Gevao, B., M. Al-Bahloul, A. N. Al-Ghadban, A. Al-Omair, L. Ali, J. Zafar and M. Helaleh (2006): House dust as a source of human exposure to polybrominated diphenyl ethers in Kuwait. *Chemosphere*, **64**, 603–608.

Hites, R. A. (2004): Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.*, **38**, 945–956.

Jones-Otazo, H. A., J. P. Clarke, M. L. Diamond, J. A. Archbold, G. Ferguson, T. Harner, G. M. Richardson, J. J. Ryan and B. Wilford (2005): Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.*, **39**, 5121–5130.

Kumar, S., J. K. Bhattacharyya, A. N. Vaidya, T. Chakrabarti, S. Devotta and A. B. Akolkar (2009): Assessment of the status of municipal solid waste management in metro cities, state capitals, class I cities, and class II towns in India: an insight. *Waste Manag.*, **29**, 883–895.

Kumari, B., V. K. Madan and T. S. Kathpal (2008): Status of insecticide contamination of soil and water in Haryana, India. *Environ. Monit. Assess.*, **136**, 239–244.

Kunisue, T., M. Watanabe, H. Iwata, A. Subramanian, I. Monirith, T. B. Minh, R. Baburajendran, T. S. Tana, P. H. Viet, M. Prudente and S. Tanabe (2004): Dioxins and related compounds in human breast milk collected around open dumping sites in Asian developing countries: bovine milk as a potential source. *Arch. Environ. Contam. Toxicol.*, **47**, 414–426.

Nakari, T. and S. Huhtala (2010): *In vivo* and *in vitro* toxicity of decabromodiphenyl ethane, a flame retardant. *Environ. Toxicol.*, **25**, 333–338.

Reddy, S., S. Basha, S. Adimurthy and G. Ramachandraiah (2006): Description of the small plastics fragments in marine sediments along the Alang-Sosiya ship-breaking yard, India. *Estuar. Coast. Shelf Sci.*, **68**, 656–660.

Safe, S. (2004): Endocrine disruptors and human health: is there a problem. *Toxicology*, **205**, 3–10.

Sahu, S. K., P. Y. Ajmal, G. G. Pandit and V. D. Puranik (2009): Vertical distribution of polychlorinated biphenyl congeners in sediment core from Thane Creek area of Mumbai, India. *J. Hazard Mater.*, **164**, 1573–1579.

Shaw, S. D. and K. Kannan (2009): Polybrominated diphenyl ethers in marine ecosystems of the American continents: foresight from current knowledge. *Rev. Environ. Health*, **24**, 157–229.

Someya, M., M. Ohtake, T. Kunisue, A. Subramanian, S. Takahashi, P. Chakraborty, R. Ramachandran and S. Tanabe (2010): Persistent organic pollutants in breast milk of mothers residing around an open dumping site in Kolkata, India: specific dioxin-like PCB levels and fish as a potential source. *Environ. Int.*, **36**, 27–35.

Tan, J., S. M. Cheng, A. Loganath, Y. S. Chong and J. P. Obbard (2007): Polybrominated diphenyl ethers in house dust in Singapore. *Chemosphere*, **66**, 985–992.

Tanabe, S., A. Subramanian, A. Ramesh, D. Mohan, P. Kumaran, V. K. Venugoplan and R. Tatsukawa (1990): Specific pattern of persistent organochlorine residues in human breast milk from south India. *J. Agricultural Food Chem.*, **38**, 899–903.

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