ORGANOHALOGEN CONTAMINANTS IN DUST SAMPLES FROM DIFFERENT INDOOR ENVIRONMENTS IN INDIA: IMPLICATIONS ON HUMAN EXPOSURE

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Introduction

Polybrominated biphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are a group of additive brominated flame retardants (BFRs) that have been widely used in various consumer products to meet fire safety standards and to avoid the rapid burning in case of fire accidents. BFRs can leach out from products or physically degrade into particles, and thus ubiquitous in the environment and biota including human. Concerns on increasing levels of BFRs in the environment and similar toxic properties with polychlorinated biphenyls (PCBs), legislated the ban/regulations on production and use on certain commercial formulations of BFRs in developed countries such as US, Canada, Japan and European nations[1,2]. Although many developed countries initiated the ban but many developing countries including India is yet to implement such regulations due to many reasons including the lack of data set. Rapid industrialization, urbanization and population growth are most likely responsible for environmental destruction in India. Though the relationship is complex, population size and growth tend to expand and accelerate these human impacts on the environment. All these in turn lead to an increase in the pollution levels. Elevated levels of persistent organic pollutants (POPs) were found in environmental[3,4] and biotic samples including human milk[5,6,7] indicating the importance of regular monitoring and the initiation of the steps to reduce the pollution levels in India. Today, electronic waste (e-waste) processing and recycling activities are of global concern because of primitive methods practiced in developing countries including India can significantly release toxic compounds into the environment. Huge amounts of domestic generation along with international input of e-waste can increase the pollution in India.

Indoor environment are vulnerable to population groups like children and pregnant women because elevated levels of PBDEs and PCBs were found in indoors than outdoor environment and also people spend most of their time indoors. Ingestion of contaminated food and dust inhalation/ingestion are the primary pathways of human exposure to BFRs. High levels of BFRs were reported in house dust from different countries, probably as a result of BFR emission from household products and adsorption by house dust[8,9]. Recently, Huke et al.[10] reported that PBDEs in dust are readily bioavailable and biologically active, implying the importance of human exposure assessment through house dust. Thus, the present study aimed to investigate the concentration and composition of organohalogen contaminants such as PCBs and BFRs [PBDEs, HBCDs, 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenylethane (DBDPE)] in dust samples collected from different indoor environments such as e-waste recycling area, commercial and residential buildings in India. We also tried to estimate the human exposure of these contaminants via dust ingestion.

Materials and methods

Sample collection

Dust samples *(n=35)* were collected from e-waste recycling, commercial and residential buildings in Chennai and Bangalore, in India during 2006 sampling survey. These two are among the world's fastest-growing cities with rapid development in the field of information technology (IT) and electronics; thus domestic generation of e-waste leads to existence of many small and large scale e-waste recycling/dismantling (both legal and illegal) units. The samples were collected using vacuum cleaner and plastic materials were avoided throughout the collection procedure. Unwanted materials from the complex mixture of dust samples were separated; fine particles were stored in amber

bottles at -20^{0}C until chemical analysis. Building characteristics including floor area, cleaning frequency, number of computers/televisions, type of flooring, ventilation facility, etc were documented at the time of sample collection.

Chemical analysis

Approximately, 0.5-1g of dust sample was extracted with a high speed solvent extractor using 50% acetone in hexane. The extract was spiked with $^{13}C_{12}$-labeled PBDEs, PCBs and HBCDs as surrogates and then loaded to multilayer silica column for the removal of unwanted material. Then the sample was further loaded to gel permeation chromatography (GPC) and eluted with a mixture of hexane and dichloromethane (1:1). The GPC fraction containing organohalogen compounds was concentrated and passed through 4g of activated silica gel packed in a glass column. The first fraction was eluted with 5% dichloromethane in hexane and second fraction with 25% dichloromethane in hexane. $^{13}C_{12}$-labeled BDE-139 was added as an internal standard to the first fraction containing PCBs and BFRs prior to quantification using a gas chromatograph equipped with a mass selective detector (GC-MSD). The second fraction containing HBCDs was spiked with deuterated HBCDs and analyzed using liquid chromatograph coupled with a tandem mass spectrometer (LC-MS/MS), based on the method published elsewhere[11]. Quantification of PCBs and PBDEs (mono- to hepta-BDEs) was performed using a GC (Agilent 6890 N) with MSD (Agilent 5973 N), and GC (Agilent 7890) coupled with MSD (Agilent 5975) for octa- to deca-BDEs, with electron impact ionization in selective ion monitoring mode (EI-SIM). Sixty two PCB congeners, forty two congeners of PBDEs (from mono to deca), BTBPE, DBDPE and three HBCD isomers (α-, β-, γ-HBCD) were quantified using the isotope dilution method to the corresponding $^{13}C_{12}$-labeled congener.

Results and discussion:

Contamination status of PCBs and BFRs

The concentrations and contamination patterns of PCBs and BFRs varied widely in dust samples from different indoor environments in India (Fig. 1). For example, BTBPE was the predominant contaminant followed by PBDEs and PCBs in dust from e-waste recycling buildings; whereas PBDEs dominated the contaminant profile in dust from commercial and residential sites (Fig. 1), indicating the presence of different sources in the respective micro-environments. BTBPE has a broad range of applications to various products, being added to acrylonitrile butadiene styrene polymers (ABS), which are used in electronics e.g., telephones, dashboards, equipments for refrigerators, toys, etc[12]. Recent economic growth with considerable contribution of information technology (IT sectors) leads to an increasing usage of electronic products including computers which may contain BFRs that finally ends in e-waste recycling buildings in India. In addition to the domestic generation of e-waste, international input also significantly contribute to BFRs pollution in India. Significantly higher (p<0.05) levels of contaminants such as 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 major emission source of PCBs and BFRs is the crude e-waste recycling/dismantling activities in India (Fig. 1).

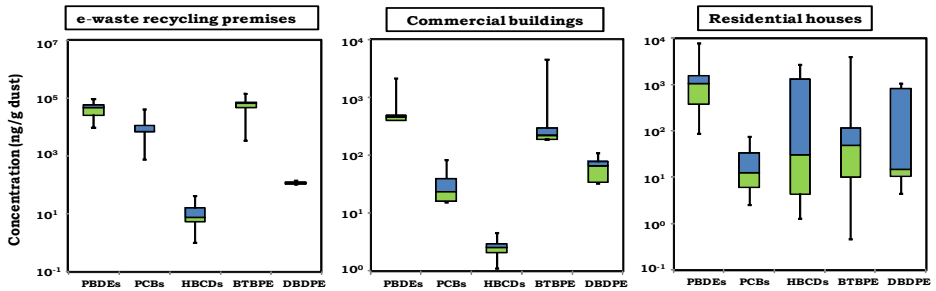

Fig. 1. Levels of PCBs and BFRs in dust samples from different micro-environments in India

High PBDEs contamination in environmental matrices from an e-waste recycling facility in various countries including China[13], Thailand[14], and Sweden[15] has been reported previously. However, HBCDs levels were relatively low in dust from e-waste recycling buildings (median: 8 ng/g) than residential dust (median: 3 and 30 ng/g) indicating the wide use of HBCDs 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) which clearly indicates that indiscriminate 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. However, the levels of DBDPE in dust samples from e-waste recycling locations were lower than Thailand and Vietnam indicating the minimal pollution of DBDPE in India (Fig. 2).

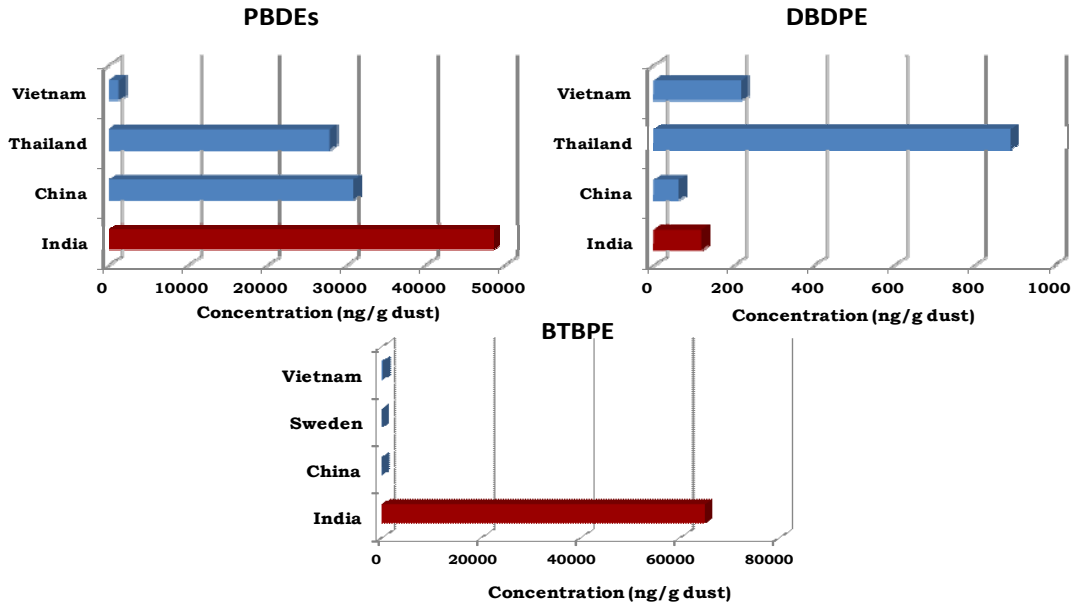

Fig. 2. Comparison of BFRs levels in dust samples from e-waste locations in various countries

PBDEs was the predominant contaminant in dust samples from commercial buildings (median: 460 ng/g dust) followed by BTBPE and DBDPE (median: 220 and 67 ng/g dust). Among dust samples from different commercial buildings, ironically BFRs levels in dust from biology lab were higher than the PC room in a college and school (data not shown). BTBPE (median: 4500 ng/g dust) dominated the profile in biology lab followed by PBDEs (median: 2100 ng/g dust). In biology lab, major BFRs containing products like computer, TV, etc were not present during our sampling but we found many hard plastic tubs (which may contain BFRs) used for dissection and this may explain high levels in the dust. In addition, the lab is located in the first floor close to the car parking area and the dust from there may also contribute elevated levels of BFRs. Batterman et al. (2009)[1] monitored 12 U.S. houses and garages and estimated total PBDE emission rate from one house with one garage to the ambient environment via airborne vapor and particulate matter was 6.5 mg/year, which is equivalent to 0.74 mg/h released from 1000 houses and garages. Among the house dust, no significant differences were observed between Chennai and Bangalore indicating an uniform contamination status. The PBDEs levels in house dust in India were comparable with Singapore, Vietnam, Germany and New Zealand but lower than Canada and US (data not shown). High contamination of BFRs in this study clearly indicates the need for more comprehensive study to find the potential sources of these emerging contaminants.

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. Relatively high proportion of Octa-BDE (23%) was found in e-waste locations than other dust samples indicating the wide recycling of octa-commercial mixture containing products in India. [16]Huang et al. (2010) reported that television sets are one of the most important emission sources for Octa-BDE. Among HBCDs isomers, α-HBCD and γ-HBCD contributed high proportion to the total. High proportion of γ-HBCD in house dust indicates recent input and direct load from products. Estimated daily intakes (EDIs) of average adult and toddler via house dust in India were comparable with Asian countries but far lower than UK and USA (data not shown). Daily intakes of BFRs via dust ingestion were much higher for toddlers than adults, particularly for the population exposed to e-waste recycling activities is of great concern. Despite the low deleterious risk of PBDE exposure via house dust as shown by the hazard quotients, this exposure pathway should be of concern because of higher BFR exposures for children[17,18] and the presence of other BFRs (such as BTBPE and DBDPE) which have not yet been fully investigated. This study is the first to provide the knowledge on contamination of indoor dusts in different microenvironments in India with evidence of e-waste recycling activities considerably contributing to emission of PCBs and BFRs into environment and exposure of workers and public. Further studies are needed to assess the heath risk for workers involved in e-waste recycling sector in India.

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