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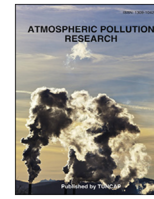

Polybrominated diphenyl ethers (PBDEs) and alternative flame retardants (NFRs) in indoor and outdoor air and indoor dust from Istanbul-Turkey: Levels and an assessment of human exposure

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A B S T R A C T

Levels of polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NFRs) were measured in ambient outdoor air, indoor air and indoor dust collected in homes and offices at urban, semi-urban and rural locations in Istanbul, Turkey. Indoor air levels of Σ_{12}PBDEs in homes and offices ranged from 36 to 730 pg/m^3 and 160 to 10 100 pg/m^3, respectively, while levels of Σ_{12}NFRs ranged from 180 to 7600 pg/m^3 and 180 to 42 400 pg/m^3, respectively. Outdoor air levels ranged from 110 to 620 pg/m^3 for Σ_{12}PBDEs and 750 to 2800 pg/m^3 for Σ_{12}NFRs. I/O ratios that are greater than 1 suggest that air concentrations detected in indoor environments are mainly from indoor sources. Indoor dust levels in homes and offices of Σ_{12}PBDEs ranged from 400 to 12 500 ng/g and 330 to 32 200 ng/g respectively and levels of Σ_{12}NFRs ranged from 320 to 31 400 ng/g and 910 to 97 900 ng/g, respectively. The I/O ratios >1 for PBDEs and NFRs may indicate that emissions of these chemicals detected in homes and offices are mainly from indoor sources. Due to childrens' frequent hand-to-mouth behaviour, lower body weight and increased dust ingestion rate compared to adults, exposure rates to target chemicals for children were greater than those of adults. Based on median concentrations of chemicals of interest in dust and air samples from Istanbul, we estimate that exposure rates of children to PBDEs and NFRs are up to 160 times higher compared to adults but none of the estimated exposure rates results for children or adults were than the recommended daily oral reference dose values of certain analytes.

1. Introduction

Flame retardants (FRs) are a class of chemicals widely used as additives in many consumer products such as polyurethane foam, plastics, spray foam insulation, electronic equipment, textiles, furniture and others (Alcock et al., 2003; Harrad et al., 2004). Polybrominated diphenyl ethers (PBDEs) have historically been the most intensively used flame retardants globally with a market demand of 56 100 tonnes, 7500 tonnes and 3790 tonnes for decabromodiphenyl ether (deca-BDE), pentabromodiphenyl ether (penta-BDE) and octabromodiphenyl ether (octa-BDE), respectively in 2001 (Morose, 2006). However, due to their persistence, bioaccummulative nature and toxicity, commercial mixtures of penta (c-penta BDE) and octa-BDEs (c-octa BDE) were added to the Stockholm Convention and have been phased out (SC, 2009) whereas commercial deca-BDE (c-deca BDE) is under review by the Stockholm Convention and have been recommended for phase-out (SC, 2013). C-penta BDE and c-octa BDE mixtures were also phased

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out in the U.S in 2004 (Great Lakes Chemical Corporation, 2005a). Application of c-decaBDE in electrical and electronic products is banned in Europe (European Court of Justice, 2008) as well as a commitment by U.S. producers and importers (Chemtura, Albermarle, and ICL Industrial Products) to end production, import and sales by the end of 2013 (USEPA, 2010). Since then, alternative chemicals have been increasingly used, including NFRs in order for manufacturers to meet flammability standards. These alternative flame retardants include "novel" flame retardants (NFRs) such as 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (ATE or TBP-AE), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE or TBP-DBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB or EH-TBB), octabromotrimethylphenyllindane (OBIND or OBTMPI), hexabromobenzene (HBB), hexabromocyclododecane (HBCDD), bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP or BEH-TEBP), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 1,2,5,6-tetrabromocyclooctane (TBCO), tetrabromoethylcyclohexane (TBECH or DBE-DBCH) and two isomers of dechlorane plus (DDC-CO) (see Tables S2–1 for traditional and practical abbreviations for these chemicals given by Bergman et al., 2012).

Despite ban and restrictions, PBDEs are still present in in-use consumer products and FRs including NFRs and PBDEs can be released into the environment via volatilization, dissolution, sorption to dust and abrasion processes (Cao et al., 2014). Studies on animals showed that PBDEs and NFRs may affect the liver, thyroid, reproductive system, and neurobehavioral developments (ATSDR, 2004; Harju et al., 2008; Nakari and Huhtala, 2010). Recent studies from different parts of the world have shown the presence of PBDEs and alternative FRs in indoor air and dust (Ali et al., 2016; Björklund et al., 2012a,b; Cequier et al., 2014; Dirtu et al., 2012; Dodson et al., 2012; Yu et al., 2012). Levels in house dust have generally been higher in the U.S. and U.K. compared with Europe and Japan, reflecting their stringent standards. Although dietary intake is the main exposure pathway to several organochlorine semivolatile contaminants, studies conducted recently (Ali et al., 2011, 2013; Dirtu and Covaci, 2010; Mercier et al., 2011) have concluded that indoor dust ingestion can be a significant exposure pathway. Due to the large specific surface area, and high organic content, dust is considered a good accumulator for flame retardants and provides a medium for their transport (Ali et al., 2012a, 2013). Several studies have shown indoor dust as a major source for human exposure to PBDEs, especially for children who spend more time on the floor and who ingest dust via hand-to-mouth activity (Allen et al., 2008; Cequier et al., 2014; Dodson et al., 2012; Harrad et al., 2010; Restrepo-Johnson and Kannan, 2009). It has also been suggested that this is likely the same for alternative flame retardants including NFRs (Cequier et al., 2014). Wu et al. (2007) and Coakley et al. (2013) reported a strong positive correlation between PBDEs concentration in human milk and dust collected from the donors' homes.

PBDEs and HBCDD have been classified as persistent organic pollutants under the Stockholm Convention and Turkey, as a signatory of the Convention, has committed to ban/phase-out these chemicals. Flame retardant chemicals were not produced in Turkey, although a recent inventory study revealed that significant amounts of PBDEs (NIP, 2014) and HBCDD (Kurt-Karakus, 2015) enter the waste stream in the country. Based on Harmonised System Codes (HS) that track chemicals imported/exported to/from the country and give information on general groups of goods and/or chemicals (but no specific or adaquate information on specific chemicals), the inventory study revealed that a total of approx. 724 tonnes of diphenyl ether was imported to the country between 1996 and 2013. However, only 177 tonnes of imported diphenyl ether was specified as penta/tetra bromo diphenyl ether and no definition was made regarding the remaining 547 tonnes of diphenyl ether product that was imported to the country in this period. Additionally, there is no data reporting where these chemicals have been used/applied (NIP, 2014). In terms of regulations to set flammibility standards and use of FRs chemicals, there exists only limited number of legislation in Turkey. According to the Turkish Standards Institution database, the only national standard regulating consumer products with regards to flame retardancy is on construction materials (TSE, 2010). A previous legislation (Official Gazzette, 2008) related to use of hazardous chemicals in electrical and electronic consumer products in Turkey which aimed to restrict PBDEs and polybrominated biphenyls (PBBs) use in consumer products was repealed in 2012 and replaced by a legislation on control of waste electrical and electronics (Official Gazzette, 2012).

Despite extensive information regarding indoor levels of PBDEs and to a lesser extent for NFRs in Europe and North America, there is little or no information regarding their concentrations in indoor air and dust in other areas of the world including Turkey. There exists limited number of studies on ambient air and soil concentrations of PBDEs in Turkey (Cetin and Odabasi, 2007a,b; Cetin, 2014), but, to our current knowledge, only two studies available reporting PBDEs levels in indoor environment The first study reports PBDEs levels from Turkey with a focus on outdoor and indoor window organic films (Cetin and Obadasi, 2011). The second study reports Σ_{14}PBDEs congeners in indoor dust collected from Kocaeli province of Turkey (Civan and Kara, 2016). There are no studies on presence and/or levels of NFRs in indoor and/or outdoor environment of Turkey. Therefore, to our best knowledge, this is the first study reporting both PBDEs and NFRs concentrations in indoor air and dust for Turkey.

The objectives of this project were: (1) to determine the concentrations of PBDEs and NFRs in indoor dust, indoor air and outdoor air in Istanbul, Turkey; (2) to compare levels of these chemicals in indoor dust in homes versus offices; and (3) to estimate the indoor exposure rates of adults and children to flame retardants through ingestion, inhalation and dermal absorption to indoor dust.

2. Materials and methods

2.1. Study area and sampling strategy

A total of 19 dust samples were collected in February–March 2012 from homes (n = 10) and offices (n = 9) in urban (Besiktas, Population in 2012: 186 067 (TUIK, 2014)), semi-urban (Bahcesehir, Population in 2014: 50 656 (TUIK, 2014)) and rural (Gokturk, Population in 2012: 19 575 (TUIK, 2014)) neighborhoods of Istanbul, Turkey (Fig. 1).

Indoor air samples were collected using polyurethane foam (PUF) passive air samplers at the same indoor locations as dust samples. One house at each of rural, semi-urban and urban settings was chosen to collect an outdoor air sample using PUF in double-dome stainless steel chambers. For this purpose, outdoor passive air sampler was left in the field along the course of indoor sampling campaign. Dust sampling from household vacuum bags can be utilized as a cost-effective and informative alternative to the standardized sampling of fresh dust by qualified workers (Fan et al., 2016). In this study, whole dust bag content of volunteers' regular use vacuum cleaner was collected for analysis (Björklund et al., 2012b; Hassan and Shoeib, 2015). Volunteers were asked to install a new dust bag in their vacuum cleaners on the day that passive indoor samplers placed in homes and in offices and if the bag is full before the harvest of air samplers, they were asked to return full bags to researchers and place an empty one untill indoor