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Levels of polybrominated diphenyl ethers and novel flame retardants in microenvironment dust from Egypt: An assessment of human exposure

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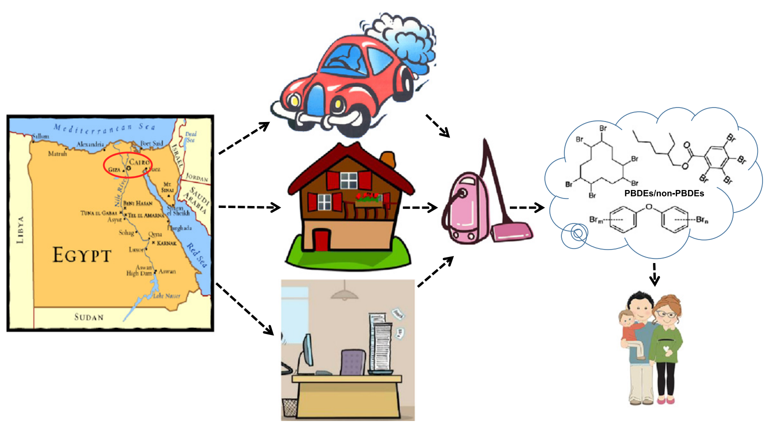
HIGHLIGHTS

- First measurements of PBDEs and non-PBDEs flame retardants in Egyptian indoor dusts.
- PBDEs were detected in all microenvironments, non-PBDEs DF ranged from 40 to 100%.
- PBDEs and non-PBDEs levels in indoor dusts were among the lowest worldwide.
- Human exposure from dust was below the oral reference dose.

GRAPHICAL ABSTRACT



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ABSTRACT

There are very few studies reporting concentrations of polybrominated diphenyl ethers (PBDEs) and novel flame retardants (FRs) or non-PBDEs in Africa and the Middle East. The present work reported concentrations of fourteen PBDE congeners and eleven non-PBDE flame retardants in dust samples collected from homes (n = 17), workplaces (n = 9) and cars (n = 5) in the greater Cairo region. The median $\sum$PBDE concentrations were 57, 425 and 1608 ng g^{-1} in homes, workplaces and cars respectively. The highest PBDE levels were observed for BDE 209, with a median concentration of 40.2, 366 and 1540 ng g^{-1} representing 70% to 95% of the total PBDEs in homes, workplaces and cars respectively. This is about 8 to 46 times greater than the median concentration of the pentaBDE (represented by the most abundant compounds in this formulation, $\sum$BDE 47, 99 and 100). In the case of non-PBDE flame retardants, a detection frequency between 52% and 100% was observed for several compounds including: hexabromocyclododecane (HBCD), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis (2-ethyl-1-hexyl) tetrabromophthalate (TBPH), 1,2-bis (2,4,6-tribromophenoxy) ethane (TBPE), ally-2,4,6-tribromophenyl ether (ATE) and Dechlorane Plus (DP). The $\sum$non-PBDE median concentrations were 8.30, 28.9 and 49.9 ng g^{-1} in homes, workplaces and cars respectively with the highest level observed for HBCD in the three microenvironments. The detection of novel flame retardants in indoor environments may be due to their wide usage after the ban of the penta and octa BDE formulation. Results show the levels of PBDEs and non-PBDEs in Egyptian dust to be among the lowest levels reported

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from other countries. Different dust exposure scenarios using 5th percentile, median, 95th percentile and maximum levels were estimated for adult and children. The estimated dust intake results were several orders of magnitude lower than the oral reference dose values.

1. Introduction

Polybrominated diphenyl ethers are a class of organic compounds, which have been used as flame retardants (FRs) in many consumer products since the mid-1970s. These products include among other things furniture, mattresses, carpet pads and electronics. Flame retardants in general can be classified as either reactive (e.g. covalently bound chemicals) or as additive which are applied to products without necessarily being chemically bound to the materials they treat. PBDEs are one of the many classes of compounds used as additive flame retardants therefore they are able to significantly migrate into the environment. PBDEs were originally produced in three commercial formulations with different levels of bromination. The penta-PBDE formulation is composed primarily of PBDEs 47, 99 (each representing about 38–49% of the formulation), 100, 153 and 154 alongside smaller amounts of tri- and hepta-PBDEs. The octa-PBDE formulation is composed primarily of a mixture of hexa- to deca-PBDE such as 153, 183, 196, 197, and 207; while the deca-PBDE blend is predominantly composed of PDBE 209 which represents 92–97% of the formulation alongside some octa-PBDEs (Krol et al., 2012, 2013).

PBDEs have been found in residential dust (Dodson et al., 2012), workplaces (Watkins et al., 2013), schools (Harrad et al., 2010), cars (Cunha et al., 2010), sea water (Möller et al., 2011) and landfill sites (Odusanya et al., 2009). PBDEs are also known to bio-accumulate and have been reported in domestic animals (Venier and Hites, 2011), wildlife (Sonne et al., 2009; Vetter et al., 2010), human serum, (Fromme et al., 2009; Johnson et al., 2010; Toms et al., 2008; Roosens et al., 2009), human tissues and breast milk (Thomsen et al., 2010). The presence of PBDEs in human milk also raises concerns of these substances being passed from mother to child. Specifically the tetra-PBDE 47, penta-PBDEs 99 and 100, and hexa-PBDEs 153 and 154 congeners are most prevalent in human tissues and compose approximately 90% of the total PBDEs (Talsness, 2008; Frederiksen et al., 2009). The deca-PBDE 209 is of special concern as exceptionally high concentrations of this congener were found in blood samples from Korea and China (Moon et al., 2007; Bi et al., 2007; Qu et al., 2007). PBDEs are thought to interfere with the thyroid hormone balance and thus contribute to neurodevelopmental problems (Eriksson et al., 2001; Hallgren et al., 2001; Meerts et al., 2001; McDonald, 2002; Lee et al., 2007). Since the thyroid hormones affect cellular metabolism and play essential roles in cell differentiation and growth, the interference with these hormones by PBDEs therefore has the potential to impact many systems in the human body (Talsness, 2008).

In response to the growing concern about their persistence, bioaccumulation and potential health effects the penta- and octa-PBDE formulations were banned in the European Union in 2004 (Prevedouros et al., 2004) and are phased out in the US (Ward et al., 2008). Recently, these two formulations were added to the list of banned chemicals in Annex A (elimination of production and use of all intentionally produced Persistent Organic Pollutants) of the Stockholm Convention in 2009 (Stockholm Convention Secretariat, 2009). The deca-PBDE on the other hand, is still in use in the US (U.S. Environment Protection Agency, 2012) and was annulled from the European Union restriction in 2008 (European Court of Justice, 2008).

The phase out of the penta- and octa-BDE formulations has led to increased use of alternate non-PBDE flame retardants. Several of the non-PBDE FRs such as hexabromocyclododecane (HBCD); 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB); bis (2-ethyl-1-hexyl) tetrabromophthalate (TBPH) and the chlorinated FR Dechlorane Plus (DP) have received considerable attention recently. The total global use in 2005 of brominated FRs including deca-BDE formulation was estimated to be 311,000 metric tons and increased to 410,000 metric tons in 2008 (Fink et al., 2008). Many of these compounds have similar physical chemical properties to PBDEs such as a high degree of halogenation and low aqueous solubility. Furthermore, most of these non-PBDEs are used as 'additive', as opposed to 'reactive' flame retardants, therefore it is expected for them to have environmental fates similar to PBDEs. Non-PBDEs have been reported in air, sea water, biota and in indoor dust (de Wit et al., 2010; Tomy et al., 2007; Ali et al., 2013; Shoeib et al., 2012; Abdallah et al., 2008; Thuresson et al., 2012; Stapleton et al., 2008). The release of flame retardants into the environment may occur during their manufacture and through migration from consumer products both during the time they are in use and after their end-of-life, by means of weathering and leaching at landfill sites.

Several studies surveying the levels of flame retardants from different industrialized countries have been reported, however data from developing countries have been very sparse. To our knowledge this study is the first investigation of the occurrences and the determination of the concentrations of PBDEs and non-PBDE FRs in indoor dust from different microenvironments in the Greater Cairo region. Here, these determined levels are compared to those previously reported in other countries and an assessment on human exposure is presented.

2. Materials and methods

2.1. Chemicals

A mixture of PBDEs 17, 28, 49, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, and 209 as well as individual PBDE 209 were obtained from Cambridge Isotope Laboratories, Inc., Ma, USA. Individual standards of non-PBDEs were purchased from Wellington Laboratories: ally-2,4,6-tribromophenyl ether (ATE), beta-tetrabromoethylcyclohexane (β-TBECH), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), beta-1,2,5,6 tetrabromocyclooctane (β-TBCO), bis (2-ethyl-1-hexyl) tetrabromo phthalate (TBPH), hexabromobenzene (HBB), gamma-hexabromocy clododecane (γ-HBCD), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) and Dechlorane *Plus* (*syn*-DP, *anti*-DP).

2.2. Dust collection

During 2013 dust samples were collected from homes and workplaces by obtaining whole vacuum cleaner bags, or by sub sampling the contents of canisters from bag-less vacuums. The dust samples were wrapped in solvent-cleaned aluminum foil and further sealed in polyethylene bags for storage at 4 °C until sieved and processed. Dust samples from cars were collected from the chairs, the roofs and the dashboards but not from the floors of the cars sampled.

2.3. Dust extraction and analysis

Details on the dust handling and sieving procedure are given elsewhere (Shoeib et al., 2011). Briefly, dust samples were sieved through a stainless steel sieve (250 μm) (U.S.A. Standard Testing Sieve). Sieved samples were kept in polypropylene tubes with screw-caps with the tops wrapped in wax paraffin sheets. The tubes were stored in polyethylene plastic bags until extraction. Samples were extracted using approximately 0.2 g sieved and homogenous dust weighed in 20 ml polypropylene test tubes and sonicated with 10 ml dichloromethane (DCM) for 30 min. The process was repeated a second time with a