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Research article

Polybrominated diphenyl ethers and "novel" brominated flame retardants in floor and elevated surface house dust from Iraq: Implications for human exposure assessment

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ABSTRACT

Concentrations of polybrominated diphenyl ethers (PBDEs) and selected novel brominated flame retardants (NBFRs) were measured in indoor dust from the living areas of 18 homes in Basrah, Iraq. This is the first report of contamination of the Iraqi environment with these chemicals. To evaluate the implications for human exposure, samples were collected from both the floor and from elevated surfaces like tables, shelves and chairs. When normalised for the organic carbon content of the dust sample, concentrations in elevated surface dust of BDE-99, BDE-209, pentabromoethylbenzene (PBEB), bis (2-ethylhexyl) 3,4,5,6-tetrabromophthalate (BEH-TEBP), and decabromodiphenylethane (DBDPE) exceeded significantly ($p < 0.05$) those in floor dust from the same rooms. This suggests that previous studies that base estimates of adult exposure via dust ingestion on floor dust, may underestimate exposure. Such underestimation is less likely for toddlers who are far more likely to ingest floor dust. Concentrations of PBDEs and NBFRs in indoor dust from Basrah, Iraq are at the lower end of levels reported elsewhere. The PBDE contamination pattern in our samples suggests that use in Iraq of the Deca-BDE formulation, exceeds substantially that of Penta-BDE, but that use of the Octa-BDE formulation has been higher in Iraq than in some other regions. Reassuringly, our estimates of exposure to our target BFRs via dust ingestion for the Iraqi population fall well below the relevant health-based limit values.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and "novel" brominated flame retardants (NBFRs) are chemicals added to a wide range of consumer products (electrical and electronic equipment, textiles, polyurethane and polystyrene foams) to meet flame retardancy standards set by various jurisdictions worldwide [1-6]. Since in most applications these chemicals are used additively - i.e. they are not covalently linked to the products in which they are incorporated - they can transfer from such products into the environment. An extensive body of studies have reported the presence of PBDEs in indoor air [7-9], indoor dust [10-21], sediments [22-24] and biota samples [25,26]. Evidence of their persistence and capacity for bioaccumulation, coupled with concerns about their adverse health effects [27-32], have led to widespread bans and restrictions on the manufacture and use of both the Penta- and Octa-BDE mixtures and their listing under the Stockholm Convention on Persistent Organic Pollutants (POPs) [33]. Moreover, manufacture and use of Deca-BDE has been progressively restricted and is currently under consideration for listing under the Stockholm Convention [34]. Such bans and restrictions on the use of PBDEs without concomitant relaxation of flammability standards, has likely resulted in increased production and use of alternatives referred to collectively as novel BFRs (NBFRs). Prime examples of such NBFRs include: pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-

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tetrabromobenzoate (EH-TBB), bis (2-ethylhexyl) 3,4,5,6-tetrabromophthalate (BEH-TEBP), 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenylethane (DBDPE) [30]. The exact global production volume of NBFRs is unclear, although one estimate placed production in the mid-2000s at about 18,000 tons per annum, with a projected growth of around 5% per year [35], Recently, NBFRs have received increasing attention due to their detection in sediments [23,36,37], indoor dust [19,20,38-41], and birds [23]. Recent studies suggest NBFRs may be endocrine disrupters [42], but overall, insufficient information is currently available regarding their fate and toxicological effects [31,43].

The similarity in physicochemical properties and applications between PBDEs and NBFRs leads to the hypothesis that human exposure to NBFRs will occur via similar pathways [35]. Specifically, human exposure to PBDEs occurs via the diet, and via inhalation of (primarily indoor) air, as well as ingestion of indoor dust. The relative significance of each pathway varies considerably according to factors such as: geographical location (dust ingestion appears more important in North America than elsewhere), age (dust ingestion is considered of greater magnitude for young children than adults), and the physicochemical properties of a given PBDE congener (exposure to decabromodiphenyl ether (BDE-209) is dominated by dust ingestion owing to its very low vapour pressure and comparative low capacity for bioaccumulation).

Thus, although the contribution of indoor dust ingestion to overall human exposure is variable, the weight of evidence suggests it likely warrants evaluation for NBFRs. Moreover, the vast majority of exposure assessments conducted to date for both PBDEs and NBFRs, have been conducted in East Asia (China, Korea, and Japan), Europe, and North America [44]. While data is emerging for other regions (including Egypt [20] and Kuwait [40,45]), to our knowledge no information exists concerning the presence of PBDEs and NBFRs in indoor dust in Iraq.

Moreover, no universally accepted standard method exists for the sampling of indoor dust for assessment of human exposure to organic contaminants [46]. To date, the majority of studies collect floor dust. However, a few studies suggested sampling dust from elevated surfaces at least 1 m above the floor in order to exclude dirt, sand and gravel [7,47,48,49,50], and in a study comparing PBDE concentrations in indoor dust collected by different methods, Bjorklund et al. (2012) [50] found that PBDE concentrations in floor dust from vacuum cleaner bags were exceeded by those in researcher-collected dust from elevated surfaces [50]. Similarly, by following the same researcher-collected method for both surfaces, Cequier et al. (2014) [51] found that the median concentration of BDE-209 and non-PBDEs in ESD ($n = 12$) are slightly higher than in FD ($n = 48$), but the difference was not significant. In contrast, concentrations of PBDEs in dust from elevated surfaces in Korean primary schools were lower than those in floor dust [52]. Elucidating whether differences in BFR contamination exist between floor and elevated surface dust is important as the two dust types likely influence human exposure in different ways. While young children are likely more exposed to floor dust, adults likely have greater contact with elevated surface dust. Hence, significant differences between the levels of contamination between floor and elevated surface dust has implications for human exposure assessment.

Against this backdrop, this study tests the hypothesis that concentrations of PBDEs and selected NBFRs in dust from elevated surfaces will exceed significantly those in floor dust from the same rooms. We also aimed to provide the first evaluation of the exposure of the Iraqi population to these contaminants. To test this hypothesis and achieve our aim, we determine concentrations of PBDEs and NBFRs in samples of elevated surface dust (ESD) and floor dust (FD) from 18 homes in Basrah, Iraq.

2. Materials and methods

2.1. Chemicals and standards

Individual standards of PBDE congeners and internal standards 2,4,4′-TriBDE (BDE-28), 2,2′,4,4′-TetraBDE (BDE-47), $^{13}C_{12}$-2,2′,4,4′-TetraBDE (MBDE-47), 2,2′,4,4′,5-PentaBDE (BDE-99), $^{13}C_{12}$-2,2′,4,4′,5-PentaBDE (MBDE-99), 2,2′,4,4′,6-PentaBDE (BDE-100), 2,2′,4,4′,5,5′-HexaBDE (BDE-153), $^{13}C_{12}$-2,2′,4,4′,5,5′-HexaBDE (MBDE-153), 2,2′,4,4′,5′,6-HexaBDE (BDE-154), 2,2′,3,4,4′,5′,6-HeptaBDE (BDE-183), DecaBDE (BDE-209) 50 ng/μL and $^{13}C_{12}$-DecaBDE (MBDE-209) 25 ng/μL, BTBPE, EH-TBB, BEH-TEBP, PBEB, and labelled internal standard $^{13}C_{12}$-BTBPE (MBTBPE), and $^{13}C_{12}$-BEH-TEBP (MBEH-TEBP) 50 ng/μL, and DBDPE 25 ng/μL were obtained from Wellington laboratories, Canada (all with purity >98%). Ethyl acetate (EA), Acetone (Ac), n-Hexane, dichloromethane (DCM), iso-octane and concentrated sulfuric acid were purchased from Fisher Scientific, UK. All solvents used during analysis were of analytical grade.

Silica gel (pore size 60 Å, 7–320 mesh) was purchased from Sigma Aldrich, Switzerland; anhydrous sodium sulfate was obtained from Sigma Aldrich, USA, and Florisil (particle size 60–100) was acquired from Fluka, USA. The NIST standard reference material (SRM 2585, "Organic Contaminants in House Dust") from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), ISOLUTE amino propyl columns, SPE cartridges and frits were purchased from Biotage (Uppsala, Sweden). Acid impregnated silica (44%, w/w) was prepared as described elsewhere [53]. Activated Florisil was prepared by baking at 450 °C for 1 h, cooling and subsequent cleaning with n-hexane (1 cycle extraction by Accelerated Solvent Extraction) and stored until use in a sealed pre-cleaned glass bottle.

2.2. Sample collection

From urban houses in Basrah province, South Iraq (Fig. S1, supporting materials), 2 dust samples were collected from each of 18 houses, between July and August 2013. In each house, one sample was collected from the living area floor (referred to here as floor dust - FD), with a second sample collected that comprised settled dust from elevated surfaces in the same living area such as tables, shelves, bookcases (referred to here as elevated surface dust - ESD). Home-owners were requested to not vacuum floors or elevated surfaces for at least 1 week before sampling. Floor dust samples were collected using a vacuum cleaner (DIRT DEVIL-DDMHH1-1100W), according to a standardised method [10]. Briefly, 1 m^2 of carpeted floor was vacuumed for 2 min, while for bare floors, 4 m^2 surface was vacuumed for 4 min. Dust was retained using 25 μm pore size nylon sample socks (Allied Filter Fabric Pty Ltd, Australia) mounted in the furniture attachment tube of the vacuum cleaner. Elevated surfaces (typically between 80 and 150 cm height) were vacuumed for 2–4 min depending on the surface area. After sampling, socks were closed with a twist tie, sealed in a plastic bag and stored at −20 °C. Before sampling, the furniture attachment and the vacuum tubing were cleaned thoroughly using an isopropanol-impregnated disposable wipe. At the time of sample collection, information on potential influences on BFR contamination such as: the number and type of putative sources like electronic devices, foam-filled furniture and floor material, ventilation system, house cleaning method, occupants and time spent in the living area was recorded. Samples were subsequently transferred to Birmingham, UK, for sieving and