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Brominated and organophosphate flame retardants in indoor dust of Jeddah, Kingdom of Saudi Arabia: Implications for human exposure☆

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HIGHLIGHTS

- First study on the incidence of FRs from different micro-environments of KSA
- First study in literature reporting emerging Br/Cl FRs and OPFRs in AC filter dust
- Chlorinated alkyl phosphate, BDE-209, and DBDPE were major chemicals.
- Lower levels were observed in house dust than those of car and AC filter dust.
- Estimated risk assessment of BDE-99 for toddlers was high than the RfD values.

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ABSTRACT

Different flame retardants (FRs) namely polybrominated diphenyl ethers (PBDEs), emerging brominated/chlorinated flame retardants (Br/Cl FRs), and organophosphate FRs (OPFRs) were analyzed in cars, air conditioner (AC) filters and floor dust of different households from Jeddah, Kingdom of Saudi Arabia (KSA). To the best of our knowledge, this is first study in literature reporting emerging Br/Cl FRs and OPFRs in AC filter dust and also first to report on their occurrence in dust from KSA. Chlorinated alkyl phosphate, penta-BDEs, BDE-209, and decabromodiphenylethane (DBDPE) were the major chemicals in dust samples from all microenvironments. ΣOPFRs occurred at median concentrations (ng/g dust) of 15,400, 10,500, and 3750 in AC filter, car and house floor dust, respectively. For all analyzed chemicals, relatively lower levels were observed in floor dust than car and AC filter dust. The profiles of FRs in car dust were different from AC filter and floor dust, which reflected their wider application as FR and plasticizer in variety of household and commercial products. For toddlers, assuming high dust intake and 95th percentile concentrations, the computed exposure estimation for BDE-99 was higher than RfD values.

1. Introduction

Brominated flame retardants (BFRs) and organophosphate flame retardants (OPFRs) are diverse group of chemicals that are used in consumer products as FRs to prevent and minimize fire hazards and/or as plasticizers (Besis and Samara, 2012; Covaci et al., 2011; Wei et al., 2015). They have found a wide range of applications in consumer products and building materials including printed circuit boards, thermal insulation boards, housing for electronic and electrical equipment, fabrics and furniture foams, wall coverings, floor finishing products, antifoaming agents and hydraulic fluids (Besis and Samara, 2012; Covaci et al., 2011; Wei et al., 2015). Most of these chemicals are used as additives rather than chemically bonded to the product matrix, thus easily released into the environment, where their persistence leads to widespread exposure to humans through various pathways such as dermal

☆ Capsule: First study on the incidence of emerging flame retardants from different micro-environments of KSA, which also highlighted that estimated exposure to BDE-99 poses via dust for Saudi toddler is high.

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contact, ingestion, and inhalation among other sources (Johnson-Restrepo and Kannan, 2009; Meeker and Stapleton, 2010). The exposure to these contaminants is of great concern due to the potential health risks to endocrine disruption, neurodevelopment, hepatic and behavioural abnormality and many of them have possible carcinogenic properties (McDonald, 2002; Meeker and Stapleton, 2010). Such evidences have contributed to list polybrominated biphenyl ethers (PBDEs) formulations (penta- and octa-BDE) under the Stockholm Convention list of persistent organic pollutants (POPs), while use of deca-BDEs has also been subjected to restrictions (European Court of Justice, 2008). Despite the legislative measures, human exposure to PBDEs is likely to continue for some time due to their persistence in the environment and presence in number of consumer materials (Ali et al., 2013a, 2014; Dirtu et al., 2012). Moreover, strict regulations have also paved way for alternative FRs as replacements for the regulated/banned formulations (Covaci et al., 2011; Wei et al., 2015). In recent years, several studies have investigated the occurrence of alternative FRs as well as PBDEs at high concentration into dust from different countries (Ali et al., 2013a; Dirtu et al., 2012; Wang et al., 2010). These alternative FRs were described less persistent and less likely to bio-accumulate than their predecessors, but recent studies have documented their occurrence in different environmental samples including air, dust, humans and household pets (Ali et al., 2013a,b; Li et al., 2015; Yang et al., 2014).

Indoor dust has been associated with human exposure to various organic contaminants and risk posed to human health by indoor contaminants particularly to the most vulnerable groups, such as toddlers and pregnant women is of great concern (Ali et al., 2013a; Stapleton et al., 2012; Vorkamp et al., 2011). People spend more time inside the home/office, while indoor they are continuously exposed to chemicals via dust ingestion, inhalation and dermal contact (Meeker and Stapleton, 2010; Mercier et al., 2011). However, no information is available about the occurrence of these FRs in the indoor environment of Kingdom of Saudi Arabia (KSA). Therefore, reporting these chemicals in indoor media from the country is important. The objectives of the study were to evaluate the levels and profiles of various FRs in indoor dust from three microenvironments of Jeddah, KSA, and estimate exposure to these chemicals for toddlers and adults via dust ingestion.

2. Experiment methodology

2.1. Materials

PBDE congeners 28, 47, 99, 100, 153, 154, 183, and 209, emerging brominated/chlorinated flame retardants (Br/Cl FRs) namely decabromodiphenylethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), dechlorane plus (DPs), and following OPFRs, tris-(2-chloroethyl)-phosphate (TCEP), tris-(1,3-dichloro-isopropyl)-phosphate (TDCPP), tris-(1-chloro-2-propyl)-phosphate (TCPP), triphenyl phosphate (TPhP), tris(2-ethylhexyl) phosphate (TEHP), tri-n-butyl phosphate (TnBP), tris(2-butoxyethyl) phosphate (TBEP), 2-ethylhexyl-diphenyl phosphate (EHDPP) were analyzed in this study.

Standards for PBDEs and emerging Br/Cl FRs were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany) and Wellington Laboratories (Canada), respectively. Standards of TnBP, TPhP, TCEP, TEHP, EHDPP, TBEP and TDCPP (mixture of 2 isomers) were purchased from Chiron AS (Trondheim, Norway), while TCPP (mixture of 3 isomers) were obtained from Pfaltz & Bauer (Waterbury, CT, USA). Purity of analytical standards for OPFRs was >98%, except for TBEP (>94%). Internal standards (ISs) BDE 77 and BDE 128 (AccuStandard Inc., USA), $^{13}C_{12}$-BDE 209, ^{13}C-TBPH, ^{13}C-anti-DP, ^{13}C-syn-DP, (Wellington Laboratories), TAP (TCI Europe, Zwijndrecht, Belgium), labelled TPP-d_{15}, TDCPP-d_{15}, TBEP-d_6, TCEP-d_{12} (Sigma) were used to quantify these chemicals.

All solvents used during the analysis were of pesticide-grade. Acetone, dichloromethane (DCM), ethyl acetate, iso-octane and toluene were purchased from Merck (Darmstadt, Germany), while *n*-hexane was purchased from Acros Organics (Geel, Belgium). Concentrated sulfuric acid (98%) (H_2SO_4) and silica gel were purchased from Merck. Empty polypropylene filtration tubes (3 mL) SPE cartridges and 500 mg/3 mL Supelclean™ ENVI™ — Florisil® cartridges were purchased from Supelco (Bellefonte, PA, USA). Silica gel was washed with Hex and activated overnight at 140 °C. Prior to each experiment, silica was heated for 2 h at 140 °C for activation. Acid impregnated silica (44%, w/w) was prepared by adding drop wise 22 mL concentrated sulphuric acid (98%) to 50 g silica under continuous stirring. All glassware was soaked for 12 h in an alkali solution (diluted RBS 35, pH 11–12) to degrade any remaining chemicals. After washing, the glassware was rinsed with water and dried at 400 °C for 5 h. All glass wares were rinsed thoroughly with *n*-hexane before use.

2.2. Sampling and sample preparation

Indoor dust samples ($N = 45$) were collected from Jeddah, KSA (household floor ($N = 15$), AC filter ($N = 15$), and cars ($N = 15$), brief details about the sampled microenvironments are given in Table S-1. For floor dust, a portion of dust from vacuum cleaner bags were collected from volunteer houses, wrapped in aluminum foil and marked accordingly. Similarly, AC filters were taken out from the AC (window/split) and dust was brushed off on spread piece of aluminum foil with pre-cleaned brush, wrapped, marked and transferred to the lab. To avoid cross contamination, brushes from the respective houses were used after pre-cleaning. For car dust, inside of the car (dash board, seats, and trunk) except floor was vacuumed and, before each sample, the vacuum cleaner was cleaned thoroughly to avoid any cross contamination. For QA/QC, field blanks using pre-washed Na_2SO_4 was used as dust. Na_2SO_4 (1 g) was spread on aluminum foil and collected with vacuum cleaner the same way as dust from vehicles. For every 5 vehicle dust samples, we collected 1 filed blank. To achieve homogenized samples, 250 μm mesh size was used to sieve all samples. Details about sampled sites were collected on a well prepared questionnaire.

The sample extraction and purification method is described in detail elsewhere (van den Eede et al., 2012). Briefly, an accurately weighed aliquot of dust (typically 50 mg) was spiked with internal standards and extracted by ultra-sonication and vortexed with *n*-hexane: acetone (3:1, v/v). Florisil was used to obtain two fractions; a 1st fraction was eluted with 8 mL Hex and a 2nd fraction with 10 mL ethyl acetate. All PBDEs and emerging Br/Cl FRs, except TBPH, were present in the 1st fraction, while TBPH and OPFRs were present in the 2nd fraction. After concentration under nitrogen, the 1st fraction was further cleaned on acid silica (44%) and analytes were eluted with 10 mL *n*-hexane: DCM (1:1, v/v). After evaporation to dryness, each fraction was re-solubilised in 100 μL of *iso*-octane prior to GC–MS analysis.

2.3. Instrumentation

Details about the instrumentation are found elsewhere (van den Eede et al., 2012). In summary, the analysis of emerging Br/Cl FRs and PBDEs was performed by 6890 Agilent (Palo Alto, CA, USA) gas chromatography (GC) coupled to a 5973 mass spectrometer (MS) operated in electron capture negative ionization (ECNI). A DB-5 column (15 m × 0.25 mm × 0.10 μm) was used for separation and the MS was deployed in selected ion monitoring (SIM) mode. The ion source, quadrupole and interface temperatures were set at 200, 150 and 300 °C, respectively. The analysis of OPFRs was performed by GC–MS in electron ionization (EI) mode. A HT-8 column (25 m × 0.22 mm × 0.25 μm) was used and the MS was operated in SIM mode with two characteristic ions acquired for each compound. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively.