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Occurrence and sources of brominated and organophosphorus flame retardants in dust from different indoor environments in Barcelona, Spain

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ABSTRACT

In this study, the simultaneous presence of eight polybrominated diphenyl ethers (PBDEs), nine new brominated flame retardants (NBFRs) and ten organophosphorus flame retardants (OPFRs) was investigated in dust samples collected from different indoor environments (homes, schools, theatres, a university and a Research Institute) in Barcelona, Spain. OPFRs were detected at the highest concentrations followed by PBDEs. ∑OPFRs ranged from 2053 to 72,090 ng g^{-1} and tris(2-chloroisopropyl) phosphate (TCIPP) was the most abundant compound. BDE-209 was the main PBDE congener detected (up to 14,990 ng g^{-1}), while other PBDEs ranged from 2.6 to 118 ng g^{-1}. Among the studied NBFRs, decabromodiphenyl ethane (DBDPE – up to 4432 ng g^{-1}) followed by bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP – up to 508 ng g^{-1}) were detected at the highest concentration, whereas a lower detection frequency was observed for 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), pentabromotoluene (PBT) and hexabromobenzene (HBB). The levels and profile of flame retardants (FRs) were characteristic of each environment, where theatres followed by homes presented the highest concentrations and schools had the lowest levels. Principal Component Analysis permitted to identify the main sources and distribution of all FRs, according to specific uses in each environment. The simultaneous presence of all FR families in indoor dust points to the need to monitor these compounds to minimize human exposure.

1. Introduction

Flame retardants (FRs) are a group of chemicals applied to different materials to reach fire safety standards adopted by many countries (BSI, 1982; OJEC, 1995, 2000). Several organic and inorganic compounds based on bromine (e. g. high brominated aromatic and cycloaliphatic compounds), chlorine (e.g. chloroparaffins, declorane plus), phosphorus (e. g. phosphate-esters, phosphonates and phosphinates, ammonium phosphate), nitrogen (e. g. melamine and melamine derivatives), boron (e.g. sodium borate, borax and zinc borates), and metallic hydroxides are used for this purpose (SpecialChem, 2013). The choice of the appropriate flame retardant, or combination of them, is dependent of the type material and the desired performance for the final product.

Some families of FRs that were used in the past or that are nowadays in use are of concern because of their toxicity to humans and to the environment. Flame retardant formulations containing polybrominated diphenyl ethers (PBDEs) were extensively applied to textiles, furniture, electronic and building materials after 1970s (Alaee et al., 2003). PBDEs present high bioaccumulation potential, are endocrine disruptors and neurotoxicants (Darnerud, 2003; Vonderheide et al., 2008; WHO, 1994) and these characteristics lead to their restriction/ban in Europe (ECJ, 2008; OJEU, 2003a, 2003b, 2005). Due to these bans, other organic flame retardants have been used as PBDE substitutes, such as new brominated flame retardants (NBFRs) and organophosphorus flame retardants (OPFRs) (Covaci et al., 2011; van der Veen and de Boer, 2012), but the safety of these compounds to humans and to the environment still needs to be elucidated. Some NBFRs are structurally similar to PBDEs indicating that these chemicals have a potential for bioaccumulation and toxicity (Ezechiáš et al., 2014). On the other hand, OPFRs may pose a risk to humans, for instance tris(2-chloroethyl) phosphate (TCEP) is classified as carcinogen (category 3) (ECHA, 2008) and tris(1,3-dichloropropyl)

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phosphate (TDCIPP) was carcinogenic at all exposure doses that were tested in rats (WHO, 1998). Thus, although the use of FRs are advantageous when considering the decreasing death and injuries associated to fires (EFRA, 2005), there is a concern regarding the exposition to these substances due to the potential toxicity that some FRs pose to humans and to the environment.

Many flame retardants are additives (not chemically bound) and thus they are released from the host materials throughout their lifetime to the surrounding environment due to volatilization and mechanical abrasion, tending to accumulate in dust particles (Liagkouridis et al., 2014; Rauert et al., 2014). The materials commonly found at homes, schools, workplaces and public places that are potential sources of OPFRs, NBFRs and PBDEs include: (i) rigid polyurethane (PU) foam – used in insulation, construction and refrigeration; (ii) flexible PU foam – used in furniture and upholstery; (iii) textiles; (iv) acrylonitrile-butadiene-styrene (ABS) and high impact polystyrene (HIPS) typically used in enclosures of electric and electronic equipments (EEE), such as computers, printers, TVs, etc.; (v) polyethylene and polyvinyl chloride (PVC), used in wiring and cables and cable jacketing; (vi) polypropylene used in cable conduit, power cables, connectors, seats, fibers (carpets, seats, etc.); (vii) polyamides used in medium voltage components, insulation, switch casings, plug connectors, terminal blocks, etc. (SpecialChem, 2013). Consequently, mixtures of flame retardants of different families are found in dust samples from indoor environments, such as homes, offices, schools and workplaces (Ali et al., 2012; Mizouchi et al., 2015; Stapleton et al., 2009).

Non-intentional ingestion of dust particles and dermal absorption was indicated as a significant human exposure route to FRs (Kim et al., 2013; Lim et al., 2014; Abdallah et al., 2015). This exposure pathway is of special concern for toddlers since their more frequent hand-to-mouth contact and close-to-ground behaviour could lead to higher amount of dust ingestion, and their lower body weigh results in a higher daily exposure. Some brominated FRs have potential to affect endocrine functions and the central nervous and reproductive systems (Lyche et al., 2015). Concerning the OPFRs, their presence in floor dust was suggested to be associated with the prevalence of asthma, atopic dermatitis and allergic rhinitis (Araki et al., 2014). Thus, studies on the occurrence of different flame retardant families in indoor dust are necessary given that these chemicals can pose a threat to human health. The aim of this work was to evaluate the co-occurrence of PBDEs, NBFRs and OPFRs in dust samples collected in homes and public places (schools, theatres and research institute/university) in Barcelona in order to identify specific compound profiles and sources of these compounds in each indoor environment.

2. Materials and methods

2.1. Chemicals

A PBDE mix (BDEs 28, 47, 99, 100, 153, 154, 183 and 209) in *n*-nonane at 1 μg mL^{-1} was acquired from Cambridge Isotope Laboratories (Andover, USA). Individual solution of 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) at 50 μg mL^{-1} in 5% toluene in nonane, decabromodiphenyl ethane (DBDPE) at 25 μg mL^{-1} in toluene, bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), pentabromotoluene (PBT), 2,4,6-tribromophenyl 2,3-dibromopropyl ether (TBP-DBPE), 5,6-dibromo-1,10,11,12,13,13-hexachloro-11-tricyclo[8.2.1.02,9]tridecene (DBHCTD) and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB) (at 50 μg mL^{-1} in toluene) were acquired from Wellington Laboratories (Guelph, Canada). Hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), tris(2-choroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tris(phenyl) phosphate (TPHP), 2-ethylhexyl diphenyl phosphate (EHDPHP) and tris(butyl) phosphate (TNBP) were acquired from Sigma Aldrich (Germany). TCIPP was acquired as a mixture of isomers (tris(2-chloroisopropyl) phosphate, bis(1-chloro-2-propyl)-2-chloropropyl phosphate, and bis(2-chloropropyl)-1-chloro-2-propyl phosphate). Tris(2-butoxyethyl) phosphate (TBOEP), tris (2-ethylhexyl) phosphate (TEHP) and tris(methylphenyl) phosphate (TMPP) were acquired from Dr. Ehrenstorfer (Augsburg, Germany). Tris(isobutyl) phosphate (TIBP) at 1000 μg mL^{-1} was acquired from Chiron (Trondheim, Norway). The surrogates [$^{13}C_6$]hexabromobenzene (MHBB) at 50 μg mL^{-1} in toluene, 3,3′,4,4′-tetrabromo[$^{13}C_{12}$]diphenyl ether (MBDE-77) at 50 μg mL^{-1} in nonane and decabromo[$^{13}C_{12}$]diphenyl ether (MBDE-209) at 25 μg mL^{-1} in toluene, were acquired from Wellington Laboratories (Guelph, Canada). Tris(phenyl) phosphate-D15 (TPHP-D15) was acquired from Sigma Aldrich (Germany). Tris (butyl) phosphate-D27 (TNBP-D27) was acquired from Cambridge Isotope Laboratories (Andover, USA). The internal standards 2,3,5,6-tetrachlorobiphenyl (PCB-65) and decachlorobiphenyl (PCB-209), both at 10 μg mL^{-1} in iso-octane, were acquired from Dr. Ehrenstorfer (Augsburg, Germany). Ethyl acetate and toluene were acquired from Merck (Darmstadt, Germany). Cyclohexane was acquired from Scharlau (Sentmenat, Spain). Florisil cartridges were acquired from Waters (5 g, 20 cc).

2.2. Sampling

Dust samples were collected in Barcelona (Spain) from five homes, four schools, three theatres, one research institute and one university. The characteristics of each are given in Table 1. Vacuum cleaner bag from the apparatus used for vacuuming in each particular environment was provided by the responsible person in each sampling place. The accumulated dust was carefully removed from vacuum cleaner bag, sieved (500 μm) and stored at −18 °C until analysis. When necessary, hair and other strange materials were manually removed using tweezers.

2.3. Extraction and analysis

Extraction was performed as described elsewhere (Cristale and Lacorte, 2013). Briefly, 0.1 g of dust was spiked with the surrogate standards and extracted with 10 mL of ethyl acetate/cyclohexane (5:2 v/v) in an ultrasonic bath (10 min) (three times). The extract was concentrated to 1 mL under N_2 flow in a Turbovap, and subjected to clean-up using Florisil cartridges. Cartridges were conditioned with 30 mL of ethyl acetate/cyclohexane (5:2 v/v) and after placing the extract on top of the cartridge, compounds were eluted with 30 mL of the same solvent mixture, then the solvent was concentrated under N_2 flow to almost dryness and reconstituted in toluene containing the internal standards PCB-65 and PCB-209 at 0.05 μg mL^{-1}. Six procedural blanks were extracted and analyzed together with the samples. OPFRs in procedural blanks were detected at concentrations from 0.2 to 14% of the observed OPFR concentrations in dust samples, and no correction considering blank contribution was done. Details concerning limits of detection of the method (MDL) and extraction efficiency were described in that previous study (Cristale and Lacorte, 2013). In short, MDL ranged from 2.0 to 275 ng g^{-1} for PBDEs, from 5.0 to 237 ng g^{-1} for NBFRs and from 3.8 to 288 ng g^{-1} for OPFRs. TBOEP had an error of $-80 \pm 3\%$ in relation to the assigned OPFRs levels for the reference material SRM 2585 – NIST (house dust), as observed by participating in an interlaboratory study (Cristale and Lacorte, 2013). Given the low recovery of TBOEP, its presence is reported in this study as semi quantitative levels.

Extracts were analyzed by GC-EI-MS/MS in a GC Agilent 7890 A