Environmental Pollution xxx (2017) 1–9

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Occurrence and human exposure to brominated and organophosphorus flame retardants via indoor dust in a Brazilian city☆

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ARTICLE INFO

Article history:
Received 26 May 2017
Received in revised form
26 October 2017
Accepted 28 October 2017
Available online xxx

ABSTRACT

Indoor dust is considered an important human exposure route to flame retardants (FRs), which has arised concern due the toxic properties of some of these substances. In this study, ten organophosphorus flame retardants (OPFRs), eight polybrominated diphenyl ethers (PBDEs) and four new brominated flame retardants (NBFRs) were determined in indoor dust from different places in Araraquara-SP (Brazil). The sampled places included houses, apartments, offices, primary schools and cars. The analysis of the sample extracts was performed by gas chromatography coupled to mass spectrometry and two ionization techniques were used (electron ionization – EI; electron capture negative ionization – ECNI). OPFRs were the most abundant compounds and tris(2-butoxyethyl) phosphate (TBOEP), tris(phenyl) phosphate (TPHP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP) and tris(2-chloroisopropyl) phosphate (TCIPP) were present at the highest concentrations. Among the brominated FRs, the most ubiquitous compounds were BDE-209, bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP) and decabromodiphenyl ethane (DBDPE). Statistical analysis revealed that there were differences among dust typologies for TBOEP, TDCIPP, ethylhexyl diphenyl phosphate (EHDPHP), BDE-209, 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), BEH-TEBP and DBDPE, which were attributed to different construction materials in each particular environment and to the age of the buildings. The highest levels of brominated FRs were observed in offices, TBOEP was at high concentration in primary schools, and TDCIPP was at high concentration in cars. A preliminary risk assessment revealed that toddlers were exposed to TBOEP levels higher than the reference dose when considering the worst case scenario. The results obtained in this study showed for the first time that although Brazil does not regulate the use of FRs, these substances are present in indoor dust at levels similar to the observed in countries that have strict fire safety standards, and that humans are exposed to complex mixtures of these contaminants via indoor dust.

1. Introduction

Indoor dust is considered an important human exposure route to semivolatile organic compounds (e.g. organochlorine pesticides, phthalates, polycyclic aromatic hydrocarbons, flame retardants, etc.) via respiration or ingestion of dust particles (Ait Bamai et al., 2014; Ali et al., 2013; Qi et al., 2014). Concerning Flame Retardants (FRs), the unintentional ingestion of indoor dust represents a human exposure pathway (Jones-Otazo et al., 2005). FRs are applied in a great variety of polymeric materials such as textiles, plastics, rubbers, electronic circuit boards and polyurethane foam, which are used in furniture, materials and coverings for buildings, electric and electronic equipments, etc. (SpecialChem, 2013). Leaching of FRs from materials to dust occurs due mechanical abrasion, direct contact migration and volatilization followed by gas/particle partitioning (Rauert and Harrad, 2015), and consequently, FRs are widely present in indoor dust (e.g. homes, workplaces, schools and transportations) (Ali et al., 2016b; Brommer and Harrad, 2015; Cequier et al., 2014; Saito et al., 2007).

☆ This paper has been recommended for acceptance by Dr. Chen Da.

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https://doi.org/10.1016/j.envpol.2017.10.110
0269-7491/

The concern on human exposure to FRs is because some of these chemicals are endocrine disruptors, neurotoxicants and carcinogenics (Chao et al., 2011; EURAR, 2009; Lyche et al., 2015; WHO, 1998). The polybrominated diphenyl ethers (PBDEs) are toxic to humans and their possible negative effects include reduced reproductive capacity in women, longer periods of menstruation, disturbances in thyroxine (T4), triiodothyronine (T3) and hormones stimulated by the thyroid system, prevalence of diabetes, and delay on neurological development (Chao et al., 2011). These toxic effects associated to their persistency and bioaccumulation potential resulted in bans and a phase out of PBDEs in many countries (OJEU, 2003; UNEP, 2009; USEPA, 2009). Consequently, industries started to use other alternative substances to get specific fire safety standards for their manufactured products and materials. Organophosphorus flame retardants (OPFRs) and new brominated flame retardants (NBFRs) have been used as PBDE substitutes, but some of these chemicals are also suspected to cause negative effects to humans. For example, tris (2-chloroethyl) phosphate (TCEP) and tris (2,3-dichloropropyl) phosphate (TDCIPP) are potential carcinogenic (EURAR, 2009; WHO, 1998).

Human exposure to complex mixtures of PBDEs, NBFRs and OPFRs present in indoor dust was reported for North American (Schreder and La Guardia, 2014), European (Cequier et al., 2014; Cristale et al., 2016; Kademoglou et al., 2017), Asian (Ali et al., 2016b) and Oceanian countries (Ali et al., 2012). The FR levels reported in these studies ranged from units of ng g^{-1} to tens of μg g^{-1} and their distribution was related to the consumption patterns of FR formulations in each country or region. In contrast, little is known about the presence of FRs in indoor dust in countries that do not regulate the use of these substances, as is the case of many South American countries, including Brazil.

The aim of this study was to generate data regarding human exposure to flame retardants via indoor dust in Araraquara (Brazil). PBDEs, NBFRs and OPFRs were determined in indoor dust collected from houses, apartments, primary schools, offices and cars. Measured concentrations were used for estimating the human exposure to FRs via dust ingestion. To the best of our knowledge, this is the first study reporting occurrence and human exposure to FRs via indoor dust in a South American country.

2. Material and methods

2.1. Chemicals

The analytical standards used in this study included: eight PBDEs (BDE-28, 47, 99, 100, 153, 154, 183 and 209); four NBFRs (bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE)); ten OPFRs (tris(2-choroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tris(butyl) phosphate (TNBP), tris(isobutyl) phosphate (TIBP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-ethylhexyl) phosphate (TEHP), tris(phenyl) phosphate (TPHP), 2-ethylhexyl diphenyl phosphate (EHDPHP) and tris(methylphenyl) phosphate (TMPP)); four surrogates (3,3′,4,4′-tetrabromodiphenyl ether (BDE-77), decabromo[$^{13}C_{12}$]diphenyl ether (MBDE-209), tris(phenyl) phosphate-D15 (TPHP-D15) and tris(butyl) phosphate-D27 (TNBP-D27)); and an internal standard (decachlorobiphenyl (PCB-209)). A detailed description of the analytical standards used is presented in the Text S1 (Supplementary Material).

Ethyl acetate (99.9% purity) was acquired from Sigma-Aldrich (Germany). Toluene was acquired from Macron (USA) and cyclohexane from JT Baker (USA). Florisil cartridges (1 g, 6 mL) were purchased from Agilent (USA).

2.2. Sampling

Dust samples were collected from 10 houses (living room and bedroom), 10 apartments (living room and bedroom), 5 primary schools (two classrooms), 5 offices (main room) and 16 cars (cabin) in Araraquara city, Sao Paulo State, Brazil. Dust samples were collected using a household vacuum cleaner Easy Box 1600W (Electrolux). Dust particles were retained in a filter paper (4–12 μm pore size, 150 mm diameter) folded as a cone and placed between the hose and the crevice tool nozzle. One filter was used in each environment and was replaced with a new one for each site. Each indoor place (houses, apartments, offices and schools) were vacuumed during a total time of 12 min and included vacuuming the floor, the surfaces and the upholstery (if present). The sampling protocol for houses, apartments and offices consisted in maintaining the vacuuming time ratio of floor, surfaces and upholstery as 3:2:1 (min), respectively. For schools since no upholstery was present the vacuuming time ratio of floor and surfaces was 4:2 (min), respectively. Cars were vacuumed during 6 min, consisting on 3 min from car seat and 3 min from other surfaces. Car floor was not vacuumed. Table 1 presents the sampling details. This vacuuming protocol was used for comparison purposes among the different environments.

After sampling, the end of the vacuum cleaner nozzle was wrapped carefully with aluminium foil to avoid loss of sample material and contamination during transportation. In the laboratory, the filter paper cone was removed from the vacuum cleaner and dust samples were sieved (250 μm mesh), placed in glass vials and stored in the freezer until analysis. In this study we analysed the dust size fraction <250 μm because it has higher adherence to human skin (Hee et al., 1985; Yamamoto et al., 2006). Tweezers were used for manual removal of hair and other bulk materials. The nozzle was cleaned with ultrapure water, dried with lint free paper tissue and wrapped in aluminium foil till next sampling.

2.3. Extraction and analysis

The extraction protocol described in a previous study (Cristale and Lacorte, 2013) was adapted to fit with the lower sample mass (50 mg of dust) extracted in this study, so that the ratio of extraction solvent/sample mass and the ratio of florisil sorbent mass/solvent volume used for elution were maintained. Details about the extraction and clean-up procedure are presented at Text S2 (Supplementary Material).

PBDEs, NBFRs and OPFRs were determined using a GC Agilent 7890A equipped with 7000A GC-MS Triple Quadrupole which can operate using electron ionization (EI) or chemical ionization (CI). A DB-5MS column of 15 m (length) x 0.250 mm (I.D.) x 0.10 μm (film) (J&W Scientific, USA) was used. GC-EI-MS/MS conditions used for determination of FRs were described elsewhere (Cristale and Lacorte, 2013). BDE-209 and DBDPE were determined using electron capture negative ionization (ECNI) mode and selective ion monitoring (SIM) as described elsewhere (Cristale et al., 2012). Table S1 (Suplementary Information) presents the instrumental conditions used in this study.

2.4. Quality control

Ten standard solutions at concentrations ranging from 0.001 to 1 μg mL^{-1} in toluene (except for BDE-209 and DBDPE that ranged from 0.01 to 10 μg mL^{-1}) were used for calibration of the GC-MS system. In order to guarantee a quantification within the linear range ($r^2 > 0.99$ and relative error < 20%) more than one calibration curve (with at least 5 points) was used when necessary.

To evaluate the extraction efficiency, a house dust sample was

Please cite this article in press as: Cristale, J., et al., Occurrence and human exposure to brominated and organophosphorus flame retardants via indoor dust in a Brazilian city, Environmental Pollution (2017), https://doi.org/10.1016/j.envpol.2017.10.110