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Brominated, chlorinated and phosphate organic contaminants in house dust from Portugal

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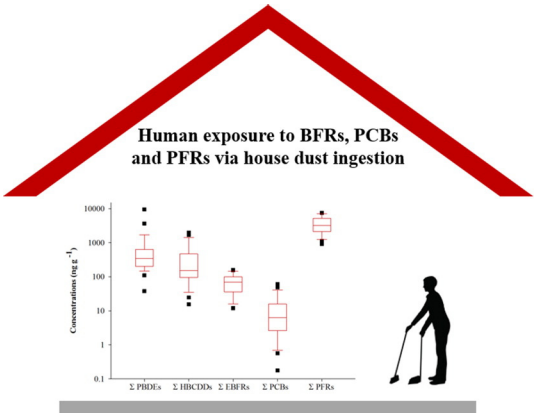
HIGHLIGHTS

- Levels of BFRs, PCBs and PFRs in 28 house dust samples from central Portugal
- PFRs were the main contaminants followed by PBDEs, HBCDDs, DBDPE, PCBs and BTBPE.
- Levels of DBDPE and PCBs higher in smaller houses and urban locations
- Intakes via dust ingestion were estimated for adults and children
- Estimated daily intakes were below RfDs

GRAPHICAL ABSTRACT



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ABSTRACT

House dust is an important matrix to evaluate the human exposure to a large number of contaminants including organochlorine compounds and flame retardants. In this study, we measured the levels of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), polychlorinated biphenyls (PCBs) and several organophosphorus flames retardants (PFRs) in 28 house dust samples collected between 2010 and 2011 in two Portuguese cities, Aveiro and Coimbra. Among the measured compounds, PFRs, particularly tris(2-ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPHP), 2-ethylhexyl diphenyl phosphate (EHDPP) and tris(methylphenyl) phosphate (TMPP), were the dominant group (median: 3200 ng g^{-1}). PBDE levels were the second highest (median: 340 ng g^{-1}) with great predominance of BDE 209 (median 270 ng g^{-1}), followed by HBCDDs (median: 150 ng g^{-1}), DBDPE (54 ng g^{-1}), PCBs (median: 6.3 ng g^{-1}) and BTBPE (median: 1.2 ng g^{-1}). Estimated daily intakes (EDIs) via dust ingestion showed a higher intake of PFRs (median: 4.6 ng kg-bw^{-1} day); however for

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PCBs
PFRs

all contaminants the EDIs were much lower than the established reference dose (RfD) values. Therefore, the studied population is exposed to non-hazardous levels of the target compounds when considering the exposure through house dust ingestion.

1. Introduction

Indoor dust is a repository of many organic and inorganic contaminants (Butte and Heinzow, 2002). As modern people tend to spend about 85–98% of their time indoors (Liagkouridis et al., 2014) exposure to indoor dust is inevitable. Therefore, house dust has been used to evaluate human exposure to a large number of compounds accumulated indoors.

Polychlorinated biphenyls (PCBs) and flame retardants (FRs) are two typical groups of compounds detected in house dust known to be hazardous to human health. FRs have been applied in various products that contain potentially flammable materials in order to reduce the devastating impact of fires. They have the ability to minimize the flame spread and the generation of smoke by slowing the combustion of polymers (Fromme et al., 2014). However, the provided safety benefits have currently been side by side with the concern of environmental contamination, toxicity and deleterious effects to animal and human health. About 200 distinct chemicals are used as FRs (Webster and Stapleton, 2012), these chemicals exhibit different structures and properties and can be inorganic or organic. This latter category includes organohalogenated and organophosphorus compounds.

PCBs unique properties such as chemical stability, high boiling point, low heat conductivity and high dielectric constants, led to their large industrial and commercial applicability (EFSA, 2005). Due to their non-flammability they were also manufactured as FRs from the late 1920s to the mid-1980s (Bergman et al., 2012), though the main application of PCBs was as dielectric oil in the transformers and capacitors. Since PCBs are classified as persistent organic pollutants (POPs), their usage was banned in the majority of industrial countries, hence they were substituted by other chemicals (EFSA, 2010).

Brominated flame retardants (BFRs), alongside with chlorinated flame retardants (CFRs), are included in the group of halogenated compounds (Bergman et al., 2012). BFRs include polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and emerging brominated flame retardants (EBFRs). PBDEs and HBCDDs stand out among the BFRs detected in the environment. However, the application of the three major commercial mixtures of PBDEs has already been banned in many countries. In 2004, the production of penta-BDE and octa-BDE mixtures was discontinued in Europe and United States (US). Four years later, the application of deca-BDE mixtures in electric and electronic devices was phased out in Europe and their use was completely banned in the US in 2013. HBCDDs commercialization was banned in August 2015 in Europe (Coelho et al., 2014).

As a consequence of these restrictions, some alternatives were introduced into the market including EBFRs and organophosphorus flame retardants (PFRs), thereby the demand for these FRs has been increasing in the last several years. For instance, the EBFRs, 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) arise as replacements for octa-BDEs and deca-BDEs, respectively (Newton et al., 2015).

Additionally, the consumption of PFRs has been growing considerably; in 2006 the European consumption of FRs was 465,000 tons of which 10% were BFRs and 20% were PFRs (van der Veen and de Boer, 2012). Similarly to BFRs, they are used in the manufacture of different products, such as plastics, polyurethane foams, thermosets, coatings and textiles. PFRs are divided into two main classes; (1) halogenated phosphates such as tris(2-chloroethyl) phosphate (TCEP) and tris (1,3-dichloro-2-propyl) phosphate TDCIPP, and (2) non-halogenated compounds, tripropyl phosphate (TPP), tri-n-butyl phosphate (TNBP), 2-ethylhexyl diphenyl phosphate (EHDPP), tricresyl phosphate (TMPP), tripentyl phosphate (TPEP), triphenyl phosphate (TPHP) and tris(2-ethylhexyl) phosphate (TEHP).

According to the vast literature published, the above-mentioned contaminants are widespread in the environment and are considered to be hazardous to wildlife and human health (e.g. Fromme et al., 2015; IARC, 2015; van der Veen and de Boer, 2012). Considering their toxicity and widespread occurrence in the indoor environment, and the lack of information regarding their indoor levels in Portuguese houses, the present study aims to evaluate the levels of selected FRs (PBDEs, HBCDDs, EBFRs and PFRs) and PCBs in house dust samples from two Portuguese cities (Aveiro and Coimbra).

2. Materials and methods

2.1. Collection of house dust samples

Dust sampling was carried out in two cities from central Portugal: Aveiro and Coimbra. Between February 2010 and November 2011, volunteers from Aveiro ($n = 18$) and from Coimbra ($n = 10$) were recruited by convenience and agreed to participate in the sampling campaign by signing an informed consent. The participants were asked to answer a questionnaire and to provide the vacuum cleaner bags that were currently in use to clean their respective residences. Hence, the bags collected in the different houses might correspond to different sampling periods (mean 90 days). In the surveyed houses all rooms were regularly vacuumed and therefore the dust samples collected reflect the contamination of the entire house. Housing characteristics, in which dust samples were collected, are described in Table 1. In our laboratory, house dust was removed from each vacuum cleaner bag and following the procedure described by similar studies (e.g. Ali et al., 2012b; Björklund et al., 2012; Brommer et al., 2012; Dirtu et al., 2012; Kim et al., 2013; Roosens et al., 2009; Van den Eede et al., 2012; Van den Eede et al., 2011), the sample was sieved through a stainless steel sieve (500 μm) to remove fibrous materials and large pieces in order to obtain a suitable degree of homogeneity. The samples were kept in clean amber glass vials and stored at −25 °C in the Environmental Specimen Bank (es-BANK) of Ehime University until chemical analysis.

2.2. Chemical analysis

Details of the analytical methods for BFRs, EBFRs, PCBs and PFRs were reported elsewhere (Asante et al., 2013; Kim et al., 2013).

2.2.1. BFRs, EBFRs and PCBs

About 2 g of each sieved dust sample were mixed with anhydrous sodium sulfate and extracted with a high speed solvent extractor (SE-100, Mitsubishi Chemical Analytech) using an acetone/hexane (1:1 *v*/*v*) solution. An aliquot of the extract corresponding to 1 g of dust was spiked with $^{13}C_{12}$-labeled PBDEs and $^{13}C_{12}$-labeled PCBs (5 ng each) and 10 ng of $^{13}C_{12}$-labeled HBCDDs as surrogates.

The spiked portion was treated with sulphuric acid (98%), washed with hexane-washed water, and then run through a multi-layer silica gel column for clean-up. The pre-clean-up solution was subjected to gel permeation chromatography (GPC: Bio-Beads S-×3, Bio-Rad, CA, 2 cm i.d. × 50 cm) with a mobile phase of dichloromethane/hexane (1:1 *v*/*v*) solution for further clean-up. The fraction containing organohalogen compounds was concentrated using a rotary evaporator and fractionated through a 4 g of activated silica gel (Wakogel DX)