Chemosphere 168 (2017) 1248–1256

Contents lists available at ScienceDirect

Chemosphere

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

Dioxin-like activities, halogenated flame retardants, organophosphate esters and chlorinated paraffins in dust from Australia, the United Kingdom, Canada, Sweden and China

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HIGHLIGHTS

- CPs were found in the highest concentrations in dust from all countries, followed by OPEs, HFRs and PBDEs.
- PBDEs showed different congener profile in dust from North America with predominance of the penta-mixture.
- CPs in dust from Sweden were predominated by the long-chain CPs while for other countries, medium-chain CPs predominated.
- PBDEs and CPs showed positive correlation with dioxin-like-activity in dust.

ARTICLE INFO

Article history:
Received 3 August 2016
Received in revised form
17 October 2016
Accepted 19 October 2016
Available online 1 November 2016

Handling Editor: J. de Boer

Keywords:
Dust
Dioxin-like activity
Halogenated flame retardants
Organophosphate esters
Chlorinated paraffins
Polybrominated diphenyl ethers

ABSTRACT

The concentrations of organic flame retardants (FRs) and dioxin-like activities in dust collected from five countries were investigated. The correlations between the concentrations of the different groups of FRs and dioxin-like activities were examined. Chlorinated paraffins (CPs, C_9 to C_{31}) were found in the highest concentration (median $\sum$CP 700 μg/g, range 280–4750 μg/g), followed by organophosphate esters (median $\sum_{13}$OPEs 56 μg/g, range 21–110 μg/g), halogenated flame retardants (median $\sum_{17}$HFRs 3.3 μg/g, range 0.87–14 μg/g) and polybrominated diphenyl ethers (median $\sum_{17}$PBDEs 2.8 μg/g, range 0.46–11 μg/g). There were no significant differences in concentrations of the FRs among the countries but differences in PBDE and CP congener profiles were found. BDE209 predominated in dust from Australia, the UK, Sweden and China, ranging from 50 to 70% of total PBDEs. The lowest percentage of BDE209 was found in the dust from Canada, representing only 20% of total PBDEs. For CPs in dust from Sweden, the long-chain CPs (especially C_{18} congeners) predominated, while for other countries, medium-chain CPs (especially C_{14} congeners) predominated. The dioxin-activities of the dusts ranged from 58 to 590 pg CALUX-TEQ/g, and had a median of 200 pg CALUX-TEQ/g. There were significant positive correlations between concentrations of PBDEs and CPs with dioxin-like activities. The dioxin-like activity may be due to the presence of polychlorinated or polybrominated dioxin/furans (PBDD/DFs) or polychlorinated naphthalenes (PCNs) in the dust. The PBDD/DFs are known impurities and degradation product of the penta-BDE mixture, and PCNs are known impurities of CPs which exhibit dioxin-like activities.

1. Introduction

Dust is a sink for many organic pollutants in the indoor environment and high concentrations of flame retardants (FRs) have been reported (Brommer et al., 2012; Johnson et al., 2010; Newton et al., 2015; Shoeib et al., 2012). The abundances and pattern of FRs

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http://dx.doi.org/10.1016/j.chemosphere.2016.10.074
0045-6535/

in dust are influenced by national fire regulations, which differ among countries. For example, deca-bromodiphenyl ethers (deca-BDEs) are phased-out in Europe and North America, but are still produced and used in China (Chen et al., 2012; Ma et al., 2012). North America used more penta-BDE relative to Europe (Law et al., 2014). Short-chain chlorinated paraffins (SCCPs, C_{10}-C_{13}) are restricted in Europe but not in China. As penta- and octa-BDE mixtures are banned under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2009), many non-BDE FRs, which are organic substances containing chlorine, bromine or phosphorous have been put on the market in large quantities worldwide. However, there is very limited information about the environmental fate, levels, production volumes, human exposure and toxicity of these substances. Few studies that have measured the levels of non-BDE FRs reported that concentrations of organophosphate esters (OPEs) in house dust from Norway were two orders of magnitude higher than for PBDEs and non-BDE brominated FRs (Cequier et al., 2014). Non-BDE halogenated FRs were ubiquitous in indoor dust, air and outdoor soils in Sweden and the UK (Newton et al., 2015). Several studies have found SCCPs and medium-chain chlorinated paraffins (MCCPs) in house dust at concentrations of micrograms per gram (Bitar, 2004; Fridén et al., 2011; Santillo et al., 2003).

Ingestion of dust is suggested to be an important human exposure pathway for poly-BDEs (PBDEs) and may pose a risk to human health (Lorber, 2008; Trudel et al., 2011). Suzuki et al. (2007) demonstrated that 2,3,7,8-tetrachloro dibenzo-*p*-dioxin (TCDD)-like activity level in Japanese indoor dust can be higher than those in contaminated sediments. Tue et al. (2010, 2013) analyzed house dust from an urban region of New York and e-waste recycling sites of Vietnam, and found that compounds with known potencies (PCDD/F, PBDD/F and co-planar polychlorinated biphenyls) only explained up to 50% of the dioxin-like activities measured *in vitro*, using the Dioxin Related Chemical-Activated LUciferase gene eXpression Analysis (DR-CALUX assay). Hence, there was still a substantial portion of unknown contaminants in dust that contributed to the overall *in vitro* dioxin-like activity.

The aim of this study was to measure the levels of the legacy (i.e. PBDEs) and non-BDE organic flame retardants in dust collected from different countries, characterize the dioxin-like activity and investigate if there were correlations between the dioxin-like activity and concentrations of the different FRs. Target FRs were i) non-BDE halogenated flame retardants (HFRs hereafter), which covers FRs containing bromine and chlorine, ii) PBDEs, iii) OPEs and iv) chlorinated paraffins (CPs), including the short-, medium- and long-chain congener groups (C_9 to C_{31}).

2. Materials and methods

2.1. Sample collection and preparation

Dust samples were kind gifts donated by collaborators from Australia ($n = 4$), UK ($n = 4$), Canada ($n = 6$), Sweden ($n = 5$) and China ($n = 5$). Samples were collected during 2008 and 2014 from offices, homes and non-residential buildings. Samples from each country were collected according to the procedure described in Harrad et al. (2008). Dust samples were obtained using vacuum cleaners with dust trapped in a nylon sampling sock inserted in the nozzle. Samples were a mix of floor dust and elevated surface dusts. Elevated surface dust refers to dust collected from surfaces of furniture, such as desks, computers, TV stands or shelves. Details of the sampling sites and dates are given in supplementary information, Table S1. All samples were sieved through a 500-μm sieve for removal of large debris and stored at −4 °C in amber glass jar until analysis.

2.2. Sample extraction

Each dust sample (0.5–2.5 g) was first mixed with 20 g of sodium sulfate (Kanto Chemical Co. Inc. Japan) and packed in a stainless steel extraction cell. Extraction was performed by using a rapid solvent extractor (SE100, Mitsubishi Chemical Analytech, Japan) with acetone/hexane mixture (1:1 v/v, 80 mL) for 40 min at 2 mL/min at 35 °C, and subsequently with toluene (80 mL) for 40 min at 80 °C at flow rate of 2 mL/min. The acetone/hexane and toluene extracts were concentrated using a rotavap, then combined and adjusted to a final volume of 10 mL in toluene.

2.3. Quantitative analysis for HFRs, PBDEs, OPEs and CPs

An aliquot of the extract representing 0.1 g of dust was fractionated for chemical quantitative analysis of HFRs, PBDEs, and OPEs. Prior to fractionation, the extracts were first solvent exchanged to isooctane and spiked with known amounts of isotopically-labelled internal standard to monitor the recovery and to quantitate the native target compounds. The isotopically-labelled internal standards and amount spiked were: $^{13}C_{12}$-BDE-155 (0.82 ng), -183 (1.5 ng), -197 (0.43 ng), and -209 (1 ng), $^{13}C_{10}$-dechlorane (DDC-CO) syn (0.9 ng), -DDC-CO anti (0.8 ng), 1.4 ng each of $^{13}C_{12}$-α-, β-, and γ-HBCDD, $^{13}C_6$-$^2H_{17}$-2-ethylhexyl 2,3,4,5-tetrabromobenzoate, EHTBB (2 ng), $^{13}C_6$-$^2H_{17}$-bis(2-ethyl-1-hexyl) tetrabromophthalate, BEH-TEBP (2 ng), and 25 ng each of d_{15}-triethyl phosphate (TEP), d_{27}-tributyl phosphate (TBP), d_{12}-tris(2-chloroethyl)phosphate (TCEP), and d_{15}-triphenyl phosphate (TPhP). We followed fractionation procedures developed by Ionas and Covaci (2013). Fractionation was achieved by silica column (Agilent Bond Elut-SI, 500 mg/3 mL cartridges). After application of the extract to the column, the column was sequentially eluted with 8.5 mL hexane to collect fraction 1, 8 mL *n*-butyl chloride to collect fraction 2 and finally 8 mL ethyl acetate to collect fraction 3. Fraction 1 was solvent exchanged to isooctane for analysis of PBDEs and most HFRs by gas chromatography (GC). Fraction 2 was further split to two equal fractions. One fraction was solvent exchanged to isooctane for analysis of EHTBB and BEH-TEBP using GC and the other fraction was solvent exchanged to acetonitrile for analysis of HBCDD using ultra-performance liquid chromatography (UPLC). Fraction 3 was kept in ethyl acetate for analysis of OPEs using GC.

CPs were analyzed in fourteen dust samples. An aliquot of the extract representing 0.05 g of dust was fractionated for chemical quantitative analysis. Prior to fractionation, the extracts were first solvent exchanged to 2 mL hexane and spiked with 10 ng of $^{13}C_{10}$-1, 5, 5, 6, 6, 10-hexachlorodecane as the internal standard. The clean-up process was adopted from Sahlström et al. (2012) and briefly described here. The extracts were treated with concentrated sulfuric acid and then cleaned-up on a SPE column packed with 2 g silica (deactivated with 2.5% H_2O) and 1 g of anhydrous sodium sulfate. The extract was loaded to the silica column and eluted by 30 mL of hexane to collect fraction 1, and subsequently eluted by 10 mL hexane/diethyl ether (1:1, v/v) to collect fraction 2. Fraction 1 was discarded and Fraction 2 was concentrated and solvent exchanged to isooctane for CP analysis.

2.3.1. Instrumental analysis of HFRs, PBDEs, OPEs and CPs

We analyzed 17 HFRs, 17 PBDEs, 13 OPEs and CPs with C_9 to C_{31} congener groups. The list of target analytes, including their full names, abbreviations, and supplier for the standard is presented in Table S2 and Text S1. Instrumental analysis for HFRs and PBDEs is described elsewhere (Sahlström et al., 2012). In brief, analysis was performed using a Trace GC Ultra coupled to a DSQ II MS (Thermo Scientific, Waltham, MA) operating in electron capture negative ion (ECNI) mode. A 15 m HT 5 fused silica column (Thermo Scientific,