



# Screening for halogenated flame retardants in European consumer products, building materials and wastes



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## HIGHLIGHTS

- PBDE, HBCDD and NFR concentrations were determined in 137 consumer products.
- Differences in HFR content between product groups, esp. textiles, plastic and EEE.
- Differences in HFRs between recycled and virgin plastics.
- Recycled plastics contained low levels of a wide range of HFRs.

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## ABSTRACT

To fulfill national and international fire safety standards, flame retardants (FRs) are being added to a wide range of consumer products and building materials consisting of flammable materials like plastic, wood and textiles. While the FR composition of some products and materials has been identified in recent years, the limited global coverage of the data and the large diversity in consumer products necessitates more information for an overall picture of the FR composition in common products/materials.

To address this issue, 137 individual samples of various consumer products, building materials and wastes were collected. To identify and characterize potential sources of FRs in indoor environment, all samples were analyzed for content of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs) and novel flame retardants (NFRs).

The most frequently detected were HBCDDs (85%), with the highest median concentration of  $\Sigma_4$ HBCDDs of  $300 \text{ mg kg}^{-1}$  in polystyrenes. The highest median concentration of  $\Sigma_{10}$ PBDEs was found in recycled plastic materials, reaching  $4 \text{ mg kg}^{-1}$ . The lowest concentrations were observed for NFRs, where the median of  $\Sigma_{12}$ NFRs reached  $0.4 \text{ mg kg}^{-1}$  in the group of electrical & electronic equipment wastes. This suggests that for consumer products and building materials that are currently in-use, legacy compounds still contribute to the overall burden of FRs. Additionally, contrasting patterns of FR composition in recycled and virgin plastics, revealed using principle component analysis (PCA), suggest that legacy flame retardants are reentering the market through recycled products, perpetuating the potential for emissions to indoor environments and thus for human exposure.

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## 1. Introduction

Halogenated flame retardants (HFRs) are chlorine or bromine based compounds added to a broad range of commercial products to increase their fire resistance. They are used to meet fire safety regulations in flammable petroleum-based materials such as

polymers – which have increased in production in the past several decades and which surround us in the form of clothing, furniture, electronics, cars and computers as well as in the form of combustible materials such as wood, paper and textiles.

Brominated compounds are frequently used organohalogenated flame retardants due to their higher trapping efficiency for free radicals and lower decomposition temperature in comparison with chlorinated compounds. Brominated flame retardants (BFRs) make up 22% of the global FR market (Posner et al., 2011), and despite recent shifts towards non-halogenated flame retardants such as

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organophosphate esters (OPEs), BFRs still dominate (>40 000 metric tons/year consumed globally in 2008, compared to ~20 000 tons/year for OPEs; (Posner et al., 2011)). Throughout the 1990s and early 2000s, the BFR market was dominated by polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBPA). However, due to environmental and human health concerns, two commercial mixtures of PBDEs were added to the annexes of Stockholm Convention on Persistent Organic Pollutants in 2009 (UNEP, 2009), while HBCDD was added in 2013 (UNEP, 2013). National bans on PBDEs (EU, 2004, 2010; Wager et al., 2012), Stockholm Convention restrictions and voluntary manufacturer phase-outs have led to a shift in current BFR usage and the consequent introduction of alternative flame retardants (FRs) to the market. The usage of HBCDD is projected to continue to 2020 (ECHA, 2014) while TBBPA and structurally-related compounds remain high-use BFRs. However, a diverse set of alternative HFRs, often structurally similar to the restricted/legacy compounds, is currently seeing wider use. These “novel” flame retardants (NFRs) include a wide variety of halogenated formulas that are new to the market or newly observed in the environment and often serve as replacements for banned PBDE formulations. Currently, there is a large number of different aromatic and cycloaliphatic HFRs with varying physico-chemical properties designed to achieve compatibility with polymers and stability during product lifetimes. Some of these substances (like TBBPA) can be covalently bound to materials during the production process, but most legacy FRs and NFRs are additive compounds, i.e. they are not bound to the material and thus have a greater potential for release from final products during their lifecycle. Many of these compounds are persistent, lipophilic and have been shown to accumulate in the environment (Besis and Samara, 2012; Covaci et al., 2009; de Wit et al., 2010; Law et al., 2003; Papachlimitzou et al., 2012; Venier et al., 2010).

HFRs are used in materials typically found in indoor environments (homes, vehicles and workplaces) where we typically spend over 20 h per day (Schweizer et al., 2007). The presence of indoor sources leads to elevated indoor concentrations of FRs, exacerbated by lower removal and degradation rates in the indoor environments due to low advective air movement, reduced photolysis and biodegradation and controlled climate. In addition to acting as a source of such compounds to outdoor environment (Bjorklund et al., 2012; Melymuk et al., 2016), the indoor environments also represent a significant potential exposure route for humans. In view of the toxicity of HFRs (Bruchajzer et al., 2011; Darnierud, 2003, 2008; Lyche et al., 2015; van der Ven et al., 2009), understanding indoor exposure is a key research concern. Indoor air and dust are frequently analyzed (Blanchard et al., 2014; Brommer et al., 2012; Brown et al., 2014; Cequier et al., 2014; Dodson et al., 2012; Fromme et al., 2014; Harrad et al., 2010; Shoeib et al., 2012; Sjödin et al., 2008; Takeuchi et al., 2014; Thuresson et al., 2012; Venier et al., 2016; Whitehead et al., 2015) to cover the main exposure routes: air inhalation and dust ingestion. Nevertheless, while the link between consumer product sources and measured indoor concentrations has been extensively investigated to define the mechanisms of this transfer (Rauert et al., 2015, 2014a, 2014b; Stubbings and Harrad, 2014), a comprehensive characterization of the levels in these sources is a missing piece. Although some work focusing on selected specific consumer products (Jonas et al., 2015; Kajiwara and Takigami, 2013; Peaslee et al., 2014; Rani et al., 2014; Stapleton et al., 2011, 2012) has been carried out, only a limited number of studies deal with a full range of products/materials commonly present in the indoor environment (Abbasi et al., 2016; Kumari et al., 2014). Knowledge of the concentrations of these chemicals in their presumed sources such as building materials and consumer products allows us to evaluate their contribution to

concentrations of HFRs in indoor air and dust, and is thus a necessary component of human exposure assessment.

To determine the typical composition and levels of HFRs in indoor materials in the Czech Republic, 137 individual samples of construction materials, electrical and electronic devices, flooring, fabric, upholstery and other daily use materials including wastes and recycled products were investigated in order to identify and characterize potential sources of HFRs in indoor environments. All materials were analyzed for their content of PBDEs, HBCDDs and NFRs to provide a broad profile of the composition of HFRs in materials with different intended applications.

## 2. Materials and methods

### 2.1. Chemicals

The target analytes included 10 PBDEs (congeners 28, 47, 66, 85, 99, 100, 153, 154, 183 and 209), 4 HBCDD isomers and 12 NFRs (TBX, TBP-BAE, PBT, PBEB, TBP-DBPE, HBB, BTBPE, s-DDC-CO, a-DDC-CO, DBE-DBCH, TBCO, DBHCTD). See Table S 1 for further details. <sup>13</sup>C labeled internal standards of PBDEs and HBCDDs were added before extraction. All the analytical standards (native and <sup>13</sup>C labeled standards) were purchased from Wellington Laboratories Inc. (Canada). Pesticide residue grade solvents were obtained from Lab-scan (Poland) and Silica Gel 60 (70–230 mesh) from Merck (Germany).

### 2.2. Sample collection

Both new and used materials were included to cover the widest range of materials used in building construction, household equipment and cars interiors. These included mainly construction materials from the past three decades (including some supplied from a company specializing in “green” low-energy buildings), new and used electrical and electronic devices, flooring, fabric, upholstery and other daily-use materials. Samples of recycled materials were also included, as their contamination from primary materials remains unclear. New materials were purchased while older and used materials were collected from various sources. A subset of 126 of these materials was also analyzed for perfluoroalkyl substances (PFASs), presented elsewhere (Bečanová et al., 2016).

A total of 137 samples were split into four categories according to use and composition. See Supplementary Material and Table S 2 for categorization and sample details.

### 2.3. Sample preparation, extraction and instrumental analysis

Samples of solid materials were crushed, chopped or ground while samples of foam and fabrics were cut into small pieces about 1–5 mm in diameter. After grinding or cutting, 5 g of each sample was extracted with dichloromethane (DCM) using warm Soxhlet extraction (60 min warm Soxhlet followed by 30 min of solvent rinsing) in a B-811 extraction unit (Büchi, Switzerland). Concentrated extracts were cleaned up using H<sub>2</sub>SO<sub>4</sub> modified silica column chromatography (elution with 40 mL DCM:n-hexane mixture 1:1). The eluate was concentrated using a stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred to a GC vial insert. Solvent was exchanged to nonane for gas chromatography/mass spectrometry (GC/MS) analysis and consequently to acetonitrile for liquid chromatography/mass spectrometry (LC/MS) analysis. Prior to instrumental analysis, injection standards (<sup>13</sup>C BDE-77, 138) were added to all samples.

PBDEs and NFRs were analyzed by GC-MS/MS using a 7890A GC (Agilent, USA) equipped with a 15 m × 0.25 mm × 0.10 μm DB5 column (Agilent J&W, USA) coupled to a Quattro Micro MS (Waters,

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