BFR LEVELS IN INDOOR ENVIRONMENT IN RELATION TO THE HOUSE EQUIPMENT

Kukučka P, Prokeš R, Audy O, Dvorská A, Oravec M, Kouhoutek J, Klánová J

Reseaech Centre for Toxic Compounds in the Environment, Faculty of Science, Masaryk University, Kamenice 3/126, 625 00 Brno, Czech Republic

Introduction

Flame retardants are compounds added to polymers, paints, textiles and other materials to improve their fireproof properties. They literally retard the progression of fire, therefore increase the chance of rescue for people to have more time to escape or extinguish the fire. The main applications are in plastic housing of electronic products such as TV sets and computers, car parts, circuit boards, electric components and cables. Included among the different flame retardants are inorganic chemicals, organic phosphate esters halogenated and non-halogenated, and chlorinated and brominated organic compounds. The flame retardants are usually sorted into 2 groups: reactive and additive flame retardants according to their use. The reactive chemicals are covalently bonded within the polymer structure and therefore less likely to leach out (and evaporate) to the environment until the product is decomposed or burnt. The additive compounds, on the other hand, are only mixed with or dissolved in the material and can more easily migrate out of the product.

Brominated flame retardants (BFRs) are a structurally diverse group of compounds including aromatics, cyclic aliphatics, phenolic derivatives. The most common BFRs are tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and polybrominated biphenyls (PBB). [1]

Polybrominated diphenyl ethers (PBDEs) have been extensively used as flame retardants in the last few decades. PBDEs are “dissolved” in polymers used in electrical and electronic devices, and in other plastic goods, coatings, cables, construction materials, and textiles. PBDEs are persistent, toxic, and bioaccumulative chemicals of anthropogenic origin, thus presenting a potential threat to wildlife and human health. High PBDE levels have also been reported in a range of environmental media and biota including fish, treated sewage sludge and even household dust. Long-term risks for human health exist because the chemicals are highly lipophilic and can persist in the human body. [2-6]

HBCDD refers to the commercial product containing three (α-, β- and γ-) diastereomers. In the HBCDD technical product, the γ ‘‘isomer’’ is the most abundant compound (75–89%), followed by the α (10–13%) and β isomers (0.5–12%); trace levels of two meso forms of HBCDD (δ- and ε-HBCDD) are also present. HBCDD is a high-production-volume BFR that is applied to products requiring combustion inhibition, such as extruded expandable polystyrene foam and textile back coatings. [7]

Although various national and international measures have been accepted to minimize the use of BFRs, they can still be found in various consumer products used in both indoor and outdoor environment. Our study included sampling of indoor and outdoor air in different types of houses and flats as well as collection and analysis of various consumer product materials (fabrics, plastics, and furnishing as well as construction materials) used in this environment.

Materials and methods

Consumer products materials

Samples of old and new materials (in total number close to one hundred) were collected from employees of our institute and from a waste separation plant. Samples were divided into groups according the use of the products and also the age of the sample. Pieces of materials were ground to obtain as homogenous sample as possible. The samples were then extracted with dichloromethane (DCM) using automated warm Soxhlet extraction (Büchi B-811, Switzerland). Extracts were cleaned-up on a column containing H_2SO_4 modified silica, DCM: *n*-hexane mixture (1:1) was used for elution. Cleaned extracts were transferred into chloroform to further remove residues of various polymers using gel permeation chromatography (GPC) (Biobeads SX3). After GPC the samples were concentrated using a gentle stream of nitrogen to a vial (1 mL). Finally the samples were analysed by GC-EI-MS/MS (Agilent 6890N GC coupled to Micromass Quattro Micro GC mass spectrometer). For HBCDD analysis the sample solvent was later exchanged to acetonitrile and samples were analysed using HPLC-ESI-MS/MS (Agilent 1200 HPLC coupled to Agilent 6410 mass spectrometer)

Air samples

Passive samplers containing PUF as a sorbent were deployed at site for 28 days. The location was ideally a living room (as the indoor environment) and nearby outdoor area (balcony, window or garden) adjacent to the living room. In some flats (3 flats), bedroom air was sampled as well. After sampling, the PUFs were stored wrapped in 2 layers of aluminium foil and zip lock plastic bag in a freezer (-18°C) until analysis.

PUFs were extracted with dichloromethane (DCM) using automated warm Soxhlet extraction (Büchi B-811, Switzerland), ^{13}C labelled BDE 28, 47, 99, 100, 153, 154, 183 and 209 congeners were added. Extracts were cleaned-up using glass column filled with 5 g of H_2SO_4 modified silica, DCM: *n*-hexane mixture (1:1) was used for elution. Cleaned extracts were evaporated using nitrogen and transferred to nonane into an insert in a vial, ^{13}C labelled syringe standards were added (final volume 50 μL). Samples were then analysed using GG-EI-HRMS (Agilent 7890A GC coupled to Micromass AutoSpec Premier mass spectrometer). For HBCDD analysis the sample solvent was later exchanged to acetonitrile and samples were analysed using HPLC-ESI-MS/MS (Agilent 1200 HPLC coupled to Agilent 6410 mass spectrometer).

Results and discussions

Consumer products materials

Levels of PBDEs in consumer product materials reached up to 0.5 μg g^{-1}. Most of the samples were below LOQ. The highest levels were found in the plastic covers of electronic devices (computers, keyboards, TV sets etc.). In the congener profile, BDE 183 prevailed. Various fabrics and tapestry samples (10 and more years old) were mostly below LOQ. More recent samples (0 to 10 years old) contained low levels of PBDEs, decaBDE prevailed in these samples. Polystyrene samples were below LOQ.

On the other hand, HBCDDs were mostly detected in insulation materials – namely polystyrene samples (EPS, XPS). Levels of up to 5 mg g^{-1} were observed. Depending on the age of the material the isomer ratio changed. While in the youngest samples γ-HBCDD prevailed, the older samples showed higher ratios for α -and β-HBCDD. Samples with the highest HBCDD content also showed trace levels of δ-HBCDD. ε-HBCDD was detected in none of the samples. Some younger textile samples (curtains and carpets) also contained HBCDDs, but on significantly lower levels (up to 0.5 μg g^{-1}) than insulation materials.

Air samples

The sampling campaign took place in summer 2010. Many of the flats don't use any air conditioning, so ventilation/air exchange is provided by open windows only. PBDE (Σ excluding decaBDE) levels in the living room samples (17) ranged between 49 and 1665 pg PAS^{-1}, bedroom samples (3) were in the range of 130 and 505 pg PAS^{-1} and outdoor samples (17) 47 to 945 pg PAS^{-1}. In the congener profile BDE 28 and 47 dominated (accounting for approx. 70% of the PBDEs analyzed). BDE 99 accounted for about 10% of the PBDEs content. The heavier PBDEs (153, 154 and 183) were mostly below LOQ values. The congener profile, however, slightly differed between individual locations. One exception was a house with forced ventilation and heat-exchange air conditioning unit, where also heavier PBDEs were observed and BDE 47 and 99 accounted for approx. 60% and 25%, respectively, of the PBDEs content. This house also showed the highest levels of PBDEs. Generally PBDEs level in air mostly depended on the equipment of the sampled location. Highest levels were found in the living rooms with highest number of electronic devices (especially in the reach of direct sunlight, close to the window) whereas lowest levels were observed in the oldest houses (more than 60 years old) with low number of electronic devices. Results are summarized in Fig. 1.

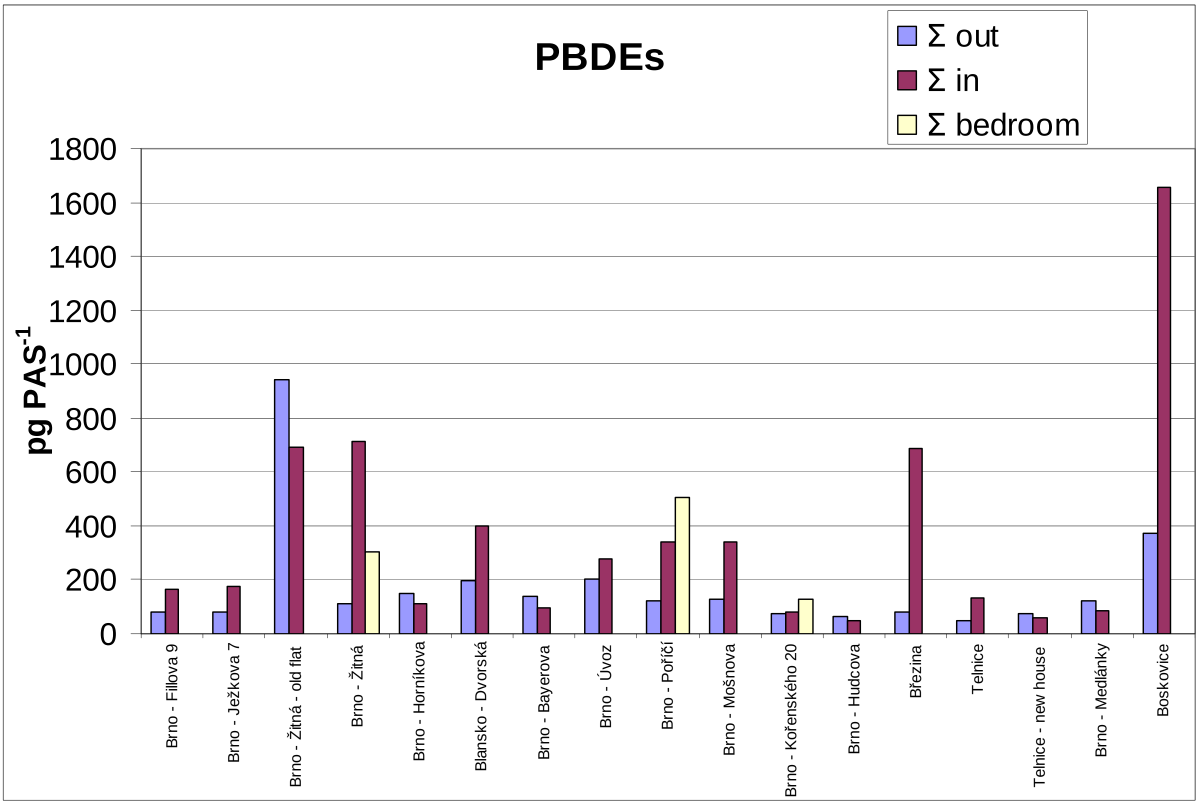

Fig. 1 PBDE levels in air samples from the summer 2010 campaign.

HBCDDs were below LOQ for all the indoor air samples and found only in 2 outdoor air samples, where the concentration reached up to 17 ng PAS^{-1} (α- and γ-HBCDD were only detected). These two samples were in the residential area where refurbishment recently took place and the houses were additionally insulated using polystyrene boards.

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