INDOOR AIR CONTAMINATION BY "OLD" AND NOVEL FLAME RETARDANTS, SHOULD WE FEAR NEW BUILDINGS?

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Introduction

Flame retardants are compounds added to polymers, paints, textiles and other materials to improve their fireproof properties. The use of flame retardants has increased due to stricter fire regulations in many countries but also increased use of plastic materials and synthetic fibres. Brominated flame retardants (BFRs) are a structurally diverse group of compounds including aromatics, cyclic aliphatics, and phenolic derivatives. The most common BFRs are tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and polybrominated biphenyls (PBB) [1-4].

PBDEs became popular BFRs due to their economical feasibility and little effect on the flexibility of the base compounds. They were resistant towards acids, bases, heat, light, reduction and oxidation. They were produced by direct bromination of diphenylether (209 possible congeners) and their production grew rapidly since the end of the 1970s. 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 household dust. Long-term risks for human health exist because the chemicals are highly lipophilic and can persist in the human body.

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.

Currently, other replacement compounds are often used, among these belong decabromodiphenylethane (DBDPE, structurally very similar to decaBDE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE, again very similar to hexaBDE) and many other new BFRs, often referred to as Novel BFRs. Chlorinated flame retardants, dechloranes, are often sorted into this group too[5-8].

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 public indoor areas, where active low volume air sampling and cascade impactors were co-employed. Indoor equipment information was recorded in a questionnaire for each site.

Materials and methods

Passive samplers containing PUF as a sorbent were deployed at site for 28 days. Low volume active air samples and cascade impactor samples were collected for 7 days. The location in flats 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. For public areas, various rooms were sampled. After sampling, the filters were stored wrapped in 2 layers of aluminium foil and zip lock plastic bag in a freezer (-18°C) until analysis.

All filters 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

Private flat samples

Levels of PBDEs in units up to thousands of pg PAS^{-1} were observed for flat samples in the two sampling campaigns. The levels in individual flats were similar for both winter and summer samples. Data analyses were performed to find possible correlation between air levels, house status, type, and electronics runtime and electronics age. Individual flats were sorted into groups. An interesting finding was observed for PBDEs levels and electronic devices age (Fig. 1), with the highest median values for the group of flats with electronic devices between 5 and 10 years old.

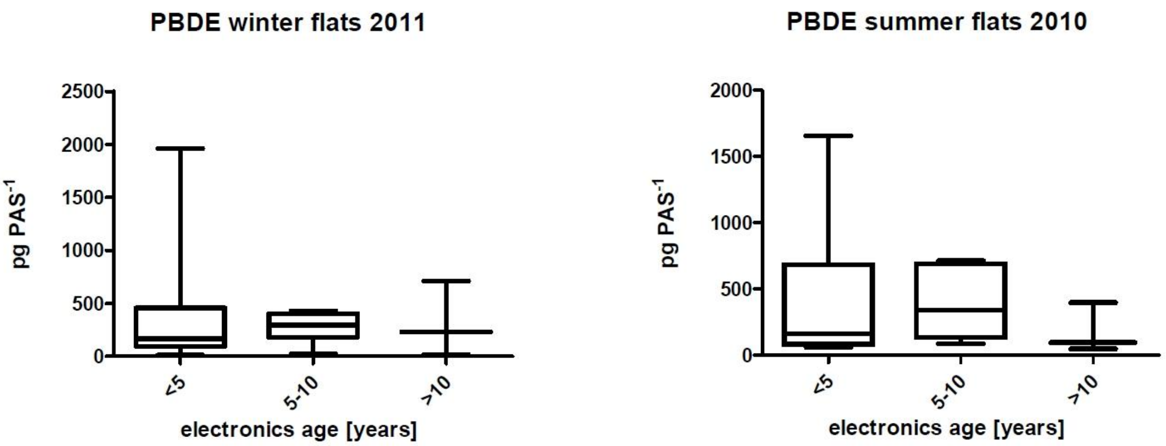

Fig. 1. PBDEs in indoor air samples in relation to electronic devices age

Levels of Novel flame retardants in flats were observed in range between hundreds of pg PAS^{-1} and units of µg PAS^{-1}. Among most prominent compounds were Dechloranes and 1,2-dibromo-4-(1,2-dibromethyl)cyclohexane (TBECH). In general, levels of Novel flame retardants exceeded those for PBDEs by 2-3 orders of magnitude.

Public indoor environment

In March 2012, a sampling campaign in a hospital was carried out. Passive samplers deployed for 28 days were complemented by low volume cascade impactors for 7 days. Selected offices, nurse daily rooms and wards were sampled. BDEs (excluding decaBDE) ranged between tens and hundreds of pg PAS^{-1}. BDE 47 and 99 contributed to more than 60% of ΣBDEs.

Dust samples collected by cascade impactors showed levels of BDEs (excluding decaBDE) between 1 and 6 pg m^{-3} (Fig. 2), with lowest levels in an office in management department. In the congener profile, BDE 99 and 183 prevailed (mostly given by the sampling technique used). Hospital is usually clean environment where dust is cleaned regularly. This is confirmed by measurements in examination room, where the higher BDEs levels than in office can be explained by more intensive room usage and low usage of the respective office. In the particle size profile BDEs levels increased with decreasing particle size.

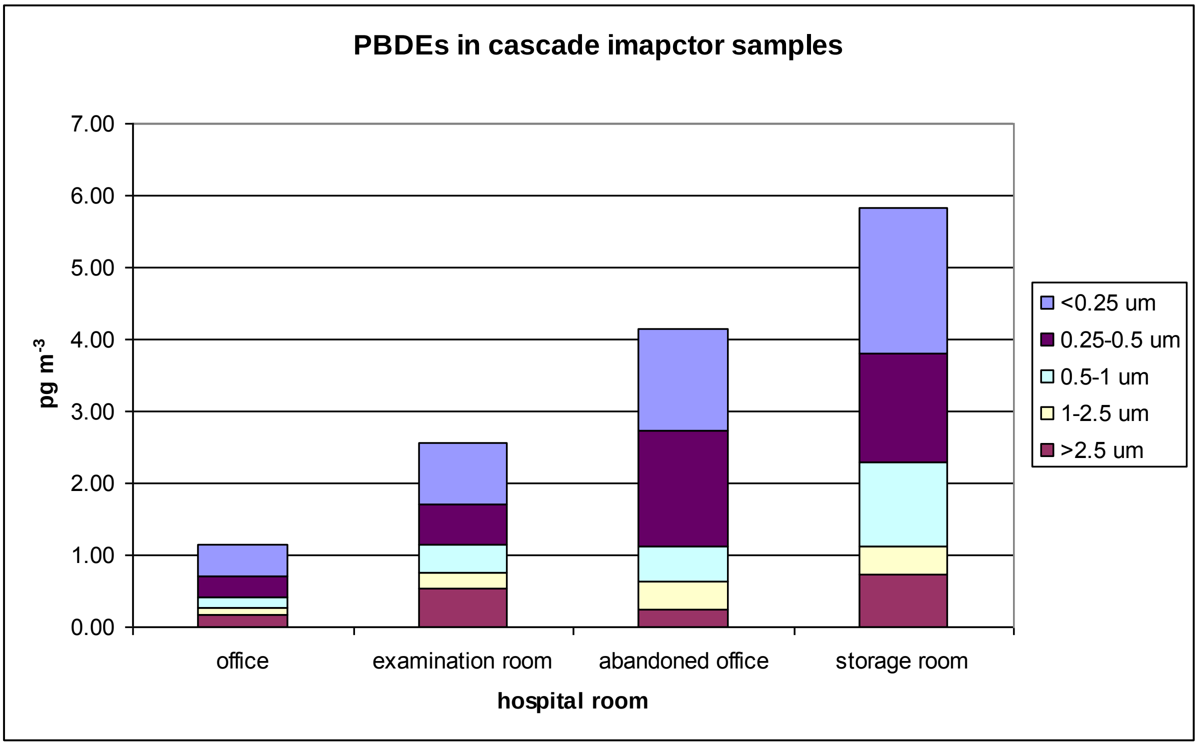

Fig. 2. PBDE levels from hospital dust collected by cascade imapctors

Acknowledgements
This project was supported by the CETOCOEN (CZ.1.05/2.1.00/01.0001) project granted by the European Union and administrated by the Czech Ministry of Education, Youth and Sports, and the INCHEMBIOL (MSM 0021622412) project of the Czech Ministry of Education, Youth and Sports.

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