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Hexabromocyclododecane and tetrabromobisphenol-A in indoor dust from France, Kazakhstan and Nigeria: Implications for human exposure

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ABSTRACT

Concentrations of hexabromocyclododecane isomers (α-, β- and γ-HBCDs) and tetrabromobisphenol-A (TBBP-A) were measured – for the first time – in indoor dust from homes, offices and cars from France, Kazakhstan and Nigeria. ΣHBCDs in French and Kazakhstani house dust (median = 1351 and 280 ng g^{-1}, respectively) were consistent with previous reports from the UK and Romania, respectively. Concentrations of ΣHBCDs in Nigerian domestic dust (median = 394 ng g^{-1}) were substantially higher than those reported from Egyptian homes. In general, concentrations of ΣHBCDs in the studied micro-environments were higher than those of TBBP-A, which may be attributed to the major application of TBBP-A as a reactive flame retardant; rendering its release to dust more difficult. Statistical analysis revealed significantly lower ΣHBCDs in French houses than those found in both offices and cars, while ΣHBCDs in cars from Kazakhstan were higher ($P < 0.05$) than those in homes and offices. Moreover, TBBP-A concentrations in car dust from Nigeria were lower than those found in homes and offices. Exposure estimates revealed higher intake of HBCDs and TBBP-A by toddlers via indoor dust ingestion compared to adults. Combined with their low body weight, this can raise concerns over the potential adverse health effects of such high exposure in toddlers.

1. Introduction

Hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A) are widely used brominated flame retardants (BFRs) with reported global market demands of 170,000 and 31,000 metric tonnes in 2004 and 2011 respectively [1]. HBCD is employed principally as an additive to expanded and extruded polystyrene foams for applications like thermal insulation of buildings, for backcoating of fabrics and to a lesser extent to high-impact polystyrene (HIPS) used in enclosures for electronic equipment. Commercial HBCD formulations consist mainly of the γ-HBCD diastereoisomer (75–89%), while the α- and β-HBCD are present in considerably lower amounts (10–13% and 1–12%), respectively. HBCD has a low water solubility (49, 15, 2 μg L^{-1} for α-, β-, and γ-HBCD), a fairly low vapour pressure (6.27×10^{-5} Pa) and is persistent in the environment (estimated $t_{0.5}$ of 51, 1440 and 5760 h in air, water and sediment, respectively). It can therefore bioaccumulate and undergo long-range atmospheric transport [2]. Oral exposure to HBCDs was reported to induce hepatic cytochrome P450 enzymes and alter the normal uptake of neurotransmitters in rat brain. It can

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cause disruption of thyroid function, reproductive system, nerve function and development in various classes of vertebrates [3]. Therefore, HBCD was recently included in Annex A of the Stockholm Convention on persistent organic pollutants (POPs) with an exemption for use in expanded polystyrene and extruded polystyrene in buildings [4].

TBBP-A is used mainly as a reactive flame retardant covalently bonded to the polymer matrix in epoxy and polycarbonate resins used in printed circuit boards and electronic equipment. It can also be used as an additive, for instance in HIPS and acrylonitrile–butadiene–styrene resins. Additive usage accounts for ~18% of TBBP-A total applications. However, even when used as a reactive flame retardant, excessive non-polymerized TBBP-A is always present which can be emitted to the environment. Due to its low water solubility (63 μg L^{-1}) and low vapour pressure (6.24×10^{-6} Pa), TBBP-A is likely to be associated with suspended particulate matter following release [5]. TBBP-A has been identified as endocrine disruptor. It also displays a high potency to bind to human transthyretin and was associated with immunotoxic and neurotoxic effects in laboratory animals [6]. The potential toxicity of TBBP-A is mitigated to some extent by its short human half-life (2.2 days) [5]. Therefore, while TBBP-A falls under the REACH registration process due to its high production volume, there are currently no global restrictions on the production and usage of TBBPA or its derivatives. However, the EU risk assessment report on TBBP-A concluded that there is a need for further information and/or testing due to possible degradation to more toxic derivatives (e.g. bisphenol-A) [5].

Several studies have reported on the levels of HBCD isomers and TBBP-A in various biotic and abiotic matrices including air, dust, soil, sediment, human milk, plasma and adipose tissue from various parts of the world, including the Arctic, indicating the ubiquity of these BFRs [6–8]. The few studies available on the levels of HBCDs and TBBP-A in indoor dust have elucidated the significance of inadvertent dust ingestion as a pathway of human exposure to these chemicals, especially for toddlers and young children [9,10]. Moreover, pharmacokinetic modelling of UK adults exposure to BFRs revealed dust ingestion to contribute 24% and 33% to the overall daily intake of HBCDs and TBBP-A, respectively [11]. This highlights the importance of assessment of human exposure to both HBCDs and TBBP-A via dust ingestion in different indoor microenvironments. Given the reported highly skewed nature of HBCD concentrations in indoor dust from commonly frequented microenvironment categories [9,12], such an assessment would provide a valuable indication of the proportion of the population that may receive elevated exposures as a result of frequenting highly contaminated microenvironments in the course of their daily lives.

Therefore, the current study aims to (a) provide first insights on the levels of HBCDs and TBBP-A in indoor dust samples collected from homes, offices and cars in France, Kazakhstan and Nigeria, (b) compare the dust levels of HBCDs and TBBP-A in the studied countries to those reported from other parts of the world, (c) estimate the daily exposure of adults and toddlers to the target BFRs in the studied countries, and (d) investigate the relative contribution of each microenvironment category to the overall human exposure to HBCDs and TBBP-A via dust ingestion.

2. Materials and methods

2.1. Sampling strategy

All the microenvironments studied comprised a convenience sample of acquaintances of the project team. Dust samples were collected from the following locations: France (Annecy), Kazakhstan (Almaty and Astana) and Nigeria (Lagos). In each country, 3 different microenvironment categories, namely homes (living rooms), offices and cars were sampled. Sampling time and sample numbers are provided in Table 1.

2.2. Sampling methods

Dust samples were collected using a Nilfisk Sprint Plus 1600 W vacuum cleaner or equivalent. Sampling was conducted according to a clearly-defined standard protocol [9] by one of the research team. In offices and homes, one m^2 of carpet was vacuumed for 2 min and in case of bare floors 4 m^2 for 4 min. In cars, only the surface of the seats with which occupants would have direct contact (i.e. not including seat backs) was sampled for 2 min. Samples were collected using nylon sample socks (25 μm pore size) that were mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie, sealed in a plastic bag and stored at −20 °C. Before and after sampling, the furniture attachment was cleaned thoroughly using an isopropanol-impregnated disposable wipe.

3. Analytical protocols

3.1. Sample preparation and extraction

Dust samples were passed through a 500 μm mesh size sieve, weighed accurately and extracted using pressurised liquid extraction (Dionex ASE-350, Hemel Hempstead, UK). Dust samples (typically between 100 and 300 mg) were loaded into pre-cleaned 66 mL cells containing 1.5 g Florisil and Hydromatrix (Varian Inc., UK) to fill the void volume of the cells, spiked with 20 ng of each of ^{13}C-labelled α-, β-, γ-HBCD and TBBP-A as internal (surrogate) standards (i.e. standards used for determination of analyte concentrations) and extracted with hexane:dichloromethane (1:9, *v*/*v*) at 90 °C and 1500 psi. The heating time was 5 min, static time 4 min, purge time 90 s, flush volume 50%, with three static cycles.

3.2. Clean up

The crude extracts were concentrated to 0.5 mL using a Zymark Turbovap® II then cleaned up by loading onto SPE cartridges filled with 8 g of pre-cleaned acidified silica (44% concentrated sulfuric acid, *w*/*w*). The analytes were eluted with 25 mL of hexane:dichloromethane (1:1, *v*/*v*). The eluate was evaporated to dryness under a gentle stream of N_2, then reconstituted in 100 μL of d_{18}-γ-HBCD (25 pg μL^{-1} in methanol) as recovery determination (or syringe) standard, used to determine the recoveries of internal standards for QA/QC purposes.

3.3. Analysis

Separation of α-, β-, γ- HBCDs and TBBP-A was achieved using a dual pump Shimadzu LC-20AB Prominence liquid chromatograph equipped with SIL-20A autosampler, a DGU-20A3 vacuum degasser and an Agilent Pursuit XRS3 C_{18} reversed phase analytical column

Table 1
Sampling information.

Country	Location	Time	Number of samples		
			Homes	Offices	Cars
France	Annecy	Aug–Oct 2008	9	11	7
Kazakhstan	Almaty and Astana	May–June 2009	10	10	11
Nigeria	Lagos	Sep–Oct 2014	10	10	10