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Human exposure to HBCD and TBBPA via indoor dust in Korea: Estimation of external exposure and body burden

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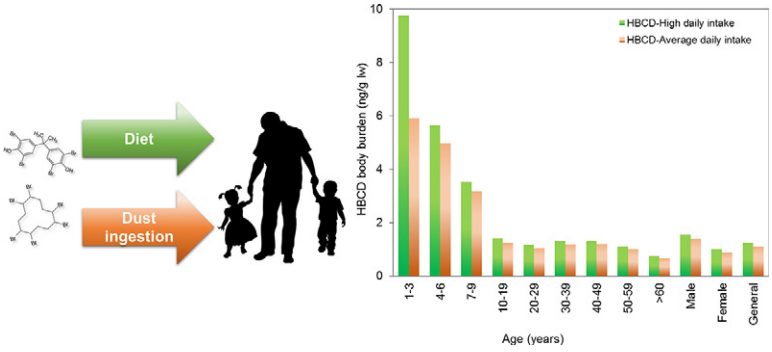
HIGHLIGHTS

- High concentrations of TBBPA were found in indoor dust in Korea.
- Food is the main contributor in ΣHBCD daily intake for Korean adults.
- The estimated ΣHBCD body burden of Korean toddlers was 7.91 ng g^{-1} lw.

GRAPHICAL ABSTRACT



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ABSTRACT

Human exposure to brominated flame retardants (BFRs) such as hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) mainly occurs through diet and dust ingestion. In this study, the BFR concentrations in 124 vacuum dust samples of six categories of indoor environments (homes, offices, kindergartens, cars, schools, and public indoor environments) and 32 surface dust samples were investigated. The median ΣHBCD concentrations ranged from 106.30 ng g^{-1} in home dust to 496.13 ng g^{-1} in office dust. The TBBPA concentrations in indoor dust (from 78.87 to 463.81 ng g^{-1}) were among the highest compared to other countries because of the high market demand for this flame retardant in Korea. The TBBPA concentrations in surface dust of living rooms were significantly higher ($p < 0.05$) than sleeping rooms, due to the presence of more electrical equipment in living rooms. The estimated daily intakes (EDI) of ΣHBCD and TBBPA (dust + diet) for toddlers were 6.18 ng kg^{-1} bw d^{-1} and 2.54 ng kg^{-1} bw d^{-1}, respectively. In general, the ΣHBCD estimated body burden of Korean adults showed good agreement with the reported ΣHBCD median concentrations in their sera. Since the developmental health effect of exposure to HBCD was categorized as "high hazard" by the US Environmental Protection Agency, the estimated high body burden of ΣHBCD in Korean toddlers (7.91 ng g^{-1} lw) warns us of possible adverse effects on the development of essential systems in their bodies.

1. Introduction

Brominated flame retardants (BFRs) have routinely been added to consumer products for several decades in a successful effort to reduce fire-related injury and property damage (Birnbaum and Staskal, 2004).

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BFRs are divided into three subgroups depending on the mode of incorporation of these compounds into polymers: i) brominated monomers, ii) reactive forms, and iii) additive forms. Reactive flame retardants, such as tetrabromobisphenol A (TBBPA), are chemically bonded into plastics. Additive flame retardants, such as hexabromocyclododecane (HBCD), are simply blended with polymers and are more likely to leach out of products (Alaee et al., 2003).

HBCD is used worldwide in expanded polystyrene (EPS) and extruded polystyrene (XPS). EPS and XPS are typically used to generate thermal insulation foam for applications in buildings and construction (Barghi et al., 2016). The commercial HBCD product is composed of three diastereomers: α-, β-, and γ-HBCD. Technical HBCD typically consists primarily of γ-HBCD; however, the isomeric profile varies depending on product application (Birnbaum and Staskal, 2004). Korea is one of the major consumers of HBCD in Asia (Oh et al., 2012). In this country, 530 tons of HBCD were consumed in 1993, and annual consumption increased to 1896 tons by 2010 (Al-Odaini et al., 2015).

Tetrabromobisphenol-A (TBBPA) is a derivative of bisphenol-A (BPA), used as a flame-retardant (Yang and Chan, 2015). TBBPA is produced by several manufacturers in Japan and China, and, until now, TBBPA use was not subject to regulatory restriction in Asia (BSEF, 2012). However, some researchers suggested that the primary toxic effect of exposure to TBBPA was the disruption of thyroid homeostasis (Ni and Zeng, 2013).

Human exposure to HBCD and TBBPA mainly occurs through dust inhalation and dust and food ingestion (Schecter et al., 2012; Goscinny et al., 2011; Abdallah et al., 2008a). It is generally accepted that diet plays a main role in human exposure to HBCD and TBBPA (Shi et al., 2009); however, diet becomes an important exposure route only when concentrations in dust and the corresponding contribution of dust to total exposure is low. Therefore, each exposure route may be country-specific (Law et al., 2014). Nevertheless, few studies have examined the contributions of diet and dust ingestion in human HBCD and TBBPA exposure. In addition, uncertainty regarding different daily dust ingestion rates (Cao et al., 2015), different methods used to assess dietary exposure, and exposure estimates of the general population (without considering a population's subgroups) make it difficult to reach correct conclusions on contributions of HBCD and TBBPA exposure routes.

In Korea, human exposure to HBCD via diet has been reported for different age groups and genders (Barghi et al., 2016). However, despite reliable evidence that documents the widespread usage of HBCD and TBBPA in Korea (Rani et al., 2014), there are no data on the cumulative exposure of these compounds to humans, specifically children. Therefore, in the first part of this study, we reported BFR concentrations in dust found in different indoor environments. In the second part, these data were used to estimate exposure to BFRs in order to compare the contributions of main exposure routes (dust and diet) in BFR daily intakes and to assess the BFR body burden of subgroups in Korea's general population, including children.

2. Materials and methods

2.1. Sample collection

Vacuum dust samples (N = 124) were collected between January–February 2009 from Seoul, Namyangju, and Yeosu (N = 34) and between March–April 2016 from Pohang and Gyeongju in Korea (N = 90) (Fig. S1). Samples were collected from six categories of indoor environments, homes (N = 46 including 4 samples from 2009), offices (N = 18), kindergartens (N = 6), cars (N = 19), public indoor environments (N = 10 including 5 samples from 2009), and schools (N = 25 collected in 2009). Dust samples (approximately 2 g) were collected from bags of vacuum cleaners that were routinely used in the respected indoor environment. Sampling from cars was carried out using a bagged hand held vacuum cleaner (Samsung 72 W) and only the surface of the seats were sampled. After each sampling, the vacuum bag was washed, dried, and used for the next sampling. All collected dust samples were sieved through a 212 μm sieve, homogenized, packed in clean aluminum foil, and stored at 4 °C until analysis in June 2016.

Surface wipes have been collected to evaluate the presence of HBCD and TBBPA in surface dust from libraries (N = 4), cars (N = 2), and homes (N = 23) from Seoul and Namyangju in 2009. Surface dust samples from homes were collected from living rooms (N = 10) and sleeping rooms (N = 13) of separate homes and were taken from randomly selected tables, chairs, and sofas. Three hand wipe samples were also collected from school students in Seoul. For surface dust sampling, wipe gauzes with dimensions of 4 × 4 in. were pre-washed with dichloromethane (DCM) using a Soxhlet extractor for >20 h. All the surface dust samples were collected by wiping the surface of indoor items using isopropanol-dipped wipe gauzes. The wiping area was 30 × 30 cm. The time since the surface was cleaned/wiped or otherwise touched prior to this study could not be determined. The gauzes were properly stored in an amber bottle to protect the target pollutants from photodegradation. Samples were kept at 4 °C until extraction was performed.

2.2. Reagents and chemicals

Solvents used for sample preparation and clean up (e.g., acetone, dichloromethane, and hexane) were HPLC-grade chemicals purchased from Honeywell Burdick. Sulfuric acid (extra pure) and anhydrous sodium sulfate (Na_2SO_4, purity 98%) were purchased from Daejung Chemicals and Metals Co., Ltd. and Kanto Chemical Co., Inc., respectively. Analytical standards (unlabeled and $^{13}C_{12}$-labeled α-, β-, γ-HBCD, TBBPA, and d_{18}-γ-HBCD) were acquired from Wellington Laboratories (Andover, MA, USA) at individual concentrations of 50 mg mL^{-1} with purities >98%. Silica gel and alumina were obtained from Merck (Darmstadt, Germany) and Sigma-Aldrich (Milwaukee, WI, USA), respectively.

2.3. Sample preparation, extraction, and clean-up

Approximately 0.1 g of dust was weighed on clean filter paper and similar to dust wipes spiked with 25 ng of isotopically labeled internal standards ($^{13}C_{12}$-α-, $^{13}C_{12}$-β-, $^{13}C_{12}$-γ-HBCD, and $^{13}C_{12}$-TBBPA). Extraction was performed by sonication for 2 × 30 min with 60 mL of 1:1 (v/v) hexane-dichloromethane (Hex-DCM). Dust extracts were concentrated and treated with sulfuric acid. Then, a silica column packed with 4 g of sodium sulfate, 2 g of deactivated neutral silica (3% water), 10 g of acidic silica (44%), 2 g of deactivated neutral silica (3% water), and 4 g of sodium sulfate from top to bottom was used to purify the samples. The extracts were eluted in one fraction using 150 mL 1:1 (v/v) Hex-DCM for HBCD and then 75 mL DCM for TBBPA. After the clean-up process, the eluate was reduced, dried and then dissolved in 120 μL of methanol for LC/MS/MS analysis.

2.4. Instrumental analysis

Instrumental analysis was carried out using an LC/MS/MS system consisting of an Agilent 1100 series HPLC binary pump (Agilent Technologies, Palo Alto, CA, USA) and a Phenomenex Synergi™ 4 μm Hydro-RP 80 Å C18 column (150 × 2.00 mm, 4 μm) coupled with an API 2000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Foster City, CA).

The mobile phase consisted of methanol, acetonitrile, and water at a constant flow rate of 180 μL min^{-1}. For the gradient program, two solvent mixtures were used: (A) 75:25 (v/v) water:methanol and (B) 50:50 (v/v) methanol:acetonitrile. The program started at an initial composition of 80% A/20% B (v/v), and the mixture was changed linearly to reach 100% B over the first 4 min. Then, this mixture was held for 10 min and a linear ramp of 4 min was used to return the mobile phase to the initial composition. The column was then equilibrated for