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Particle size distribution of brominated flame retardants in house dust from Japan

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This article is dedicated to the memory of my respected supervisor, Dr. Hidetaka Takigami, who sadly passed away after completion of this study. I would like to express my sincere gratitude for all of his support in the past.

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ABSTRACT

The present study was conducted to examine the concentrations, profiles, and mass distributions of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs) based on the particle sizes of house dust samples from five homes in Japan. After removal of impurities from house dust from vacuum cleaner bags, selected indoor dust samples were size fractionated (>2 mm, 1–2 mm, 0.5–1 mm, 250–500 μm, 106–250 μm, 53–106 μm, and <53 μm). Fluffy dust was collected separately for particle size analysis. PBDEs, HBCDs, and PBDFs were detected in all the samples analyzed. In general, PBDE levels of particulate and fluffy dust were comparable and the highest concentrations were found in 106–250 μm or 53–106 μm fractions. HBCD concentrations in fluffy dust were higher than those in particulate dust, and their levels were the highest in 106–250 μm and 250–500 μm factions, respectively. The highest concentrations of all three compound groups were not found in particles <53 μm in size, suggesting that the distribution of brominated flame retardants does not depend solely on the surface area-to-volume ratios of dust particles. The concentrations of PBDEs and PBDD/Fs depended principally on the concentrations in particles <53 μm in size because the predominant mass of particulate dust were found in this fraction. The mesh size used for sample preparation will thus have little effect on the concentrations as long as particles <53 μm are included. In contrast, HBCD concentrations increased by as much as 80% when particles >250 μm in size and fluffy dust were included. The conclusion is that particulate dust <250 μm in size without fluffy dust should be used to analyze dust for brominated flame retardants.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are among the brominated flame retardants (BFRs) that are widely used as synthetic additives to reduce the flammability of plastics, textile coatings, and electronic appliances. However, despite the benefits of BFRs, their use problematic because of their persistence, tendency to bioaccumulate, and possible adverse effects on wildlife and humans, even in remote areas. The use of PBDEs and HBCDs has been phased out because of international regulations such as the Restriction of Hazardous Substances (RoHS) Directive (Directive 2002/95/EC) of the European Commission [1] and the Stockholm Convention on Persistent Organic Pollutants (POPs) [2]. However, even though the use of the BFRs of concern has been phased out, special attention should be paid to the potential for their emission from treated products to indoor and outdoor environments, which will continue for a long time. Another environmental and health concern is that PBDEs have the potential to form polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) in combustion processes and under thermal stress during extrusion, molding, or shredding [3] as well as via photolysis in various matrices such as solvents, sediment, soil, house dust, and treated-articles [4–8]. The toxicity of these resultant compounds is estimated to be similar to that of

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chlorinated dioxins [9]. In addition, PBDD/Fs have been found as impurities in commercial PBDE mixtures [10]. Recently, PBDD/Fs were identified for possible future inclusion in the list of toxic equivalency factors (TEFs) and for consideration in the toxic equivalency (TEQ) concept proposed by World Health Organization [11].

Humans are exposed to various chemicals, including BFRs, in daily life through multiple media, including food, water, and air. House dust is also a significant source of exposure to BFRs for humans, and especially for young children, who frequently touch their hands to their mouths. House dust is a complex heterogeneous mixture of biologically derived, particle-bound matter; indoor aerosols; and soil particles with a composition strongly dependent on seasonal, environmental, and personal factors [12,13]. It has been reported that BFR concentrations in human blood and breast milk are significantly correlated with those in indoor dust [14], the suggestion being that indoor dust reflects the lifestyles and activities of the people who reside there. Dust has therefore been used as an indicator of indoor contamination over the past decade [15]. However, it is usually not easy to obtain a representative dust sample from a home for chemical analysis because the composition of house dust is inhomogeneous throughout a home as well as between homes [16]. The concentrations of contaminants in dust are influenced by many factors, including sampling season [17], building structure, the room in the home, furnishing materials, heating and ventilation, how well and how often the area is cleaned, and the experimental design of the sampling. Since there is no universally accepted standard method for the collection and pretreatment of dust samples, many studies of indoor environmental contaminants have employed their own unique sampling strategies which sometime lead to difficulties in the interpretation of contaminant levels. The result of a dust analysis might depend strongly on the particle size distribution used for the chemical analysis [16–21], however, research in this area is limited and more research is needed to generalize the fact. Moreover, whether it is appropriate to include fluffy dust (lint) in the sample to be analyzed is always problematic for the chemical analyst.

At the moment there are three hypothesized pathways of BFR transfer from products to dust: (1) volatilization of BFRs from the treated product, with subsequent partitioning to dust; (2) transfer via direct contact between the treated product and dust [22,23]; and (3) abrasion via physical wear and tear of the treated product, resulting in the transfer of particles or fibers of the treated product directly to dust [24,25]. Pathways 1 and 2 are thought to depend basically on the surface area of the dust. Because chemical contaminants are usually adsorbed onto the surface of particles, finer particles with larger surface area-to-volume ratios have more capacity to retain chemical contaminants, the result being higher contaminant concentrations in finer particles [26,27]. So far, no studies have focused on which pathways account for most of the transfer of BFRs from products to indoor dust.

Based on this background, the aims of this study were to (1) elucidate the particle size dependence of the levels of BFRs and related substances in Japanese house dust; (2) obtain clues as to the characteristics of the sources of BFRs in the dust; and (3) propose a range of particle sizes best suited for BFR chemical analysis. To the authors' knowledge, this study is the first to include an analysis of the particle size distribution of PBDD/Fs in dust, and the first to compare the distribution of BFRs in particulate and fluffy dust separately.

2. Material and methods

2.1. Samples

House dust samples were collected in 2009 from vacuum cleaner bags of vacuum cleaners that were routinely used at five homes in the Kanto region of Japan (designated HD-01, -02, -03, -04, and −05). After manual removal of debris, hair, and small pebbles with tweezers from the dust of individual bags, the dust was sequentially sieved into seven fractions based on particle sizes (>2 mm, 1–2 mm, 0.5–1.0 mm, 250–500 μm, 106–250 μm, 53–106 μm, and <53 μm) with a vibratory sieve shaker (Model PRO, FRITSCH, Yokohama, Japan). To enhance the sieving efficiency, 10 zirconium oxide grinding balls (10 mm in diameter) were placed on the top sieve, which had the largest mesh size (2 mm). Sieving was continued until the weight of dust on the top sieve stopped decreasing and became constant. Fluffy dust was also separately allocated to each of the particle fractions (Fig. 1). It may be inappropriate to classify fluffy dust on the basis of 'particle' size, because fluffy dust is fibrous. To the extent possible, however, particulate and fluffy dust were included in each size fraction, and the size fractions were separated for purposes of chemical analysis. Prior to extraction, samples were weighed and then stored in a cold, dark place.

2.2. Chemical analysis

PBDEs, HBCDs, and PBDD/Fs in the size-fractionated dust samples were extracted by using a rapid solvent extractor (SE-100, Mitsubishi Chemical Analytech Co., Ltd., Japan). First, approximately 0.5 g–2 g of each sample was mixed with 10 g of anhydrous sodium sulfate (for PCB analysis, Kanto Chemical Co., Inc., Japan). The mixture was transferred to an extraction column, and the column was then filled with acetone/hexane (1:1). For the next 40 min the solvent was gradually replaced with toluene at a flow rate of 2 mL min^{-1}. The temperature of the extraction column was then increased to 80 °C and held for 10 min. The extraction with toluene continued for another 30 min at a flow rate of 2 mL min^{-1}. After the addition of $^{13}C_{12}$-labeled PBDE (MBDE-MXE, Wellington Laboratories, Inc., Canada), PBDD/Fs, and HBCD mixtures (MaHBCD, MbHBCD, and MgHBCD, Wellington Laboratories) as internal standards, a portion of the crude extract was quantitatively transferred onto a multilayer column that consisted of Wakogel DX (Wako Pure Chemical Industries, Ltd., Japan), 22% sulfuric acid–impregnated silica gel (6 g, Wako Pure Chemical Industries, Ltd.), 44% sulfuric acid–impregnated silica gel (4.5 g, Wako Pure Chemical Industries, Ltd.), and 2% potassium hydroxide–impregnated silica gel (3 g, Wako Pure Chemical Industries, Ltd.) that had been pre-washed and conditioned with 50 mL of 5% dichloromethane/hexane. PBDE and PBDD/F homologs were eluted in the first fraction with 70 mL of 5% dichloromethane/hexane; HBCD diastereomers were eluted in the second fraction with 60 mL of 50% dichloromethane/hexane. The PBDE and PBDD/F fraction was evaporated and loaded onto a sulfoxide silica gel column (3 g, Supelclean Sulfoxide, Sigma-Aldrich Co., LLC) for further clean up. The first fraction of sulfoxide silica gel clean-up was eluted with 9 mL of hexane and discarded. The second fraction of sulfoxide silica gel clean-up was eluted with 50 mL of 10% acetone/hexane and was collected. This fraction was evaporated to incipient dryness and further loaded onto an active carbon-dispersed silica gel reversible column (Kanto Chemical Co., Inc., Japan), where it remained for 30 min. After PBDE homologs were eluted with 80 mL of 25% dichloromethane/hexane, the column was turned upside down, and then PBDD/F homologs were eluted with 60 mL of toluene. After evaporation to incipient dryness, each fraction for