TRI- TO DECABROMINATED DIPHENYL ETHERS AND HBCD IN INDOOR AIR AND DUST FROM STOCKHOLM MICROENVIRONMENTS

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Introduction

PentaBDE, OctaBDE, DecaBDE and HBCD are additive brominated flame retardants (BFRs) in textile coatings, foams, and plastics that are used in TVs, computers, various electric and electronic equipment, insulation sheets, upholstery, bed-ticking, carpeting, etc. These products are found in homes, public buildings such as day care centers and schools, office buildings as well as in cars, subways, trains, airplanes, and other means of transport. PBDEs, primarily the tri-heptaBDEs have been measured in indoor air in several studies of North American and UK homes, public buildings and in one study, cars[1-6]. In a few studies, BDE-209 has been included but HBCD has not. PBDEs and HBCD have also been found in indoor dust in studies from North America and a few European countries[1-3;5;7-13]. Data from Sweden are few but show the presence of PBDEs in air and dust[14;15]. The aim of this project was therefore to sample and quantify polybrominated diphenyl ethers (PBDEs), particularly decabromodiphenyl ether (BDE-209) and hexabromocyclododecane (HBCD) in indoor air and dust from homes, offices, apartments, day care centers, and cars in Stockholm, Sweden. The results were used to estimate general human exposure to these compounds from indoor environments.

Materials and methods

Indoor air (gas and particle phase) and dust samples were collected from 54 homes (10 houses, 44 apartments from 11 different buildings), 10 day care centers, 10 offices (different buildings) and 17 new cars (7 makes) from Stockholm City. Apartment buildings were chosen so half of the apartments sampled had characteristics of "sick building syndrome" and half were classified as "healthy homes". Air sampling of PBDEs and HBCD was done using a low volume active air sampler connected to a personal pump with a flow rate of 1-15 L/min[14;16]. The sampler train contained two polyurethane foam plugs (PUFs) for collecting target compounds in the vapor phase and a glass fiber filter for collecting target compounds on particles[17]. To increase the mass of sample, four sampling trains were placed in parallel on one pump with a flow rate of 12 L/min (3 L/min per sampler). The sampler was suspended at least 1 m above the floor with the filter end pointing down. Air from buildings was sampled for 8 (offices, day care centers) or 24 hours (houses, apartments) during winter 2006 (heating season). Cars were sampled for 8 hours in June 2006; 5 cars were sampled twice, once indoors and once outside standing in strong sunshine with the windows closed to reach a higher indoor temperature. Dust samples were collected after air sampling was complete, using cellulose filters in styrene-acrylonitrile holders inserted in a polypropylene nozzle (Krim. Teknisk Materiel AB, Bålsta, Sweden), which was attached to the intake nozzle of an industrial strength vacuum cleaner [18]. Sampling was done from surfaces at least one meter above the floor, such as bookshelves, moldings and counters, in order to eliminate dirt, gravel and sand. Dust was only available from 4 cars of 4 different makes. Surrogate standards of Dechlorane and ^{13}C-BDE209 were added to samples, which were then extracted twice in DCM for 30 minutes in an ultrasound bath. Extracts were cleaned up on acid/silica (H_2SO_4/SiO_2-gel (1:2, w/w)-cartridges. Samples were spiked with injection standard of BDE-77 and the sample volume reduced prior to analysis on GC/MS. Samples were analyzed for tri-decaBDEs (BDE-28, 47, 99, 153, 183, 197, 206, 207, 208, 209) and total HBCD using a GC-MS with negative chemical ionization, (GC-ECNI-MS)[19;20], with ammonia as reagent gas. The system used was a Finnigan MAT SSQ 7000 MS instrument coupled to a Hewlett-Packard 5890 II GC. The GC column used was a 15 m DB-5MS fused silica column (J&W Scientific, 0.25 mm i.d., film thickness 0.25 µm). Analyses were performed by monitoring m/z 237 and 239 for the surrogate standard of Dechlorane and 494.3 and 496.3 for ^{13}C-BDE209. The analysis of nonaBDE and BDE-209 was done by monitoring m/z 484.2 and 486.2. The injection standard of BDE-77 and the rest of the brominated analytes (PBDEs and HBCD) were analyzed by monitoring m/z 79 and 81. Results for air samples are given as total (gas and particle phase) concentrations.

Results and discussion

Air: PBDEs were detected in all air samples, but HBCD concentrations were very low or below the detection limit. The BFR concentrations were log-normally distributed within each microenvironment class. The median concentrations of the different BFRs found in air samples from the different indoor environments are presented in Fig. 1. The median ΣPBDE concentrations vary by two orders of magnitude between the different indoor environments, with lowest concentrations in apartments (63 pg/m^3), higher in houses (330 pg/m^3) and cars (520 pg/m^3) and highest in day care centers (1400 pg/m^3) and offices (4000 pg/m^3). Offices had the highest maximum ΣPBDE value (7300 pg/m^3). When broken down into the three technical PBDE products, median ΣPentaBDE concentrations are similar in houses (31 pg/m^3) and apartments, intermediate in day care centers and cars and highest in the offices. Again, offices had the highest maximum ΣPentaBDE concentration (1000 pg/m^3). Median ΣOctaBDE concentrations are lowest in houses and apartments, intermediate in day care centers and cars and highest in offices. Offices also have the highest maximum ΣOctaBDE value (3600 pg/m^3). Median ΣDecaBDE concentrations are lowest in apartments, ten times higher in houses and cars, 30 times higher in day care centers and 100 times higher in offices. Offices have the highest maximum value (5800 pg/m^3). Within the different classes of microenvironments, there was considerable variation in BFR concentrations and proportions.

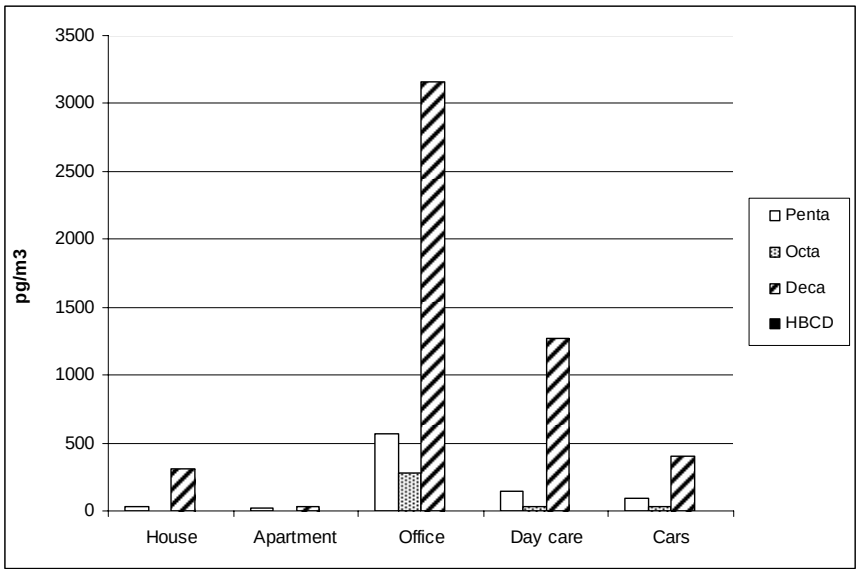

Fig. 1. Median concentrations in air (pg/m^3) from houses, apartments, offices, day care centers and cars. Penta is the sum of BDE-28, -47, -99, -153. Octa is the sum of BDE-183 and -197. Deca is the sum of BDE-206, -207, -208, -209.

No differences were seen in air concentrations in cars sampled indoors or standing in the sun or in concentrations between apartments from "sick" or "healthy" buildings. For all microenvironments, the compound found in highest concentrations in air was BDE-209. The BDE congener patterns in the majority of samples are similar to those of the technical products, indicating that these are being released in some manner from materials containing these flame retardants, either by outgassing or by other possible processes. Concentrations of all BDE congeners were correlated to each other but not to HBCD.

Dust: PBDEs and HBCD were detected in dust samples and concentrations were log-normally distributed within each microenvironment class. The median concentrations of the different BFRs found in dust samples from the different indoor environments are presented in Fig. 2. The median ΣPBDE concentrations are lower in houses (510 ng/g dw) than in apartments (1400 ng/g dw), cars (1400 ng/g dw), offices (1200 ng/dw) and day care centers (1200 ng/g dw). The maximum values vary considerably, with apartments having the highest maximum value (102 000 ng/g dw). When broken down into the three technical PBDE products, median ΣPentaBDE concentrations are lowest in cars, similar in houses and apartments, somewhat higher in offices and highest in the

day care centers. Median ΣOctaBDE concentrations are lowest in cars, are higher and similar in houses, apartments and day care centers and highest in offices. Offices also have the highest maximum ΣOctaBDE value (260 ng/g dw). Median ΣDecaBDE concentrations are lowest in houses, somewhat higher in offices and day care centers and highest in cars and apartments. Apartments have the highest maximum value (102 000 ng/g dw), which is due to one apartment having a very high concentration of BDE-209 (100 000 ng/g dw). Median HBCD concentrations are lowest in apartments and cars, somewhat higher in houses and highest in offices and day care centers. Within the different classes of microenvironments, there was considerable variation in BFR

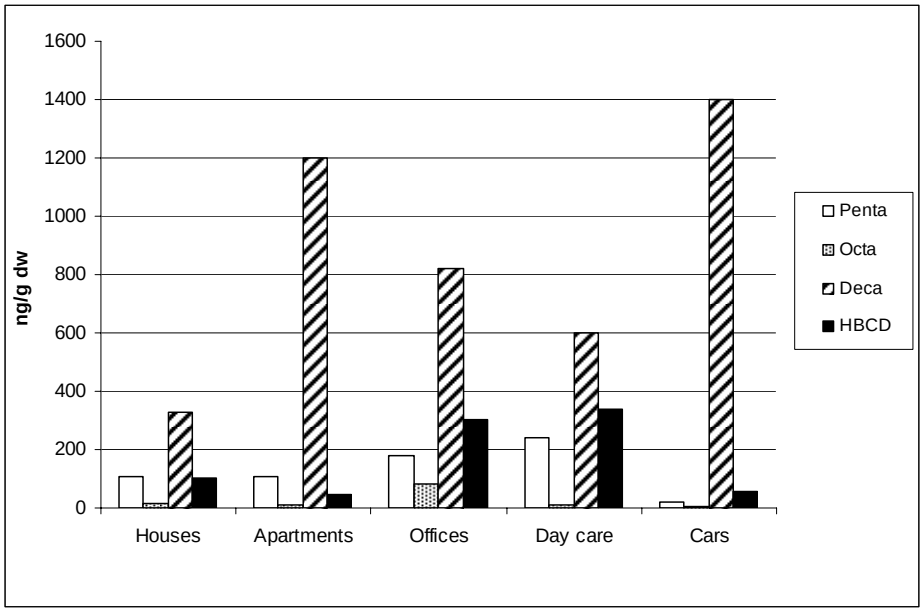

Fig. 2. Median concentrations in dust (ng/g dry weight) from houses, apartments, offices, day care centers and cars. Penta is the sum of BDE-28, -47, -99, -153. Octa is the sum of BDE-183 and -197. Deca is the sum of BDE-206, -207, -208, -209.

concentrations and proportions. As with air samples, no differences were seen in concentrations in dust between apartments from "sick" or "healthy" buildings. For all microenvironment types, the BFR found in highest concentrations in dust was BDE-209. There is considerable variation in BFR concentrations and profiles within and between each type of microenvironment. HBCD was found in the majority of dust samples and sometimes was the predominant BFR in the sample. BDE-209 was found in all dust samples and was the predominant compound in most of them, with particularly high concentrations found in one apartment, but also elevated concentrations in a few other locations. The predominance of BDE-209 in dust is due to its low volatility, which makes it more likely to be found on particulates at room temperature[2] as well as the fact that DecaBDE is the predominant technical product in use. As for air, all microenvironments have outliers for various BFRs. The BDE congener patterns in the majority of samples are similar to those of the technical products, indicating that these are being released in some manner from materials containing these flame retardants. Correlations were seen between concentrations of BDE congeners within a technical product, but not between the different technical products or HBCD.

Air vs dust: No statistically significant correlations were found for concentrations of any individual BDEs, HBCD or sum parameters when comparing paired air and dust samples from all microenvironments together. No statistically significant correlations were seen when paired air and dust samples were compared for houses, apartments, offices or day care centers, separately.

Intakes: Estimated intakes were calculated using median ΣPentaBDE concentrations in air and dust, mean dust ingestion rates for adults and children[21;22], air inhalation rates[8] and mean dietary intake in Sweden[23]. Inhalation

and dust ingestion play minor roles compared to diet in adult exposure, but dust ingestion may represent up to 20% of toddler intake. When the worst case scenario is used (high dust ingestion, maximum dust concentrations), dust ingestion in toddlers may represent up to 90% of intake. For HBCD exposure, adult exposure is mainly from the diet[24] as well, with only 6% of toddler exposure coming from dust ingestion. But in the worst case scenario, dust ingestion in toddlers may represent up to 80% of HBCD intake. For the BDE congeners in OctaBDE and DecaBDE, particularly BDE-209, no dietary intake estimates are available to compare inhalation and dust ingestion with.

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