Measurement of the Flame Retardants Polybrominated Diphenyl Ethers (PBDEs) and Hexabromocyclododecane (HBCDD) in House Dust

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Introduction

Current monitoring of polybrominated diphenyl ethers (PBDEs) has shown that concentrations are increasing in the environment very rapidly with doubling times as short as three to five years [1,2]. North America consumes a large percentage of the global market demand for PBDEs, and as a result, concentrations of PBDEs in human milk and serum are an order of magnitude higher in women from North America relative to Europe[3-5]. Within sampled populations, PBDE levels in human serum have been shown to range over an order of magnitude, and high levels cannot always be attributed to occupational exposure, age or diet [4,5]. One source that may be responsible for these observations is exposure in the home. These compounds are liberally applied to many common household items such as furniture, mattresses, computers and TVs to retard or hinder the outbreak of fire. Over time, these flame retardants may leach out into the home environment, where they may be inhaled or ingested, resulting in elevated levels in human serum.

Very few studies have examined PBDE levels within the home and only one study has measured the concentrations of two PBDE congeners in house dust[6]. The present study was undertaken to measure a suite PBDE congeners in house dust from a variety of homes and to assess the contribution of the three commercial PBDE mixtures (penta-, octa- and decaBDE) to the house dust composition. In addition, we also measured the concentrations of hexabromocyclododecane (HBCDD), another flame retardant. Correlations with properties of the houses

such as year of construction, square footage, carpeting coverage and number of computers in the house were also examined for any positive influences.

Materials and Methods

Seventeen house dust samples were collected using a small handheld vacuum (Euro-Pro model, 900 Watts) equipped with a hose, filter basket and HEPA filter. A standard coffee filter was inserted between the filter basket and HEPA filter to collect fine particle dust from each house. Under these conditions, dust was collected that passed through a 1 mm mesh in the basket. Between sample collections the vacuum was thoroughly cleaned with hot water and a methanol rinse and new filters were used for each sample. In each house, dust was collected in the main family room by vacuuming the rugs or hardwood floors until sufficient mass (0.1-0.5 g) was collected on the filter (approximately 5-15 min.). After vacuuming, the dust was scraped off the filter into pre-cleaned glass jars using methanol rinsed spatulas and taken back to NIST for extraction and quantification. All dust samples were extracted using pressurized fluid extraction with dichloromethane and the extracts were cleaned using silica sep-pak cartridges. A ^{13}C labeled BDE 209 (2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether, BDE 209L) and a ^{13}C labeled chlorinated diphenyl ether (2,2',3,4,5-pentachlordiphenyl ether, CDE 86L) were added to each sample as internal standards.

House dust standard reference materials (SRM 2583 and 2584) were also extracted and measured for PBDEs. These SRMs were prepared at NIST but were initially collected under the direction of the Research Triangle Institute and the U.S. Environmental Protection Agency. The collection process involved sampling of numerous vacuum cleaner bags from houses, cleaning services, motels and hotels in the states of North Carolina, Maryland, Ohio, New Jersey, Wisconsin and Montana. These house dust materials were originally collected and prepared as a SRM for lead in house dust.

Quantification of BDE congeners was performed using a gas chromatograph equipped with a mass spectrometer. Analysis was made using negative chemical ionization operated in the selected ion monitoring mode, and BDEs were quantified using ions 79 and 81 (bromide ions) for the majority of the BDEs with the exception of BDE 209 which was monitored with ions 487 and 409. A 15 m x 0.25 mm (i.d.), 5% phenyl methylpolysiloxane capillary column (0.25 µm thickness) was used for the separation of the BDE congeners, and all injections

were performed with on-column cool injection.

Results and Discussion

Preliminary data on 22 PBDE congeners measured in the 17 house dust samples found total BDE concentrations ranging from 780 ng/g dry mass to 29,700 ng/g dry mass (Table 1). The contribution of pentaBDE (percentage of BDE 47, 99 and 100 to the total concentration) ranged from 7 % to 88% of the total BDE burden among the houses while the contribution of the decaBDE product (percentage of BDE 209 to the total concentration) ranged from 10 % to 86 % among the house dust samples. The sum total of pentaBDE and decaBDE congeners contributed at least 82% of the total PBDE burdens in all house dust samples. Concentrations of BDE 209 alone in the house dust samples ranged from 160 ng/g dry mass to 8,500 ng/g dry mass. These concentrations are in the median to high range of concentrations typically observed in contaminated sediment and sewage sludge[7-8] and suggest that home environments may play a significant role in human exposure to these flame retardants. The concentrations of all three nonaBDE congeners (BDE 208, 207 and 206) and two octaBDE congeners (BDE 197 and 196) were determined in all house dust samples and found to range from 0 % to 6% of the total PBDE burdens. Additionally, other BDE congeners were observed in the chromatograms that are not present in the commercial mixtures (BDE 17, 28, 49, 66 and 119).

Factors that could be affecting levels of PBDEs in the home were examined. These factors included age of the house, area, number of TVs and computers within the residence, type of flooring (i.e. carpeting versus hardwood floors) and number of foam containing furniture pieces. No significant correlations were apparent with these factors. However, the homes with the greatest percentage of BDE 209 in dust (>50%) were all collected from small apartments and condos (600 to 1080 sq. ft) in which the owners were all young professionals with computers that were used on a frequent basis (>5 hours a week).

Concentrations of BDE 209 in the two SRMs were comparable to the mean level measured in the house dust samples. However, levels of the pentaBDE congeners were lower in concentration relative to the mean levels measured in the house dust samples collected. This may reflect a difference in the time of sampling as the SRMs were collected and ten years ago. Value assignments for the PBDE

congeners will be made for these two SRMs and presented.

Hexabromocyclododecane (HBCDD), another flame retardant used in similar applications as PBDEs was also measured in the house dust samples. Concentrations ranged from < 3.0 ng/g dry mass to 800 ng/g dry mass, were not correlated to PBDE levels, and were not correlated to any other factor examined in this study.

References

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Table 1. BDE congener concentration (ng/g dry mass) measured in house dust samples (n=17) and SRMs (n=6).

	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 183	BDE 197	BDE 206	BDE 209	HBCDD
Min.	3	17	117	28	12	5	<D.L	<D.L	160	<D.L
Max.	117	7,600	14,000	2,100	1,500	168	77	238	8,700	925
Mean	21	1,200	1,700	270	180	30	14	48	2,100	140
SRM 2583	15 ± 0.9	226 ± 13	400± 27	64 ± 4	53 ± 4	18 ± 2	9.3 ± 0.9	39 ± 4	2230 ± 190	< D.L.
SRM 2584	14 ± 1.0	205 ± 5	340 ± 8	54 ± 1	1	23 ± 1	2	36 ± 5	2050 ± 160	< D.L.