

Concentration of Polybrominated Diphenyl Ethers (PBDEs) in House Hold Dust – Inhalation a Potential Route of Human Exposure.

Andreas Sjödin¹, Olaf Päpke², Ernest McGahee III¹, Richard S. Jones¹, Chester R. Lapeza¹, Jean-François Focant¹, Richard Y. Wang¹, Yalin Zhang¹, Larry L. Needham¹, Thomas Herrmann², and Donald G. Patterson Jr.¹,

¹ Centers for Disease Control and Prevention (CDC); National Center for Environmental Health (NCEH); Division for Laboratory Sciences (DLS); 4770 Buford Hwy; Atlanta, GA, 30341; U.S.A.

² ERGO Research, Geierstrasse 1, D 22305 Hamburg, Germany.

Introduction

Polybrominated diphenyl ethers (PBDEs) are congeners of a class of environmental contaminants that have been present in the environment for decades. PBDEs were first identified in the River Viskan in Sweden ¹ and has since then been recognized as an environmental contaminant with a global distribution as shown by the detection of this compound class in aquatic and terrestrial environments in Europe ² and North America. ³

Human PBDE levels have been shown to be increasing in Sweden ⁴, Norway ⁵ and in the United States. ⁶ This indicates a wide spread human exposure to this class of chemicals. Technical pentaBDE and octaBDE have been withdrawn from the market in Europe ⁷ and the single producer of these products in the United States has agreed to phase-out manufacturing of these products by the end of 2004. No restrictions for commercial DecaBDE are planned in the United States.

However, PBDEs will still be present in consumer products sold prior to the phase out of pentaBDE and octaBDE for decades to come. Hence it is of utmost importance to identify the exposure routes to humans especially in the United States where much higher levels of PBDEs have been observed in people. An average level of 34 ng/g lipid has been observed in human serum pools collected in 2002 ⁶ and values in the range of 2.9-272 ng lipid (average 41ng/g lipid) have been observed in human milk. ⁸ This can be contrasted to levels observed in Swedish milk pools (2.3 ng/g lipid) collected in 1997. ⁴

Human exposure to persistent chemicals like polychlorinated biphenyls has traditionally been considered to be mainly through food consumption and other direct exposure routes such as inhalation and/or dermal exposure are only of quantitative more importance in the case of occupational exposures. However, this may or may not be true for PBDEs which are still being used in the modern indoor environment. This is further supported by the relatively low concentrations recently reported in foodstuffs sampled in the United States. ⁹

Our approach was to use the contents of vacuum cleaner bags as an indication of indoor PBDE contamination. The results from this study have to be followed up by air sampling

and biomonitoring studies to answer if PBDE exposure through inhalation of dust and/or dermal contact could be a major exposure route in the United States.

Materials and Methods

Vacuum cleaner bags were collected in Germany (N=10) and in Atlanta, United States (N=10). The bags from the 20 different households were opened and the content transferred to a household sieve with a hole size of ~2mm. The sample was sieved by shaking and particulate matter was collected on aluminum foil. After a sufficiently large sample of particulate matter had been collected on the foil, the sample was transferred to a Ziploc[®] bag and stored at room temperature until analysis. Between each sample the sieve was cleaned and the aluminum foil replaced.

The samples (0.2g) were extracted by transferring the sample to an accelerated solvent extraction[®] (ASE) cell (11mL) filled with Hydromatrix (Varian Inc; Palo Alto, CA). The samples were extracted using ASE (Dionex; Sunnyvale, CA) employing hexane as the solvent using the following settings: Temperature, 100°C, purge volume 60%, nitrogen purge time 60 seconds, pressure 1500psi, no preheat time and static extraction time 5 minutes and three repeated extraction cycles. The cell and inert content had been cleaned prior to adding the dust sample by extracting the cell using the same parameters as for the sample extraction. Blank samples (N=3) comprised of only Hydromatrix were also included among the unknowns.

Three samples from the United States and three samples from Germany were extracted a second time in order to verify complete extraction.

The collection vial used at the extractor were weighed before and after extraction in order to calculate exact amount of solvent collected, i.e., approximately 30mL. Concentrated sulfuric acid (5mL) was added to the dust samples and the samples subsequently rocked for 5 minutes. A small aliquot was drawn from each sample (100µL) and added to GC-vials containing ¹³C-labeled triBDE to decaBDE internal surrogate standards (750pg/congener). The samples were evaporated to 10µL and analyzed by gas chromatography high-resolution mass spectrometry (GC/HR-MS) on a MAT95 (ThermoFinnigan MAT, Bremen, Germany). The level of PBDEs in the samples was calculated as ng/g dust taking into account the dilution step.

Results

The sum PBDE concentration in dust samples collected in Germany, mainly Northern Germany, ranged from 17-550 ng/g dust (median 74) while a concentration range of 530-29,000 ng/g dust (median 4,200) was found in the samples collected in the United States. 2,2',4,4'-TetraBDE (BDE-47) and decaBDE (BDE-209) were the most abundant PBDE congeners recovered. The pentaBDE pattern observed in the dust samples was similar to that found in the technical products, i.e. 2,2',4,4',5-pentaBDE (BDE-99) is similar in concentration to that of BDE-47 (Table 1 and Figure 1). The observed difference in concentration between Germany and the United States was statistically significant (U-Test).

Table 1. Concentration of polybrominated diphenyl ethers (PBDEs) in dust samples given as ng/g dust.

Compound	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
United States (N=10)							
Median	430	880	150	140	77	73	2,000
Min	230	69	<15	5	<7	<8	120
Max	3,000	3,700	660	650	260	4,000	21,000
Germany (N=10)							
Median	<14	10	<6	<6	<6	<5	60
Min	<14	<4	<6	<6	<6	<5	<5
Max	22	38	7	22	<6	121	410

Abbreviations: BDE-47, 2,2',4,4'-tetrabromodiphenyl ether; BDE-99, 2,2',4,4',5-pentaBDE; BDE-100, 2,2',4,4',6-pentaBDE; BDE-153, 2,2',4,4',5,5'-hexaBDE; BDE-183, 2,2',3,4,4',5',6-heptaBDE; BDE-209, decaBDE.

For the six samples that were extracted twice, PBDEs in the second extract were found at levels below the quantification limit defined as 3 times the standard deviation of blank samples or at levels below the instrumental detection limit.

Discussion

Significantly higher levels of PBDEs were observed in the dust collected in the United States as compared to Germany, cf. Table 1 and Figure 1. This illustrates that exposure to dust is a potential exposure route of PBDEs for humans. The higher importance of direct exposures has been shown in the past in isolated occupational settings, i.e., recycling of electronic goods.¹⁰ This occupational study, however, addressed exposure to congeners with a high degree of bromination such as heptaBDE through decaBDE. The main exposure route of the lower brominated species such as BDE-47 and BDE-99 has to date been assumed to be the food, as has been shown to be the case for Swedish and Latvian fishermen consuming large quantities of fish caught in the Baltic Sea.¹¹

Considering the intake of an adult of between 10 to 100 mg of dust (dust contains e.g. 4000 ng/g PBDEs) we may expect an intake via dust of up to 400 ng per day per person. This intake may add to the intake via food of between 50 and 100 ng per day per person as reported by various authors.^{12,13}

We can not conclude what exposure routes are more important to humans in the United States and Germany, but we can conclude that in indoor dust the levels of PBDEs are much higher in the United States than in Germany (Table 1 and Figure 1). In light of these findings and the fact that higher levels are reported in people living in the United States¹⁴ that this potentially important route of exposure has to be studied in-depth in the future.

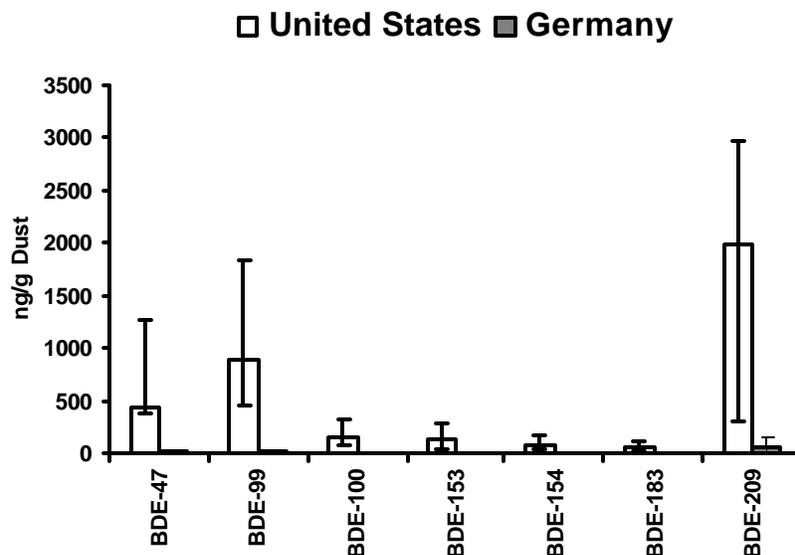


Figure 1. Concentration of polybrominated diphenyl ethers in dust samples from Germany and the United States. Error bars indicates quartile range.

References

- (1) Andersson, Ö. and Blomkvist, G., *Chemosphere*, 1981, **10**, 1051-1060.
- (2) Asplund, L., Athanasiadou, M., Sjödin, A., Bergman, Å. and Börjeson, H., *Ambio*, 1999, **28**, 67-76.
- (3) Norstrom, R. J., Simon, M., Moisey, J., Wakeford, B. and Weseloh, D. V. C., *Environ Sci Technol*, 2002, **36**, 4783-4789.
- (4) Meironyté, D., Norén, K. and Bergman, Å., *J Toxicol Environ Health*, 1999, **58 Part A**, 329-341.
- (5) Thomsen, C., Lundanes, E. and Becher, G., *Environ Sci Technol*, 2002, **36**, 1414-1418.
- (6) Sjödin A., Jones R. S., Focant J.-F., Lapeza C. R., Wang R. Y., McGahee E. E. I., Zhang Y, Turner W. E., Slazyk B., Needham L. L., and Patterson Jr D. G. *Environmental Health Perspectives*, *In press*.
- (7) Cox, P. and Efthymiou, P., *Official Journal of the European Union*, 2003, **OJL 42**, 45-46.
- (8) Schecter, A., Pavuk, M., Pöpke, O., Ryan, J. J., Birnbaum, L. and Rosen, R., *Environ Health Perspect*, 2003, **111**, 1723-1729.
- (9) Schecter A., Pöpke O., Ryan J. J., Tung K. C., Birnbaum L., Staskal D., and Rosen R. *Third International Workshop on Brominated Flame Retardants*, *In press*.
- (10) Sjödin, A., Hagmar, L., Klasson-Wehler, E., Kronholm-Diab, K., Jakobsson, E. and Bergman, Å., *Environ Health Perspect*, 1999, **107**, 643-648.
- (11) Sjödin, A., Hagmar, L., Klasson-Wehler, E., Björk, J. and Bergman, Å., *Environ Health Perspect*, 2000, **108**, 1035-1041.
- (12) Bocio, A., Llobet, J. M., Domingo, J. L., Corbella, J., Teixidó, A. and Casas, C., *J Agric Food Chem*, 2003, **51**, 3191-3195.
- (13) Ryan, J. J. and Patry, B., *Organohalogen Comp*, 2001, **51**, 226-229.
- (14) Sjödin, A., Patterson Jr, D. G. and Bergman, Å., *Environ Int*, 2003, **29**, 829-839.