ANALELE ŞTIINŢIFICE ALE UNIVERSITĂŢII "Al. I. CUZA" IAŞI
Seria Chimie, Tomul XVI, 2008

Estimation of Daily Intake of Selected Brominated Flame Retardants (BFRs) through Food Consumption and Indoor Dust Ingestion in Romania

Alin C. Dirtu [a,b*] and Adrian Covaci [b]

[a] *Department of Chemistry, "Al. I. Cuza" University Iasi, 11 Carol I Bd, Iasi 700506, Romania*

[b] *Toxicological Center, Department of Pharmaceutical Sciences, University of Antwerp, Universiteitsplein 1, Wilrijk-Antwerp 2610, Belgium*

Abstract: The present study aimed at estimating the human exposure to selected brominated flame retardants (including polybrominated diphenyl ethers – PBDEs, especially decabrominated diphenyl ether – BDE 209, and total hexabromocyclododecane – HBCD) in Eastern Romania through food consumption (mainly food of animal origin) and indoor dust ingestion. The estimation of daily intake for these contaminants was hereby assessed based on monthly food consumption recommendations by the Romanian authorities and on studies focused on dust ingestion by humans. The results of the present study show that the intake of lower PBDE congeners is higher through food consumption, while the ingestion of indoor dust is dominant for BDE 209. The levels found for total HBCD were lower when compared to PBDEs, showing that this flame retardant has a limited application range in products commercialized in Romania.

Keywords: BFRs; PBDEs; BDE 209; Food; Dust.

[*] Correspondence to:
Alin C. Dirtu, tel: +40 232 201308, fax: +40 232 201313, e-mail: alin.dirtu@chem.uaic.ro

Introduction

Polybrominated diphenyl ethers (PBDEs) were firstly introduced on the market as flame retardants (FRs) in 1960s and since then, their environmental levels have been continuously increasing. Their presence in human tissues is of particular concern because of their toxicological potential regarding neurodevelopment and the endocrine system.[1]

Due to their lipophilic nature, these chemicals are mainly found in lipid-rich food of animal origin, such as meat, fish and dairy products, which constitute an important part of our diet. It has been suggested that food, and in particular food of animal origin, is responsible for more than 90% of the average human intake of PCBs, a class of chemicals with relatively similar structure as PBDEs.[2] Besides lipid-rich food, for the human intake of FRs, indoor dust ingestion has been shown to be an important source.[3] The importance of the different routes of human exposure to PBDEs (diet and inhalation/ingestion) is not completely understood at present and opinions about the contribution of the dietary intake vary among publications.[4] In general, the proportion of the total intake that is diet-related, was estimated between 73% [5] and 93% [6]. The rest of the intake originates from inhalation and ingestion of dust, which may concentrate large quantities of PBDEs.[7-9] However, the contribution of dust inhalation/ingestion to the total PBDE exposure is susceptible to large variability depending on several factors, such as life style (indoor–outdoor), age (toddler–adult), home environment, and workplace exposure.[9]

Therefore, the present study aimed at estimating of human exposure in Eastern Romania to selected brominated flame retardants (including polybrominated diphenyl ethers – PBDEs, especially decabrominated diphenyl ether – BDE 209, and total hexabromocyclododecane – HBCD)

through food consumption (mainly food of animal origin) and indoor dust ingestion. The estimation of daily intake for these contaminant was hereby assessed based on monthly food consumption recommendations by the local authorities and on studies focused on dust ingestion by humans.

Experimental

Samples collection

A number of 50 food samples (each sample was obtained by pooling 3 sub-samples of the same food item) and 18 indoor dust samples were collected in June-September 2007 from Iasi, Romania. Selected food samples included several meat products (pork, beef and chicken steak, salami and pork sausages), diary products (cheese, butter, milk cream), vegetable cooking oil and eggs. Food samples were collected from 3 large-chain supermarkets and also from villages around Iasi city, Romania. The samples were homogenized immediately after collection and stored at −20 °C until analysis.

Investigated analytes

The following analytes were targeted for analysis: decabrominated diphenyl ether (BDE 209) and total hexabromocyclododecane (HBCD). Lower PBDEs (congeners: 28, 47, 100, 99, 154, 153, and 183) were also investigated in collected samples, but reporting of their levels are not the main purpose of this study. They are presented in order to underline the contribution of BDE 209 to the sum of concentration for PBDEs from food compared to indoor dust samples. Internal standards used for analyte quantification were BDE 128 and ^{13}C-BDE 209.

Analysis methodology

The methods used for the analysis of food and indoor dust have

previously been described.[10,11] Depending on the type of sample, 0.2 to 4 g of homogenized food and 0.25 g of dust were dried using anhydrous Na_2SO_4, spiked with internal standards and Soxhlet extracted with *n*-hexane/acetone mixture (3:1, *v/v*). For food analysis, an aliquot (~1/8th) of the extract was used for gravimetrical lipid determination. Clean-up was achieved by column chromatography on acid silica (45% H_2SO_4, *w/w*). The cleaned extract was concentrated and the solvent was changed to *iso*-octane before injection into the gas chromatographic (GC) system. An overwiew of the analysis methodology applied for the determination of BDE 209 and total HBCD is presented in Figure 1.

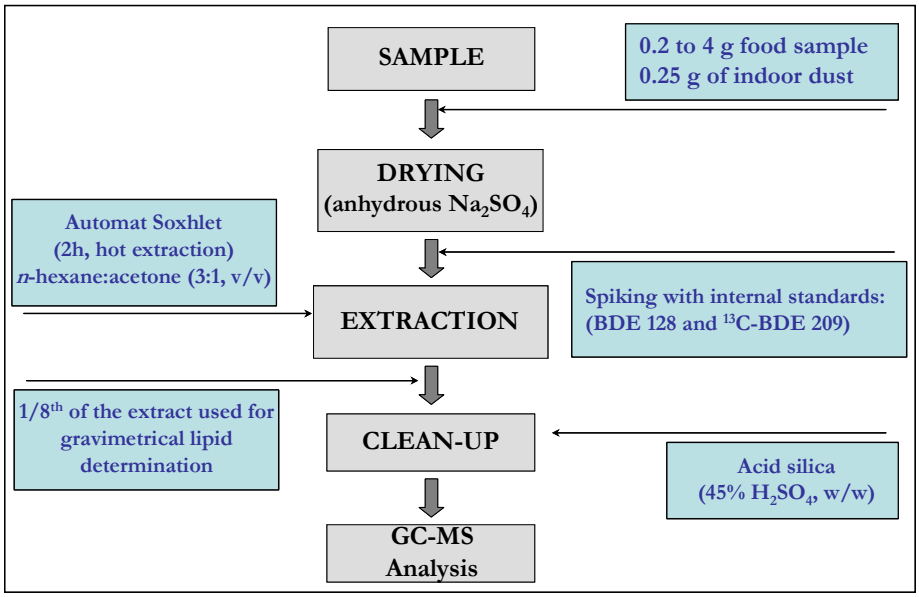

Figure 1. Analysis methodology used for determination of BDE 209 and total HBCD from food and indoor dust samples.

Instrumentation

Instrumental analysis was performed using a Hewlett Packard 6890 gas chromatograph coupled to a HP 5973 mass spectrometer with electron

capture negative ionization source (GC/ECNI-MS) operated in selected ion monitoring mode. The ion source, quadrupole and interface temperatures were 250, 150 and 300 °C, respectively. For the analysis of BDE 209 and total HBCD a 12 m × 0.18 mm × 0.20 μm AT-5 capillary column was used. Helium was used as carrier gas at constant flow (1.0 mL min^{-1}) with an initial pressure of 14.40 psi, while methane was used as reagent gas in the mass spectrometer. The electron multiplier voltage was set at 2200 V. One μL extract was injected in solvent vent mode (initial injector temperature at 90 °C, stay 0.05 min, then to 300 °C at a rate of 700 °C min^{-1}, vent flow 75 mL min^{-1}). The split valve was closed after 1.5 min. Ions *m/z* 484.7/486.7 and 494.7/496.7 were monitored for BDE 209 and ^{13}C-BDE 209, respectively. Ions *m/z* 79 and 81 were monitored for HBCD and BDE 128 (IS).

Quality assurance/Quality control

The quality control (QC) was done by regular analysis of procedural blanks (one in each batch of eight samples) and replicate samples (one in each batch of eight samples), for which a RSD < 10% was considered acceptable. Instrumental QC was done by regular injection of solvent blanks and standard solutions. The efficiency and capacity of the method was demonstrated by successful participation in international inter-laboratory exercises on the determination of PBDEs and PCBs in biota.[6] Recoveries for individual analytes were between 80% and 104% (RSD < 12%). Procedural blanks of BDE 209 and HBCD were consistent (RSD < 15%) and therefore the mean procedural blank value was used for subtraction. After blank subtraction, the limit of quantification (LOQ) was set at 3 x SD of the blank, which ensures >99% certainty that the reported value is originating from the sample. This, however, implies varying LOQs

depending on the sample intake and on the each investigated analyte. In case of analytes presented in samples at levels below method LOQ, the concentrations were replaced with values corresponding to ½ LOQ.

The method performance for dust analysis was also assessed via analysis of standard reference material SRM 2584 (house dust) which has indicative values for PBDEs[12] and for which a good agreement was obtained between our measured values and those reported in the literature.

Results and discussions

This is the first study which estimates the dietary exposure of Romanian population to BFRs through food and indoor dust ingestion. Since no differences in the concentrations of BFRs were observed between food samples from different supermarkets and vendors, median values were calculated using all analytes regardless the origin.

Levels and profiles

Results for food and indoor dust were expressed as median values in ng/g of sample (wet weight basis in case of food samples) (Table 1). Contrarily to dust, BDE 209 and HBCD could not be detected above the LOQ in any food samples. Therefore, a value of ½ LOQ were further used for statistical calculations, in order to obtain preliminary information regarding the exposure level of such contaminants through food consumption in Romania compared to similar studies from other European countries. The main contributor to the sum PBDEs in dust samples was BDE 209, with a contribution between 94 and 99 % that largely comprise the Deca-BDE commercial formulation. However, the BDE 209 levels measured in Romanian indoor dust samples are much lower than those in dust samples collected from United Kingdom or United States.[13] Similar

trends in dust were found also for HBCD[14], for which the levels were lower than PBDEs, showing that this BFR has a limited application range in products commercialized in Romania.

Intake estimation

To estimate the intake of contaminants through food consumption, concentrations (in wet weight basis) and the official recommendation of the monthly food consumption for an adult were used.[15,16] For toddlers, we considered 70% of the adult diet.

Table 1. Median levels of organohalogenated contaminants (ng/g *ww*) of the different food samples and also indoor dust samples considered for this study.

		N	Lipid (%)	ΣPBDEs	BDE 209	HBCD
Meat products	beef steak	2	10	0.26	<LOQ	<LOQ
	chicken	6	2	0.13	<LOQ	<LOQ
	pork	7	15	0.15	<LOQ	<LOQ
	salami	6	21	0.15	<LOQ	<LOQ
	pork sausage	3	23	0.12	<LOQ	<LOQ
Diary products	butter	3	71	0.11	<LOQ	<LOQ
	cheese (sheep)	5	26	0.11	<LOQ	<LOQ
	cheese (cow)	8	19	0.14	<LOQ	<LOQ
	vegetable oil	2	100	0.11	<LOQ	<LOQ
	milk cream	2	30	0.17	<LOQ	<LOQ
Eggs		3	9	0.03	<LOQ	<LOQ
Indoor dust		18	-	12	480	190

To make a preliminary evaluation of the magnitude of exposure to OBCs through dust ingestion to the population of Iasi City, Eastern Romania, we have assumed (in the absence of experimental data) 100% absorption of intake.[13] We have used average adult and toddler dust ingestion figures of 20 and 50 mg/day and high dust ingestion figures for adults and toddlers of 50 and 200 mg/day.[13,17] The estimation of daily intake (ng/day) of BFRs for adults and toddlers through food consumption and dust ingestion is presented in Table 2.

For the intake of PBDEs, the results for indoor dust ingestion are different when compared to food consumption for tri- to hepta-BDEs and for BDE 209. Therefore, for lower PBDE congeners, food consumption is of a higher importance in both cases (adult and toddler daily intake), while indoor dust ingestion is more important when intake of BDE 209 is considered (Figure 2 and Figure 3). The results show that food consumption contribute with more than 90% to the intake of lower PBDEs, while indoor dust ingestion can contribute with more than 85% to BDE 209 intake (in case of toddlers and considerring high dust intake scenario).

The results for intake of BDE 209 through dust ingestion estimated in the present study are comparable with similar studies applied on domestic dust samples from Canada, but they are much lower compared to studies applied on samples from UK or US (Table 3).[13,18]

Table 2. Estimation of daily intake (ng/day) of BFRs for adults and toddlers through food consumption and dust ingestion**.**

		RDC[a] (g)	ΣPBDEs	HBCD
Adult	Meat products	190	22	40
	Butter	16.7	1.8	4.2
	Cheese	110	14	28
	Vegetable oil	20	2.2	5
	Eggs	25	0.02	0.02
	Daily total – food		**40**	**77**
	Indoor dust-average intake	0.02[b]	**30.3**	**6**
	Indoor dust-high intake	0.05[b]	**75.8**	**15**
Toddler	Meat products	133	15	28
(6-24 months)	Butter	11.7	1.3	2.9
	Cheese	77	10	20
	Vegetable oil	14	1.5	3.5
	Eggs	17.5	0.01	0.01
	Daily total – food		**28**	**54**
	Indoor dust-average intake	0.05[b]	**75.8**	**15**
	Indoor dust-high intake	0.2[b]	**304**	**61**

[a]-RDC=Recommended daily consumption (g);[15,16] [b]-average and high dust ingestion figures (g) for adult and toddler.[13,17]

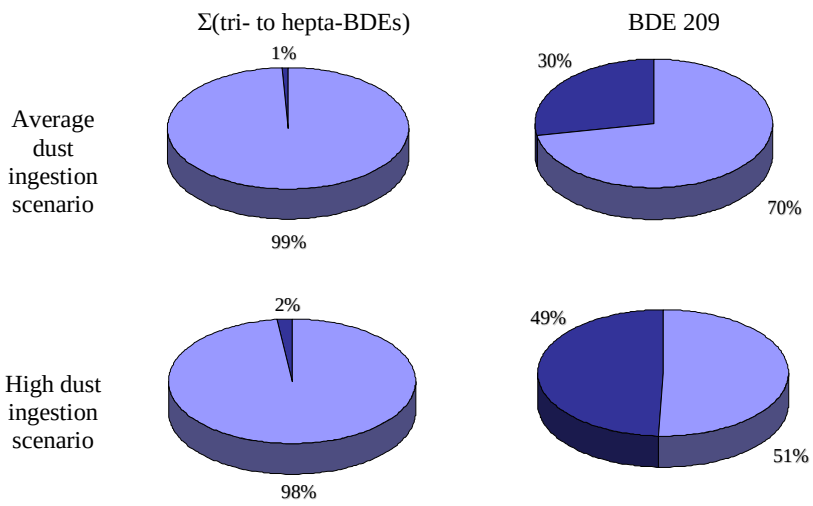

Figure 2. Contribution of food ( ) and indoor dust ( ) to daily intake of sum tri- to hepta-BDEs and BDE 209 for adults.

Because the most analyses were done on fresh unprocessed foods, which were not boiled, cooked, baked or fried prior to analysis, the data used to estimate the dietary exposure to BFRs might slightly overestimate the actual dietary exposure.[19] Also, because in our food basket collected for analysis we did not include any fish samples, we assume that present results might be underestimated, since it is known that fish can accumulate high amounts of BFRs. However, fish represents only a very small part of the daily diet for the Romanian population (less than 1%) compared with other types of food of animal origin.[15]

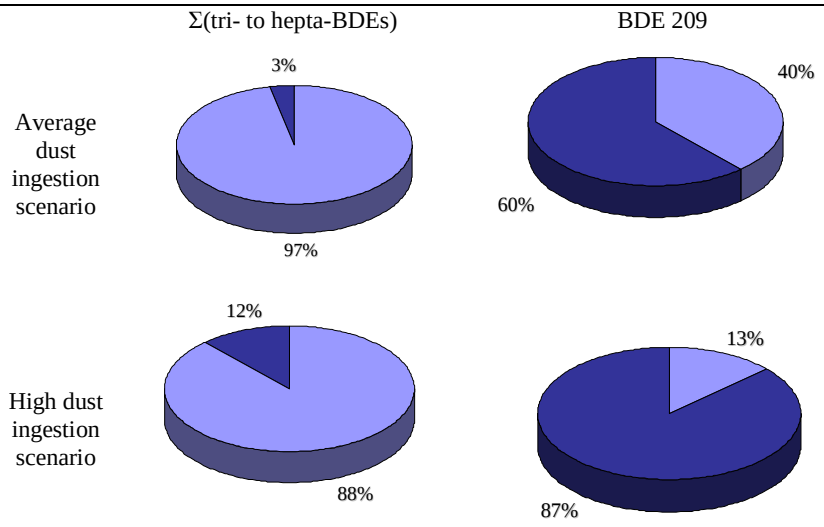

Figure 3. Contribution of food ( ) and indoor dust ( ) to daily intake of sum tri- to hepta-BDEs and BDE 209 for toddlers.

Table 3. Estimation of daily intake (ng/day) of BDE 209 for adult and toddler through indoor dust ingestion in various locations including Iasi, Romania**.**

Country/Region	Ingestion of BDE 209 (ng/day)			
	Adult		Toddler (6-24 months)	
	Mean	Median	Mean	Median
Canada (low dust ingestion)	13	11	33	28
Canada (high dust ingestion)	33	28	130	110

UK (low dust ingestion)	900	56	2200	140
UK (high dust ingestion)	2200	140	9000	560
US (low dust ingestion)	32	26	80	65
US (high dust ingestion)	80	65	320	260
Romania, Iasi (low dust ingestion)	**30**	**10**	**75**	**24**
Romania, Iasi (high dust ingestion)	**75**	**24**	**300**	**96**

Conclusions

This is the first study which reports the estimation of dietary exposure of population from Romania to BFRs both through food and indoor dust ingestion. The main contributor to the sum PBDEs in dust samples was BDE 209, with a contribution between 94 and 99 % that largely comprise the Deca-BDE commercial formulation. The results of the present study shows that the intake of lower BDEs is higher through food consumption and the intake of BDE 209 is higher through indoor dust ingestion. The results for intake of BFRs through dust ingestion estimated in the present study are comparable with similar studies applied on domestic dust samples from Canada, but they are much lower compared to studies applied on samples from UK or US.

References

1. Darnerud, P. O., *Environ. Int.*, **29**, 841 (2003).
2. Liem, A. K. D., Fürst, P., and Rappe, C., *Food Addit. Contam.*, **17**, 241 (2000).
3. Stapleton, H. M., Jones-Otazo, H., Clarke, J. P., Diamond, M. L., Archbold, J. A., Ferguson, G., Harner, T., Richardson, G. M., Ryan, J. J., and Wilford B., *Environ. Sci. Technol.*, **39**, 5121 (2005).
4. Voorspoels, S., Covaci, A., Neels, H., and Schepens, P., *Environ. Int.*, **33**, 93 (2007).
5. Wijesekera, R., Halliwell, C., Hunter, S., and Harrad, S., *Organohalog. Compd.*, **55**, 239 (2002).
6. Harrad, S., Wijesekera, R., Hunter, S., Halliwell, C., and Baker, R., *Environ. Sci. Technol.*, **38**, 2345 (2004).
7. Stapleton, H. M., Dodder, N. G., Offenberg, J. H., Schantz, M. M., and Wise, S. A., *Environ. Sci. Technol.*, **39**, 925 (2005).
8. Wilford, B. H., Shoeib, M., Harner, T., Zhu, J. P., and Jones, K. C., *Environ. Sci. Technol.*, **39**, 7027 (2005).
9. Jones-Otazo, H. A., Clarke, J. P., Diamond, M. L., Archbold, J. A., Ferguson G, Harner T, Richardson, G. M., Ryan, J.J., and Wilford, B., *Environ. Sci. Technol.*, **39**, 5121 (2005).
10. Voorspoels, S., Covaci, A., and Schepens P., *Environ. Sci. Technol.*, **37**, 4348 (2003).
11. Covaci, A., Gheorghe, A., Voorspoels, S., Maervoet, J., Steen Redeker, E., Blust, R., and Schepens, P., *Environ. Int.*, **31**, 367 (2005).
12. Stapleton, H. M., Harner, T., Shoeib, M., Keller, J. M., Schantz, M. M., Leigh, S. D., and Wise, S. A., *Anal. Bioanal. Chem.*, **384**, 791 (2006).

13. Harrad, S., Ibarra, C., Diamond, M., Melymuk, L., Robson, M., Douwes, J., Roosens, L., Dirtu, A. C., and Covaci A., *Environ. Int.*, **34**, 232 (2008).
14. Abdallah, M. A. E., Harrad, S., Ibarra, C., Diamond, M., Melymuk, L., Robson, M., and Covaci A., *Environ. Sci. Technol.*, **42**, 459 (2008).
15. Official Monitor of Romania, no. 59bis from 22.03.1996, Ord. no. 1955.
16. Mihailescu A, *Editure A' 92*, Bucharest, 2004.
17. Stapleton, H. M., Jones-Otazo, H., Clarke, J. P., Diamond, M. L., Archbold, J. A., Ferguson, G., Harner, T., Richardson, G. M., Ryan, J. J., and Wilford, B., *Environ. Sci. Technol.*, **39**, 5121 (2005).
18. Dirtu, A. C. and Covaci, A., *Organohalog. Compd.*, **70**, 562 (2008).
19. Zabik, M. E., Booren, A. M., Zabik, M. J., Welch, R., and Humphrey, H., *Food. Chem.*, **55**, 231 (1996).