DIETARY INTAKE OF PBDEs BY THE POPULATION OF CATALONIA, SPAIN. TEMPORAL TREND

Bocio A[1], Domingo JL[1], Martí-Cid R[1], Mata E[2], Teixidó A[2], Llobet JM[3]
[1]Laboratory of Toxicology and Environmental Health, "Rovira i Virgili" University, Reus, Catalonia, Spain; [2]Department of Health, Generalitat de Catalunya, Catalonia, Spain; [3]Toxicology Unit, University of Barcelona, Barcelona, Catalonia, Spain

Abstract
In the present study, the concentrations of polybrominated diphenyl ethers (PBDEs) were determined in 58 food samples belonging to 11 eleven food groups. These samples were randomly acquired in 12 cities of Catalonia (Spain) between March and June of 2006. The dietary intake of PBDEs was estimated for the population of this region, and the results were compared with those of a previous survey performed during 2000. The highest concentration of total PBDEs was found in fish and shellfish (426.9 ng/kg wet weight), followed by oils and fats (258.7 ng/kg wet weight), and eggs (80 ng/kg wet weight). The dietary intake of PBDEs for a standard male adult of 70-kg body weight was 85.7 ng/day (or 1.2 ng/kg body weight/day). On a body weight basis, it means a notable decrease: 30%, with respect to the daily intake of the 2000 survey (102.0 ng/day, or 1.2 ng/kg/body weight/day).

Introduction
PBDEs, a class of brominated flame retardants, have been used in a variety of consumer products, being produced in notable quantities. In recent years, a marked increase in the levels of PBDEs in human biological tissues and fluids, especially in breast milk, has been observed in some countries. This increasing presence of PBDEs in human tissues is of particular concern due to their association with endocrine disruptors, reproductive and developmental toxicity, neurotoxicity, and potential cancer already reported in rodent studies. Until recently, it was thought that the predominant route of exposure of human to virtually all Persistent Organic Pollutants (POPs) (including PBDEs) was through food consumption. Consequently, in 2000 we determined the concentrations of PBDEs in a number of food samples (11 food groups) acquired in Catalonia (Spain).[1] The dietary intake of PBDEs was subsequently estimated for the general population living in that Spanish region. The most important contribution to the dietary PBDE intake corresponded to fish and seafood, being approximately one-third of the total.[1]

Recently, our previous survey was extended in the number of analyzed edible marine species. The levels of PBDEs were measured in 14 species of fish and seafood.[2] In order to establish the temporal trend in the total dietary intake of PBDEs by that population, food items belonging to the remaining 10 food groups assessed in our 2000 survey were also analyzed. We here present the results of the this new survey concerning PBDE levels in a number of foodstuffs, as well as the dietary intake of these pollutants by the population of Catalonia. A comparison of the dietary intake of PBDEs with those corresponding to our previous survey is also presented.[1]

Materials and Methods
Sampling. In March-June 2006, food samples were randomly acquired in local markets, big supermarkets, and grocery stores from twelve representative cities (Barcelona, Hospitalet de Llobregat, Vilanova i la Geltrú, Mataró, Sabadell, Terrassa, Girona, Tarragona, Reus, Tortosa, Lleida, and Manresa) of Catalonia. For collection of samples, two groups were made up. The first group included meat of beef (steak, hamburger), pork (loin, sausage), chicken (breast), and lamb (steak); fish (hake, sardine) and shellfish (mussel); vegetables and tubers (lettuce, tomato, potato, green beans, cauliflower); fruits (apple, pear, orange), and eggs. The second group included cow milk (whole, semi-skimmed) and dairy products (yoghurt, cheese); cereals (bread, pasta, rice); pulses (lentils, beans); fats (margarine) and oils (olive, sunflower), and meat products (ham, hot dogs, salami). In the first group, most products are usually retailed and their origins could be very diversified in the different cities. Therefore, in that group, two composite samples were analyzed for each food item, except in fish and shellfish where three composite samples for each species were analyzed. Each composite was made up of 24 individual samples, which were collected in twelve different places. In contrast, most food items included in the second group corresponded to brands/trademarks that could be obtained in many different places. Consequently, in this

group, only one composite sample was analyzed for each food item. These composites were made up of 24 individual samples of similar weights, which were collected in four different places of a same city. The sums of the tetra-to-octabrominated congeners were determined for each sample. A total of 58 samples were analyzed.

Analytical techniques. The determination of PBDEs was based on US EPA method 1625 and CARB Method 429. The extraction and clean-up was carried out under light exclosure conditions in order to avoid losses on light sensitive compounds (PBDE). Appropriate isotope-labeled extraction standards ($^{13}C_{12}$-PBDE) were added to the homogenized sample in order to control the whole sample preparation process. The sample was extracted using hexane/acetone as solvent. The extract was then concentrated to determine PBDE levels. A clean-up procedure of the extracts was carried out using adsorption chromatography on a mixed silica column and adsorption/fractionation on alumina. The final step was a reduction of the fraction volume to the analytically needed amount. The cleaned extracts were analysed by HRGC/HRMS using Agilent GCs (5890 and 6890) coupled to Waters Autospec Ultima HRMS systems with selected ion recording at resolution 10000. The samples were injected onto non-polar DB5MS-type GC columns. The quantification was carried out using the corresponding isotope-labeled compounds as internal standards.

Dietary exposure estimates. Consumption data by the general population of Catalonia of the analyzed foodstuffs were taken from Serra-Majem and co-workers.[3] When a concentration was under the limit of detection (LOD), daily intakes were calculated assuming the respective values would be equal to none-half of that LOD.

Results and Discussion

Table 1 summarizes the concentrations of PBDEs in the 11 groups of analyzed foodstuffs. Results are presented as the sum of tetra- to octaBDEs for the 2000 and for the current survey. In the current study, the highest concentration of total PBDEs was found in fish and shellfish (426.9 ng/kg wet weight), followed by oils and fats (258.7 ng/kg wet weight), and eggs (80 ng/kg wet weight). In our previous survey, the highest PBDE levels were found in oils and fats (587.7 ng/kg ww), fish and shellfish (383.1 ng/kg ww), and meat and meat products (109.3 ng/kg ww). The lowest concentrations of total PBDEs were observed in fruits (5.8 ng/kg ww) and milk (9.3 ng/kg ww) in the 2000 and 2006 surveys, respectively. Data of food intake and dietary intake of PBDEs for a standard male adult of 70-kg body weight (previous and current surveys) are shown in Table 2. In the 2000 study, total dietary intake was 102 ng/day, or 1.5 ng/kg body weight/day, whereas in the current survey these intakes were 85.7 ng/day and 1.2 ng/kg body weight/day, respectively. On a body weight basis, it means a notable decrease: 30%, which was mainly due to the notable reduction in the contribution of oils and fats (24.1 vs. 10.6 ng/day), and meat and meat products (20.2 vs. 8.6 ng/day). In contrast, the greatest increase corresponded to vegetables (1.8 vs. 4.1 ng/day).

Table 1. PBDE concentrations (ng/kg wet weight) in Food Samples Collected in Catalonia, Spain[a]

food group	vegetables		tubers		pulses		cereals		fruits		fish and shellfish		meat and meat products		eggs		milk		dairy products		oils and fats	
	(n=8)[b] *2000*	*(n=10) 2006*	*(n=2) 2000*	*(n=2) 2006*	*(n=2) 2000*	*(n=2) 2006*	*(n=4) 2000*	*(n=4) 2006*	*(n=6) 2000*	*(n=6) 2006*	*(n=6) 2000*	*(n=6) 2006*	*(n=15) 2000*	*(n=15) 2006*	*(n=2) 2000*	*(n=2) 2006*	*(n=2) 2000*	*(n=2) 2006*	*(n=2) 2000*	*(n=2) 2006*	*(n=3) 2000*	*(n=3) 2006*
tetraBDE	4.0	1.9	0.5	5.0	2.3	4.5	2.2	5.6	0.4	0.7	171.2	224.1	23.5	7.4	17.3	10.0	8.0	1.7	10.7	8.7	169.7	20.5
pentaBDE	1.4	2.3	0.5	15.1	0.6	2.9	2.2	5.4	0.4	1.3	143.8	130.4	24.9	10.6	25.8	13.6	5.1	1.6	23.4	8.7	157.7	48.2
hexaBDE	0.4	1.6	0.9	2.5	1.1	2.1	4.5	2.6	0.7	1.3	56.1	58.4	13.5	5.3	11.9	7.3	0.5	0.8	2.0	4.9	139.7	25.3
heptaBDE	0.7	0.8	1.8	1.3	2.2	1.1	8.9	1.3	1.4	0.7	6.2	6.3	24.0	4.3	4.4	5.4	1.1	0.4	4.0	2.5	77.0	12.7
octaBDE	1.4	11.6	3.7	15.0	4.5	12.9	17.9	15.8	2.9	7.8	5.8	7.7	23.4	19.300	4.7	43.8	2.1	4.9	7.9	29.6	43.7	152.0
sum PBDE	7.9	18.2	7.4	38.9	10.7	23.5	35.7	30.7	5.8	11.7	383.1	426.9	109.3	46.844	64.2	80.0	16.9	9.3	47.9	54.3	587.7	258.7

[a]For each food group, one value is given. The upper value was calculated assuming that when a congener was below the detection limit the contration was equal to one-half of the respective limit of detection.

[b]n= number of composite samples analyzed.

Until recently, studies concerning the dietary intake of PBDES by the population of a certain region or country have been very limited.[4] The reported intakes ranged between a median value of 90.5 ng/day in a UK study using duplicate diet samples and 44 ng/day in Canada, although in that study the number of foodstuffs included was essentially limited to samples of animal origin.[5,6] Recently, Schecter and co-workers estimated a PBDE intake from food in US males of 70 kg (aged 20-59 years) between 1.17 and 1.26 ng/kg/day, while in a market-basket study in Belgium, Voorspoels and co-workers estimated PBDE intakes between 23 and 48 ng/day (lower and upper bound, respectively).[7,8]

Table 2. Estimated Dietary Intake of PBDEs by the Adult Population of Catalonia, Spain[a]

food group	daily consumption[b] (g)	PBDE intake[c] (ng/day)	
	2000 and 2006	2000	2006
vegetables	226 (15.7)	1.8	4.1
pulses	24 (1.7)	0.3	0.6
cereals	206 (14.3)	7.4	6.3
tubers	74 (5.1)	0.6	2.9
fruits	239 (16.6)	1.4	2.8
fish and shellfish	92 (6.4)	35.2	39.3
meat and meat products	185 (12.8)	20.2	8.6
eggs	34 (2.4)	2.2	2.7
dairy products	106 (7.3)	5.1	5.8
milk	217 (15.0)	3.7	2.0
fats and oils	41 (2.8)	24.1	10.6
total intake	**1444 (100)**	**102.0**	**85.7**
		1.5[d]	**1.2**

[a]Results are given for a male adult of 70-kg body weight. [b]In parentheses, percentages of total consumption. [c]Data were calculated assuming ND = ½ LOD. [d]Total intake expressed in ng/kg body weight/day.

With respect to the contribution of the dietary PBDE intake to the total daily exposure of the general populations to these POPs, recent studies in the US support the hypothesis that both diet and the indoor environment play prominent roles. The importance of these two routes may depend on individual exposure factors such as diet and exposure to dust, as well as on the concentrations of PBDEs in the food and dust they encounter.[8] In a recent study, Lorber reported that in a US population, exposure to PBDEs in house dust accounted for 82% of the overall estimated intake (7.7 ng/kg body weight/day), being the exposure through dietary intake 1.3 ng/kg body weight/day.[9] It opens an interesting line of research concerning PBDE exposure.

Acknowledgements
This study was supported by the Catalan Food Safety Agency, Department of Health, Generalitat de Catalunya, Barcelona, Catalonia, Spain.

References

1. Bocio A, Llobet JM, Domingo JL, Corbella J, Teixidó A, Casas C. *J. Agric. Food Chem.* 2003; 51:3191.
2. Domingo JL, Bocio A, Falcó G, Llobet JM. *Environ. Sci. Technol.* 2006; 40:4394.
3. Serra-Majem L, Ribas L, Salvador G, Castells C, Serra J, Jover L, Treserras R, Farran A, Román B, Raidó B, Taberner JL, Salleras L, Ngo J. *Direcció General de Salut Pública. Departament de Sanitat i Seguretat Social. Generalitat de Catalunya, Barcelona*. 2003.
4. Domingo JL. *J. Chromatograph. A.* 2004; 1054:321.
5. Wijesekera R, Halliwell C, Hunter S, Harrad S. *Organohalogen Compd.* 2002; 55:239.
6. Ryan JK, Patry B. *Organohalogen Compd.* 2001; 51:226.
7. Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, La Guardia M, McClean MD, Webster TF. *Environ. Sci. Technol.* 2007; 41:1584.
8. Voorspoels S, Covaci A, Neels H, Schepens P. *Environ. Int.* 2007; 33: 93.
9. Lorber M. *J. Expo. Sci. Environ. Epidemiol.* 2007 (in press).