

Brominated Flame Retardants in European Food Samples Collected in 2007 to 2009

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Introduction.

Brominated Flame Retardants (BFRs) are widely used as flame retardants in polymer materials, textiles, electronic boards and various other materials. Typical components used are Polybrominated Biphenylethers (PBDEs), Hexabromocyclododecane (HBCD) Polybrominated Biphenyls (PBBs, formerly used) and Tetrabromobisphenol A (TBBPA). Technical PBDE preparations are produced as mixtures of mainly penta-, octa- or decabromobiphenyl ethers¹. PBDEs are structurally similar to other environmental pollutants like dioxins and PCBs, they are lipophilic and persistent components and widespread in the environment. Due to findings of increasing values in humans (Noren and Meironyte, 2000; Schröter–Kermani et al., 2000), the investigations of food for this group of components got raising importance. In general, there is limited information for PBDE and other BFRs in actual food from Germany. Because of the importance of fish and dairy products for the estimated dietary intake of PBDEs and other BFRs by adults (Bocio et al. 2003), further actual information is needed.

TBBPA is currently the most widely used BFR with an estimated global use of 170.000 tones in 2004. TBBPA is mainly used as a reactive flame retardant bonded to the polymer matrix in epoxy and polycarbonate resins used in electronic equipments and in printed circuit boards (BSEF). Since more than a decade, Polybrominated Biphenyls (PBBs) are not used on the market anymore.

Materials and Methods.

Samples

All samples were analyzed within the normal analytical day to day procedures. The samples originate from different countries from Northern Europe (fish, mussel) or Western Europe (milk, cheese, fish oil, lamb liver). The samples were received in the laboratory between 2007 and end 2009.

Table 1: Type and Number of Food samples analyzed (collected in 2007/2008/2009)

Sample	PBDEs	PBBs	HBCD	TBBP A
Cheese	10			
Milk	38	15	15	15
Fish	48	4	1	7
Fish oil	37			
Lamb liver	12		12	
Mussel	2	2	2	5

Analytical Methods

All analyses were performed following the isotope dilution method. The samples were freeze dried and a mixture of ¹³C₁₂-labeled internal standards were added to the homogenized fraction of the dried sample material prior to soxhlet-extraction.

PBDEs / PBBs

24 native PBDE standards (BDE Nos. 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153 154, 156, 183, 184, 191, 196, 197, 206, 207, 209) were obtained from Wellington Laboratories, Canada. 8

internal $^{13}\text{C}_{12}$ -labeled standards - BDE Nos. 28, 47, 99, 153, 183, 196, 207 and 209 - were delivered by Wellington, Canada. The number of 24 individual congeners is relatively large. The measurements here are only performed for the 9 predominant PBDEs mainly applied as internal standards. 13 native PBB standards (PBB Nos. 18, 26, 30, 31, 49, 52, 53, 80, 101, 103, 153, 155, 209) were obtained from Ehrenstorfer GmbH, Germany.

Clean up of all lipid extracts was performed on combined acid on silica-, silica- and alumina columns. The final extract was reduced in volume by a stream of nitrogen, the final volume was 50 μl containing $^{13}\text{C}_{12}$ BDE 138 as recovery standard. The measurements were performed using high-resolution gas chromatography/low resolution mass spectrometry (HRGC /LRMS) using a DB 5 (30 m; 0,25 mm ID; 0,1 μm film) column for gas chromatographic separation. The identification of BDEs and PBBs was based on retention time and isotope ratio. Recoveries measured for the internal standards used range between 70 and 117 %.

HBCD (GC/MS-NCI)

The native HBCD standards (α -, β -, γ -HBCD-Isomers) and two $^{13}\text{C}_{12}$ labeled standards (γ -HBCD, BDE-138) were obtained from Wellington Laboratories, Canada. The internal standard, $^{13}\text{C}_{12}$ -labeled γ -HBCD, was added to the homogenized fraction and the extraction was performed by Soxhlet with hexane: acetone (4:1). The lipid extract was further purified with sulphuric acid, followed by alumina oxide (2 % water) clean-up. The final extract was reduced in volume by a stream of nitrogen, the final volume was 50 μl containing $^{13}\text{C}_{12}$ - BDE 138 as recovery standard.

The measurements were performed using high-resolution gas chromatography /low resolution mass spectrometry (HRGC /LRMS) with negative chemical ionization (NCI) mode using a DB 5 (15 m, 0.25 mm ID, 0.1 μm film) column for gas chromatographic separation. The identification of total (sum of the HBCD-Isomers) was based on retention time and isotope ratio. Recoveries measured for the internal standards used range between 60 and 105 %.

HBCD (LC/MS-MS)

The native HBCD standards (α -, β -, γ -HBCD-Isomers) and one $^{13}\text{C}_{12}$ labeled standard (γ -HBCD) were obtained from Wellington Laboratories, Canada. The internal standard, $^{13}\text{C}_{12}$ -labeled γ -HBCD, was added to the homogenized fraction and the extraction was performed by Soxhlet with hexane: acetone (4:1). The lipid extract was further purified with sulfuric, followed by alumina (2 % water) clean-up. The final extract was reduced to dryness under a gentle stream of nitrogen, dissolved in 100 μl of methanol for LC/MS-MS analysis.

The measurements were performed using liquid chromatography/electro spray ionization with tandem mass spectrometry detection (LC/ESI-MS/MS) using a security guard cartridge (C18 x 2.0 mm i.d., Phenomenex) and a Synergy 4u Fusion RP C-18 column (100 mm x 2.0 mm i.d., 80A, Phenomenex) column for liquid chromatographic separation.

Tetrabrombisphenol A

The native TBBPA standard and two $^{13}\text{C}_{12}$ labeled standards (TBBP-A, BDE-138) were obtained from Wellington Laboratories, Canada. The internal standard, $^{13}\text{C}_{12}$ -labeled TBBP-A, was added to the homogenized fraction and the extraction was performed by Soxhlet with hexane: acetone (4:1). The lipid extract was further purified with sulphuric acid, followed by silica gel clean-up. The final extract, containing $^{13}\text{C}_{12}$ labeled BDE 138 as recovery standard, was derivatized with BSTFA, forming TMS-derivatives, prior to GC-MS analysis.

The measurements were performed using high-resolution gas chromatography /low resolution mass spectrometry (HRGC /LRMS) with negative chemical ionization (NCI) mode using a DB 5 (15 m, 0.25 mm ID, 0.1 μm film) column for gas chromatographic separation. The identification of the TBBPA-TMS derivative was based on retention time and isotope ratio. Recoveries measured for the internal standards used range between 80 and 110 %.

Results and Discussion.

The analytical results for all samples and all parameters are reported in **Table 2** to **Table 5**

PBDEs

Table 2: Concentrations of PBDEs in various samples, Northern Europe, values are given in pg/g lower bound (lipid based, for fish and mussel wet weight based)

	Fish n = 48, pg/g wet weight		Fish oil n = 37, pg/g wet weight		Milk n = 38, pg/g lipid		Cheese n = 10, pg/g lipid		Lamb liver n = 12, pg/g lipid		Mussel n = 2 pg/g wet weight	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Lipid content (%)	11	0,1- 67	100	100	2,4	1,5 - 3,8	31,3	11,8 - 38	8	5,6 - 12		
BDE-28	64	<0,7-370	150	<0,5-1390	7,3	<0,5-12	<5	<5	16	<10-23	1,4	1,2-1,6
BDE-47	1070	9-10500	1790	14-19600	49	15-142	60	27-146	153	36-348	52	42-61
BDE-49	146	1,4-880	499	4-5390	<1	<1	<7	<7	12	<10-12	11	10-12
BDE-99	49	4,5-143	188	7-1140	29	11-124	33	12-113	161	24-571	27	19-36
BDE-100	183	1,0-1640	377	6-3730	10	<2-27	24	21-27	56	<20-112	13	10-15
BDE-153	25	<2-70	106	6-903	22	<1,1-75	27	25-28	119	<30-286	5,4	5,4-5,4
BDE-154	164	<2-1530	267	5-3970	13	<1,8-24	<15	<15	39	<30-39	6,0	6,0-6,0
BDE-183	28	<3-33	34	<20-174	<10	<10	<20	<20	<500	<500	<3	<3
BDE-209	153	<20-2240	<500	<500	<20	<20	na	na	na	na	<50	<50
Total BDEs	1880	17-17400	3370	42-36300	130	26-404	143	85-314	557	60-1392	115	94-137

< : <LOQ (Limit of quantification) na: not analyzed

PBBs

Table 3: Concentrations of PBBs in various samples, Northern Europe, values are given in pg/g, wet weight

	n	Mean	Median	Min	Max
Mussel					
PBB-30	2	< 1	< 1	< 1	< 1
PBB-52	2	< 1	< 1	< 1	< 1
PBB-101	2	< 2	< 2	< 2	< 2
PBB-153	2	< 3	< 3	< 3	< 3
PBB-209	2	< 30	< 30	< 30	< 30
Fish					
PBB-30	4	< 2	< 2	< 1	< 5
PBB-52	4	6,1	7,5	< 2	7,6
PBB-101	4	3,0	2,6	< 2	4,7
PBB-153	4	<5	< 5	< 2	1,3
PBB-209	4	< 60	< 60	< 30	< 100
Milk					
PBB-30	15	< 3	< 3	< 3	< 3
PBB-52	15	< 5	< 5	< 5	< 5
PBB-101	15	< 8	< 8	< 8	< 8
PBB-153	15	< 10	< 10	< 10	< 10
PBB-209	15	< 60	< 60	< 60	< 60

< : <LOQ (Limit of quantification)

HBCD

Table 4: Concentrations of total HBCD in various samples, Northern Europe, values are given in ng/g , wet weight, lower bound Collection of samples between 2008 and 2009

	n	Total HBCD		Individual Isomers		
		Mean	Range	Mean		
				α	β	γ
Milk	15	<0,02	<0,02	na	na	na
Fish	1	0,6	0,6-0,6	0,48	0,09	0,08
Lamb liver	12	<0,05	<0,05	na	na	na
Mussel	2	0,58	0,15-1,01	0,41	0,12	<0,06

< : <LOQ (Limit of quantification) na : not analyzed

Tetrabromobisphenol A

Table 5: Tetrabromobisphenol A (TBBPA) in fish, mussel and milk samples. Values given in ng/g wet weight, collection of samples between 2007 and 2008

Sample	n	Mean	Median	Min	Max
Haddock	2	<0.005	<0.005	<0.005	<0.005
Cod	2	<0.005	<0.005	<0.005	<0.005
Halibut, Greenland	1	<0.005			
Redfish	1	<0.005			
Fish liver	1	0.31			
Mussel	3	0.26	0.20	0.15	0.44
Cows milk	15	<0.005	<0.005	<0.005	0.006

< : <LOQ (Limit of quantification)

PBDEs are found in all food samples analyzed here. Highest concentrations are detected for PBDEs (total) in fish and fish oil samples at mean values between 2000 and 3000 pg/g wet weight (Table 2). PBBs have only been detected in fish samples showing the congeners 52, 101 and 153. In general PBBs were measured at about 1000-fold lower concentrations.

The data reported here are in good agreement to findings reported by other authors. (Nylund et al., 2001, de Wit, 2002, JECFA, 2006, Russel et al., 2008, Schecter et al., 2006, Paepke et al. 2009)

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