POLYBROMINATED DIPHENYLETHERS (PBDES) IN FISH SAMPLES OF VARIOUS ORIGIN

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Introduction

Polybrominated diphenylethers (PBDEs) are widely used as flame retardants in polymer materials, textiles, electronic boards and various other materials. Technical PBDE preparations are produced as mixtures of mainly penta-, octa- or decabrombiphenyl ethers[1]. PBDEs are structurally similar to other environmental pollutants like dioxins and PCBs, they are lipophilic and persistent components and widespread in the environment. For certain congeners bioaccumulation has been observed[2]. Due to recent findings of increasing values in humans[3, 4], food investigations for this group of components become raising importance. An early investigation for PBDEs in food from the German market has been performed by Krüger[5]. In general, here is only limited information for PBDE of actual food in Germany. Because of the importance of fish for the estimated dietary intake of PBDEs by adults[6, 7], actual information for Germany is needed. This papers gives an impression of the contamination of a limited number of fish samples bought on the German market in mid 2003.

Methods and Materials

Samples

All samples were provided in summer and autumn 2003. Herring and trout were bought as whole fish. Analyzed was the eatable part of samples.

Table 1: Fish samples from the German market

Sample	Origin
Herring, whole	North See
Salmon	Chile
Plaice	North-East Atlantic
Trout, whole	North-East Atlantic
Ocean Perch (Rosefish)	North Atlantic
Ocean Perch	North Atlantic
Halibut	North-East Atlantic
Halibut	North Atlantic
Halibut	North Atlantic
Coalfish	North Atlantic
Pike-perch	Denmark
Victoria Perch	Kenya
Catfish	Netherlands

Analytical Methods
All analyses were performed following the isotope dilution method. 12 native standards (BDE Nos. 17, 28, 47, 66, 77, 85, 99, 100, 138, 153 154, 183 were obtained from Cambridge Isotope Laboratories, Andover, USA. One native standard - BDE No 209 - was from Wellington Laboratories, Guelph, Canada. 6 internal C^{13} labeled standards - BDE Nos. 28, 47, 99, 153, 154 and 183 - were delivered by Wellington, Canada, one – BDE No 209 – was from Cambridge. Solvents were delivered by Merck (n-pentane), Promochem (cyclohexane, dichloromethane) Baker (diethylether), and Mallinckrodt (ethanol, toluene). Silica gel, aluminia oxide, sodium sulfate and potassium oxalate were obtained from Merck.

A total of 10 - 100 g fish tissue was homogenized and mixed with sodium sulfate. Before column extraction a mixture of 7 internal BDE standards was added to the sample (100 pg / sample for each congener with the exception for Deca-BDE: 10.000 pg). For column extraction a mixture of cyclohexane and dichloromethane was applied. The extract was washed with water and dried over sodium sulfate. After solvent evaporation gravimetric lipid determination was performed.

Clean-up of the lipid extract was performed by acid treated and activated silica gel and aluminia oxide column. The final extract was reduced in volume by a stream of nitrogen,

the final volume was 50 µl containing C^{13} labeled BDE 139 (Wellington) for recovery standard.

The measurements were performed using high-resolution gas chromatography /high resolution mass spectrometry (HRGC /HRMS, HP 5890 coupled with VG Autospec) at RP = 10 000 using a DB 5 (30 m, 0,25 mm ID, 0,1 µm film) column for gas chromatographic separation. The two most abundant masses were used for measurement (M^+ for Tri- and Tetra-BDE, and M-2BR^+ for Penta- to Deca-BDE). The identification of BDEs was based on retention time and isotope ratio. The quantification was performed using internal and external standards. Recoveries measured for the internal standards used range between 70 and 117 %.

Reduction of solvents and control of blank data is an important step in quality control when analyzing PBDEs at ultra trace levels. Solvents and reagents were tested before the laboratory procedures. All glassware was rinsed by solvents prior to use. Silica gel and sodium sulfate were pre-washed. Rotary evaporators were not used to reduce the risk of contamination. No plastic equipment was used. For quality control a laboratory blank and a QC pool of human milk fat was run with each batch of ten samples. Quantification was only done if sample data was at least twice the blank value.

Results and Discussion

The results of the investigation are presented in table 2. The table gives the lipid content in g/100 g (%) and the concentration for all congeners in ng/g on lipid weight basis. In addition to the congeners reported in table 2, PBDE Nos. 85 and 138 have been measured as well. For all samples no detectable amounts were found for these congeners at a detection limit of 0,02 and 0,03 respectively.
The concentration for the total of PBDEs found ranges between 0,42 ng/g for halibut and 47,6 ng/g for rosefish

These data are mostly in good agreement with data published by other investigators. The highest values are found for samples originating from the San Francisco Bay Area[13] and in bream from the river Elbe[14] as shown in Table 3. Fish from the river Elbe is normally not available commercially.

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Table 2. Concentrations of PBDE congeners in fish samples from the German market, 2003 (ng/g lipid)

Sample	Lipid content %	BDE No.											Total BDE
		17	28	47	66	77	99	100	153	154	183	209	
Herring	20,7	0,13	0,45	7,43	0,56	0,03	2,61	2,15	0,12	0,40	n.d.	n.d.	13,9
Salmon	12,7	0,01	n.d.	1,01	0,06	n.d.	0,37	0,20	0,02	0,09	n.d.	n.d.	1,76
Plaice	2,3	0,15	0,28	3,57	0,32	n.d.	1,23	0,57	0,19	0,35	0,04	n.d.	6,65
Trout	9,6	0,05	0,27	5,61	0,33	n.d.	1,98	0,93	0,14	0,42	n.d.	n.d.	9,74
Ocean Perch	3,6	0,02	1,57	34,7	0,40	0,01	1,09	4,77	0,95	3,76	0,04	0,36	47,6
Ocean Perch	3,2	n.d.	0,39	11,2	0,18	n.d.	0,28	1,9	0,29	2,1	n.d.	0,04	16,4
Halibut	13,6	n.d.	n.d.	0,34	0,02	n.d.	0,05	n.d.	n.d.	0,02	n.d.	n.d.	0,42
Halibut	11,1	n.d.	0,19	3,0	0,13	n.d.	0,28	0,34	0,07	0,34	n.d.	n.d.	4,35
Halibut	11,2	0,05.	0,47	6,0	0,35	n.d.	0,73	1,12	0,23	0,91	n.d.	n.d.	9,86
Coalfish	0,51	0,02	n.d.	1,54	0,02	n.d.	0,46	0,13	0,03	0,03	n.a.	0,42	2,66
Pike-perch	0,56	0,08	0,23	20,5	0,64	0,10	4,17	4,22	0,85	3,85	0,11	2,79	37,6
Victoria Perch	1,8	n.d.	n.d.	0,67	0,01	n.d.	0,15	0,10	0,10	0,25	0,21	1,04	2,53
Catfish	3,1	n.d.	0,21	3,77	0,27	n.d.	1,45	0,73	0,16	0,38	0,12	1,18	8,27

n.d. = not detected n.a. = not analyzed

Table 3. PBDEs in fish samples, other studies (in ng/g, lipid)

Area	Author	Year of collection	Sample	n	Mean values (Range)
Norway (13 Lakes)	Schlabach et al. 2001 (9)	1999	Trout	1/ lake	43,2 (7,9 – 124)[1]
Baltic Sea (7 Sites)	Nylund et al. 2001 (10)	1999	Herring	12-20 /site	17,0 (12 – 30,7)[2]
German Market	CVUA Annual Report, 2001 (11)	2001	Plaice	44	30 (151)[3]
			Rosefish	64	14 (196)[3]
Scotland	Jacobs et al., 2002. (12)	1999	Salmon	8	53,6 (1,1 – 85,2)[1]
Belgian Market		2001		5	19,6 (3,1 – 52,1)[1]
San Francisco Bay Area	Holden et al.,2003 (13)	2002	Perch Halibut Bass Shark	6 4 4 1	696 2235 1925 489
River Elbe	Lepom et al. 2002 (14)	2001	Bream	22	198 (26 – 728)[1]
			Eel	5	6,3 (3,6 – 21,4)[1]

[1] = range of individual data [2] = range of means [3] = maximum value

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