Polybrominated Diphenyl Ethers (PBDEs) in Fish, Fish Oil, Fish Meal and Fish Feed Samples of Various Origin

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Introduction

PolybrominatedDiphenyl Ethers (PBDEs) are widely used as flame retardants in polymeric materials, textiles, electronic boards and various other materials. Due to findings of increasing values of PBDEs in humans [1], food investigations for this group of components become of raising importance. An early investigation for PBDEs in food from the German market has been performed by Krüger [2]. But in general, only limited actual information for PBDEs of fish and fish related products is available. Because of the importance of fish for the estimated dietary intake of PBDEs by adults [3], actual information about fish and fish related products is needed as they are used as food or feedingstuff.

PBDEs were analysed in fish, fish oil, fish meal and fish feed samples of various origins. All samples were investigated within the routine analytical service of a commercially focused institution like Ergo thus giving indications of the recent market situation.

Materials and Methods

Samples

All samples analysed for PBDEs were received in September 2003 to January 2005 within our routine analytical service. Exceptions are stated. The samples were more than 100 fish and fish related products (like fish oil, fish meal and fish feed) of different origin.

Analytical methods

The analytical method used for determination of PBDEs in fish and fish related samples (fish oil, fish meal, fish feed) has been described before [4,5]. All analyses were performed following the isotope dilution method: Before extraction or solving, a mixture ^{13}C-labelled internal standards was added to the sample. Fish samples were homogenized with sodium sulphate and a column extraction by means of cyclohexane/dichloromethane followed. Fish meal samples were soxhlet extracted by means of n-hexane/acetone. Fish oil samples were dissolved in hexane. After extraction or solving a column-clean up (acid treated and activated silica gel and aluminium oxide) was performed. The measurements were performed using high-resolution gas chromatography / high-resolution mass spectrometry (HRGC / HRMS). The identification of PBDEs was based on retention time and isotope ratio.

Results and Discussion

The study emphasis was on BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-209 as these congeners dominate the total PBDE content respectively are discussed recently. Table 1 presents a brief evaluation of the total PBDE data obtained in Ergo routine analysis. Results are given on fresh weight basis (Table 1a) as well as on lipid basis (Table 1b).

Table 1: Evaluation of fish, fish oil, fish meal and fish feed data obtained in Ergo routine analysis:

a) Sum of PBDEs * (ng/g, fresh weight based)

Matrix	n **	5 Percentile	25 Percentile	Median	Mean	75 Percentile	95 Percentile
Fish	59	0,015	0,051	0,13	0,68	0,76	3,5
Fish oil	36	0,35	4,2	14	12	17	20
Fish meal	18	0,12	0,25	1,3	1,5	2,0	4,0
Fish feed	22	0,072	1,7	3,3	3,4	5,3	6,5

* expressed as total of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-209;

** years of sample receipt: 2003-2005

b) Sum of PBDEs * (ng/g, lipid based)

Matrix	n **	5 Percentile	25 Percentile	Median	Mean	75 Percentile	95 Percentile
Fish	59	0,86	1,6	6,2	12	19	35
Fish oil	36	0,35	4,2	14	12	17	20
Fish meal	17	1,02	1,7	12	12	17	26
Fish feed	18	0,18	3,8	15	12	18	25

* expressed as total of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-209;

** years of sample receipt: 2003-2005

Notice: Mean values of 12 ng/g, lipid based, for all investigated matrices were controlled. Not rounded mean values showed small differences.

The concentration for the total of PBDEs found in more than 100 individual samples range between 0,41 ng/g and 78 ng/g lipid at 5.5 and 12 ng/g lipid (median and mean) for fish samples. Data on lipid basis showed a quite similar pattern of contamination of all investigated matrices. The highest concentration found for the total of PBDEs (outside of the routine analyses) resulted at 22 800 ng/g lipid in a fish oil sample.

Samples from the southern hemisphere showed much lower PBDE-contents than samples from the northern hemisphere.

Figure 1 and 2 present the pattern of total amounts of PBDEs as well as the part of BDE-47 examplary for two matrices.The congener patterns of nearly all samples were dominated by the 2,2',4,4'-tetrabromo (BDE-47) congener. Normally the fully brominated component BDE-209 is of minor importance in fish samples. Surprisingly in one individual fish sample the BDE-209 has been found to be the dominating congener at a value of 4,800 ng/g lipid. Detailed information will be given for patterns resulting from different samples of the same species. On the other hand the patterns of different fish species will be compared as well.

Figure 1: PBDEs in fish samples obtained in Ergo routine analysis

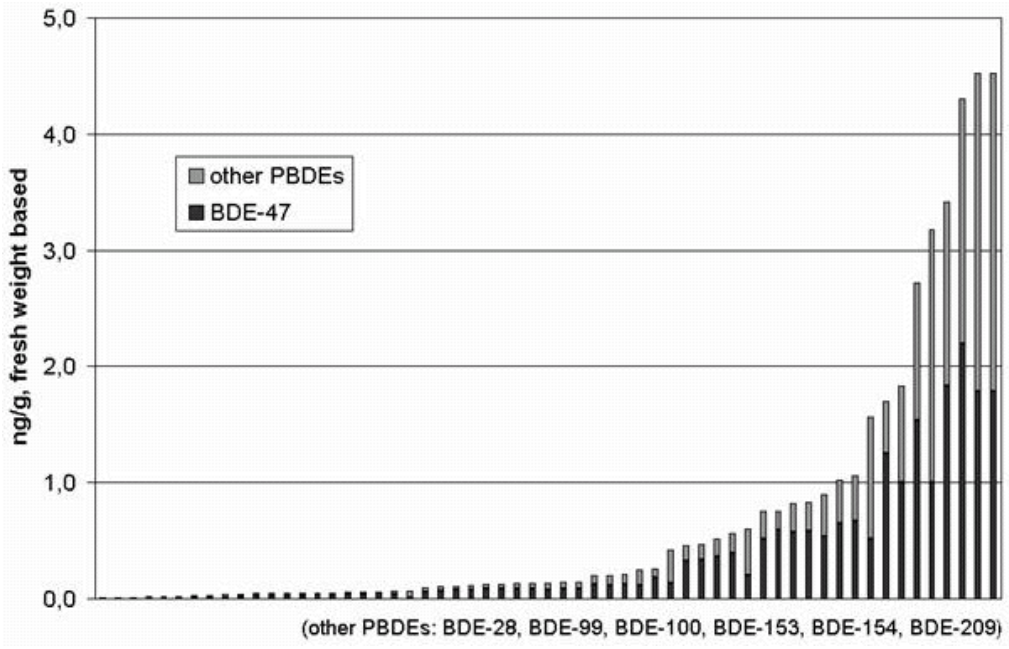
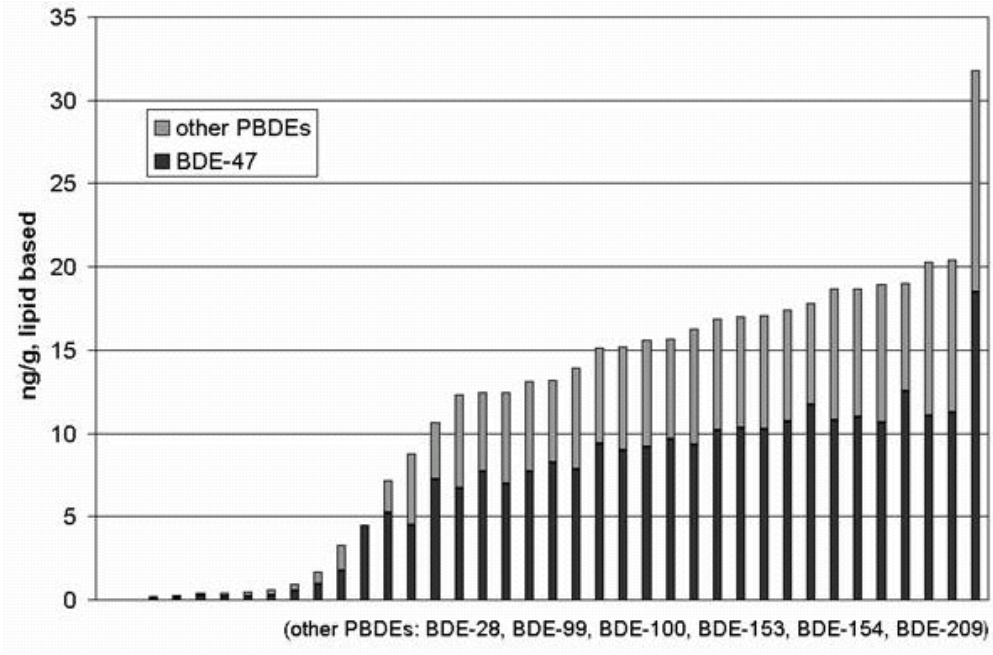


Figure 2: PBDEs in fish oil samples obtained in Ergo routine analysis



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