ACTUAL LEVELS OF POLYBROMINATED DIPHENYL ETHERS (PBDES) IN FISH AND FISH RELATED MATRICES AND TEMPORAL TRENDS

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Introduction

Polybrominated Diphenyl Ethers (PBDEs) are commonly used as flame retardants in consumer products such as foam cushions, carpets, computers and various other materials. Due to their lipophilic and persistent character PBDEs accumulate in the human body. [1] Investigations of food as a possible major pathway for human exposure to this group of environmental contaminants became therefore of raising importance. An early investigation for PBDEs in food from the German market was performed by Krüger. [2] Until now, the knowledge on representative PBDE concentrations in various food categories is still limited. Relatively high levels were found in fatty fish. But in general, only limited actual information for PBDEs of fish and fish related products is available contrary to the importance of fish for the estimated dietary intake of PBDEs by adults. [3]

PBDEs were analysed in fish, fish oil, fish meal and fish feed samples of various origins as they are used as food or feeding stuff. 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 April 2006 within our routine analytical service. The samples were more than 350 fish and fish related products (like fish oil, fish meal and fish feed) of different origin. Pertaining to the matrix fish all samples were taken into account but not smoked, cooked or otherwise prepared fish.

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 alumina) 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. PBDE-concentrations were calculated on fresh weight as well as lipid basis. Box-Whisker-plots are shown so that the lower quartile is presented by the 25th percentile, the second one by the median and the upper quartile by the 75th percentile, whiskers extending to the 5th and 95th percentiles.

Results and Discussion

The study emphasis was on BDE-28, BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209as 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). The concentration for the total of PBDEs found in more than 350 individual samples range between 0,39 ng/g and 81 ng/g lipid at 15 and 17 ng/g lipid (median and mean) for fish samples. Data on lipid basis show a comparable pattern of contamination of all investigated matrices. Fish and fish related samples from the southern hemisphere (that means typically samples from South America) show significant lower PBDE-levels than samples from the northern hemisphere (mainly Europe and North America) (Figure 1).

Table 1: Evaluation of fish and related matrices: data obtained in Ergo routine analysis:
a) Sum of PBDEs * (ng/g, fresh weight based)

Matrix	n **	Mini-mum	5th Pct	25th Pct	Median	Mean	75th Pct	95th Pct	Maxi-mum
Fish	150	0,002	0,017	0,21	0,98	1,2	1,6	3,4	6,0
Fish feed	58	n.d.	0,10	1,1	2,5	2,7	3,9	6,1	8,2
Fish meal	36	0,051	0,14	0,81	1,7	1,8	2,3	4,5	6,0
Fish oil	103	n.d.	0,25	7,3	16	18	25	46	54

* expressed as total of BDE-28, BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209
** Years of sample receipt: 2003-2006 n.d. not detectable

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

Matrix	n **	Mini-mum	5th Pct	25th Pct	Median	Mean	75th Pct	95th Pct	Maxi-mum
Fish	149	0,39	2,6	7,5	15	17	22	41	81
Fish feed	54	n.d.	0,42	3,2	8,3	9,6	16	23	26
Fish meal	35	0,42	0,98	2,3	11	11	15	24	31
Fish oil	103	n.d.	0,25	7,3	16	18	25	46	54

* expressed as total of BDE-28, BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209
** Years of sample receipt: 2003-2006 n.d. not detectable

Figure 1: Differences of PBDE-levels between southern and northern hemisphere in fish related samples

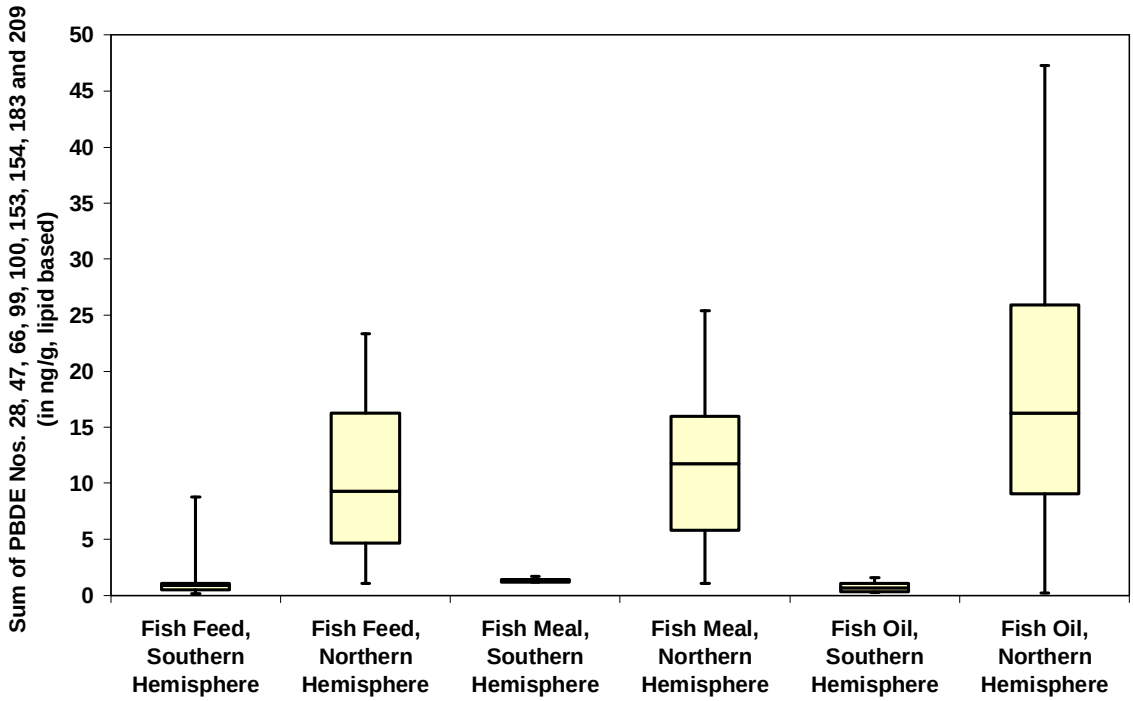

Figure 2: PBDEs in fish samples obtained in Ergo routine analysis (total PBDE-values given on fresh weight basis)

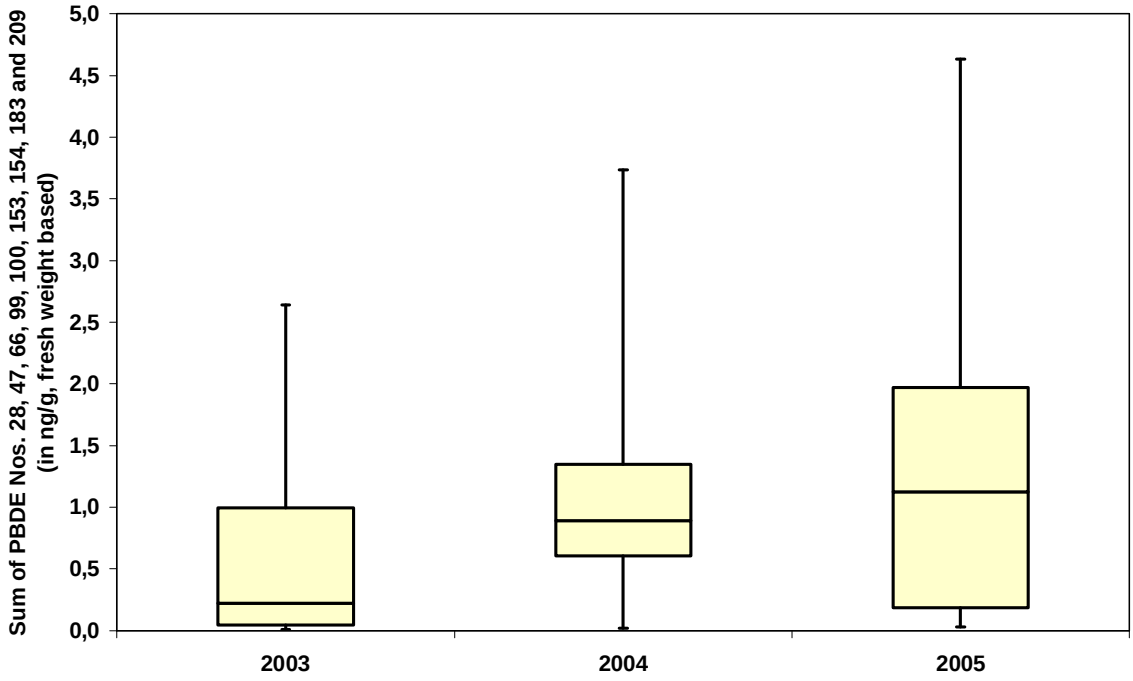

Figure 3: PBDEs in fish samples obtained in Ergo routine analysis (total PBDE-values given on lipid basis)

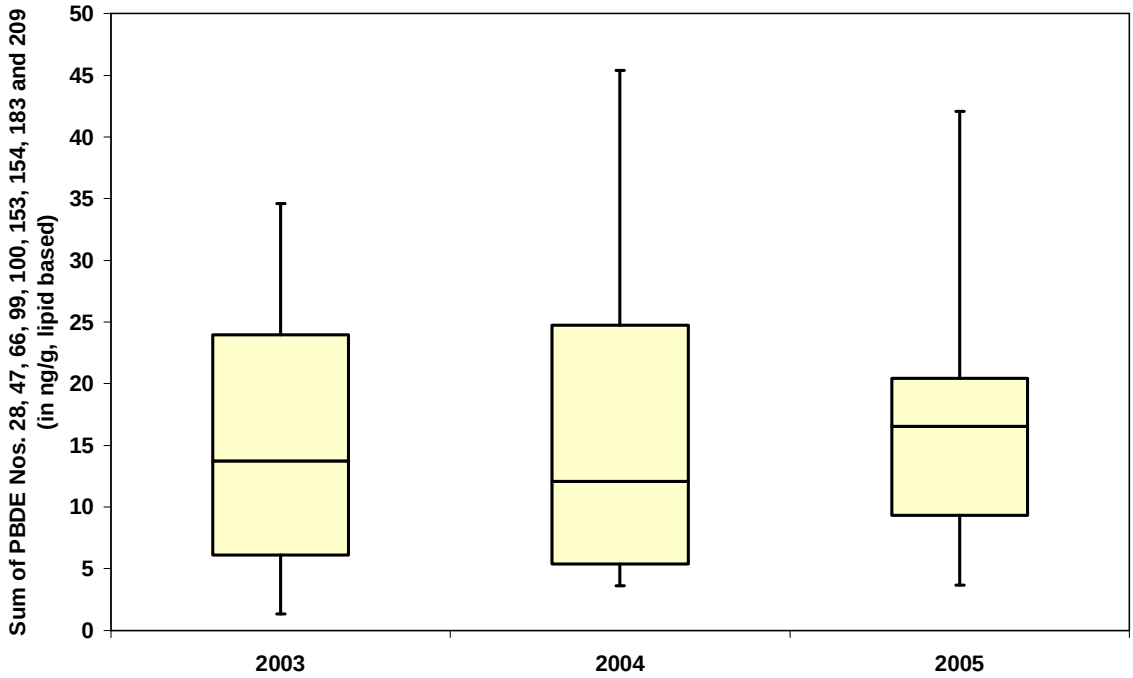

Figure 2 and 3 present the distribution of total amounts of PBDEs in fish depending on the year of sample receipt. Because of only limited data (n=4), samples from 2006 were not taken into account as well as samples identified as from southern hemisphere. Due to the lipophilic character of PBDEs and their bioaccumulation in fatty tissues, their concentrations are normally given on a lipid basis. For fish, however, it has proven good to use the edible part as the basis, especially for risk assessment purposes because the fat content of fish differs significantly. While cod may contain only 0,2 % of fat, the lipid content of eel might range up to 30 % and even higher. This is important because lean fish accumulates PBDEs and other lipophilic compounds in a much lower amount of fat compared to fatty fish resulting in higher contaminant levels on a fat basis. In contrast, basing the contaminant levels on the fresh or whole weight, allows a more reliable estimation on human exposure by consumption of fish. Distributions are therefore given on fresh weight basis (Figure 2) as well as on lipid basis (Figure 3).

Regarding the distribution of PBDEs in the edible part of fish, a temporal trend could be assumed because the median of the annual PBDE-levels increased slightly from 2003 to 2005. But regarding the distribution on lipid basis, a temporal trend is not noticeable. The reason is that the determined fat contents of the analysed samples increased quite proportional with the determined PBDE-values. This could happened by simply receiving more fatty fish samples within the Ergo routine service in later years on the one hand ,on the other hand fish having a higher lipid content could also gain in importance for human consumption.

According to data published by the Fisheries Department of the Food and Agriculture Organization of the United Nations (FAO), the world average per capita demand for all seafood could amount to 18,4 kg in 2010, compared with 16,1 kg in 1999/2001. [6] Against this background and taken into account that, basing the contaminant levels on the fresh or whole weight, allows a more reliable estimation on human exposure by consumption of fish, temporal trends of PBDEs in fish and fish products should be watched closely in the future.

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