

Investigation of Polybrominated Diphenyl Ethers in UK Retail Food Samples

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Introduction

The UK Food Standards Agency has been investigating the occurrence of brominated flame retardants in food since they were identified as an emerging risk to the food chain in the early 2000s. The Agency has previously reported levels in composite samples of fish and shellfish (Food Standards Agency 2006a), in shellfish from specific geographical sources (Fernandes *et al.* 2007) and in Total Diet Study food groups (Food Standards Agency 2006b). The Total Diet Study showed that some polybrominated diphenyl ethers (PBDEs) were detectable in most food groups, notably carcass meat, meat products and offal. Here we report, for the first time, levels of PBDEs in a range of individual food samples purchased from retail outlets around the UK.

Materials and Methods

Sampling

The sampling plan for this survey was compiled by Ventress Technical, who also purchased the samples. The sampling plan was weighted towards those foods in which, on the basis of previous surveys, the compounds of interest were most likely to be found. A total of 100 samples were obtained during 2007 and, based on the analytical results for those samples, a further 15 samples were obtained in 2008.

Analysis

Analyses for a range of brominated flame retardants and related chemicals were carried out by the Food and Environment Research Agency (Fera). PBDEs (17 congeners, see Table 1) were measured to the same analytical quality assurance

Table 1. Frequency of positive results

Congener	Food (number of samples)									
	Fish & shellfish (38)	Offal (20)	Meat (17)	Eggs (7)	Milk & dairy (10)	Vegetable oils (3)	Cereals (2)	Vegetables (16)	Jam (2)	Total (115)
PBDE-17	26	0	0	0	0	0	0	2	1	29
PBDE-28	38	0	0	0	0	0	0	3	1	42
PBDE-47	38	19	15	6	10	1	1	7	2	99
PBDE-49	38	1	2	5	1	0	0	5	1	53
PBDE-66	36	1	2	1	1	0	0	5	1	47
PBDE-71	7	0	0	0	0	0	0	1	1	9
PBDE-77	21	0	0	0	0	0	0	2	1	24
PBDE-85	2	1	0	2	0	0	0	0	1	6
PBDE-99	35	19	16	7	10	1	1	7	2	98
PBDE-100	38	15	12	7	8	0	0	6	2	88
PBDE-119	33	0	1	0	0	0	0	3	1	38
PBDE-126	0	0	0	0	0	0	0	0	0	0
PBDE-138	0	1	3	3	0	0	0	1	0	8
PBDE-153	34	17	16	7	10	0	1	8	2	95
PBDE-154	38	9	11	5	3	1	0	4	2	73
PBDE-183	18	15	12	6	1	0	0	5	1	58
PBDE-209	10	6	1	5	3	0	1	4	1	31

criteria as dioxins and polychlorinated biphenyls (Ambidge *et al.* 1990). Samples were fortified with internal standard mixtures of $^{13}\text{C}_{12}$ -labelled PBDEs 28, 47, 99, 153, 154, 183 and deca-BDE (BDE 209) and solvent-extracted. Crude extracts were cleaned on modified silica and fractionated on activated carbon. The fractions containing PBDEs were further purified using acid and base hydrolysis and activated alumina. Following concentration and the addition of a sensitivity standard, PBDEs were quantified using gas chromatography-high resolution mass spectrometry (HRGC-MS). Further details of the analytical method can be found elsewhere (Fernandes *et al.* 2004).

Results and Discussion

Results

Of the congeners measured, only BDE 126 was not detected in any samples. Every other congener was found in at least six samples (Table 1). The most frequently-occurring congeners were BDE 47, present in 86% of samples, BDE 99 (85%), BDE 100 (77%), BDE 153 (83%) and BDE 154 (63%). Other than BDE 126, the least abundant were BDE 71 (8%), BDE 85 (5%) and BDE 138 (7%).

The total concentrations of PBDEs are shown in Table 2a (fish and shellfish) and 2b (other foods). It is unsurprising that the highest levels were found in oily fish, notably herring (maximum 15.0 $\mu\text{g}/\text{kg}$), eel (9.4 $\mu\text{g}/\text{kg}$) and whitebait (7.2 $\mu\text{g}/\text{kg}$). In other foods, the highest levels were in meat, liver and cheese, but none were above 1 $\mu\text{g}/\text{kg}$. In general, BDE 47 (2,2',4,4'-tetra-BDE) was the most abundant individual congener in fish, followed by BDE 49. BDE 99 and BDE 100 (penta-BDEs) were also frequent but at lower levels. The more brominated congeners such as BDE 153 and BDE 154 (hexa-BDEs) were more abundant in meat, whilst in eggs and milk products there was a relatively consistent detection of the

Table 2a. Total PBDE in fish and shellfish, $\mu\text{g}/\text{kg}$ whole weight

Species (No. of samples)	Lower bound		Upper bound	
	Mean	Range	Mean	Range
Eel (fresh) (2)	2.26	0.41, 4.10	2.28	0.43, 4.12
Eel (smoked) (2)	7.77	6.14, 9.41	7.99	6.52 - 9.46
Herring (4)	5.07	1.42 - 15.0	5.11	1.53 - 15.0
Mackerel (4)	2.43	0.83 - 4.13	2.45	0.84 - 4.16
Atlantic salmon, farmed (4)	2.05	0.56 - 3.61	2.09	0.59 - 3.69
Atlantic salmon, wild (2)	0.60	0.56, 0.65	0.67	0.67, 0.68
Alaskan salmon (wild) (2)	0.08	0.06, 0.10	0.09	0.08, 0.10
Sardines (2)	0.62	0.49, 0.76	0.64	0.48, 0.80
Sprats (2)	1.61	1.57, 1.65	1.63	1.60, 1.66
Trout (farmed) (2)	1.54	1.31 - 1.77	1.58	1.32, 1.84
Whitebait (2)	3.98	0.72, 7.24	3.99	0.73, 7.24
Carp (1)	0.03	-	0.05	-
All oily fish (29)	2.59	0.06 - 15.0	2.63	0.05 - 15.0
Cod (2)	0.03	0.02, 0.04	0.04	0.04, 0.04
Haddock (1)	0.00	-	0.02	-
Plaice (2)	0.07	0.04, 0.10	0.11	0.05, 0.17
Sole (2)	0.05	0.02, 0.08	0.08	0.07, 0.09
All whitefish (7)	0.04	0.02 - 0.10	0.07	0.04 - 0.17
Crab (1)	1.58	-	1.69	-
Prawns (1)	0.03	-	0.11	-

frequently-occurring congeners, albeit at lower levels (rarely greater than 0.1 µg/kg). All PBDE congeners were detected less often and at lower concentrations in foods of non-animal origin.

Table 2b. Total PBDE in other foods, µg/kg whole weight

Food (No. of samples)	Lower bound		Upper bound	
	Mean	Range	Mean	Range
Milk (2)	0.02	0.008, 0.03	0.06	0.02, 0.09
Cheese (8)	0.11	0.008 - 0.26	0.18	0.08 - 0.32
Meat (17)	0.09	0 - 0.77	0.12	0.02 - 0.15
Liver (14)	0.06	0 - 0.62	0.07	0.02 - 0.64
Other offal (6)	0.03	0.002 - 0.07	0.05	0.01 - 0.15
Eggs (7)	0.26	0.007 - 0.70	0.29	0.07 - 0.71
Vegetable oils (3)	0.04	0 - 0.12	0.59	0.43 - 0.90
Jam (2)	0.09	0.001, 0.17	0.09	0.002, 0.17
Cereals (2)	0.03	0.01, 0.05	0.06	0.06, 0.06
Potatoes & products (6)	0.03	0 - 0.06	0.10	0.01 - 0.21
Vegetables (10)	0.02	0 - 0.13	0.03	0.01 - 0.14

In contrast to the results for the Total Diet Study, in which BDE 209 (deca-BDE) was usually the most abundant congener, notably in the meat products food group, and also in contrast to the results of the farmed and wild fish and shellfish survey, in which BDE 209 was reported in almost all fish species, BDE 209 was detected in only about one quarter of the samples tested in this survey. It was found most often in offal, fish and eggs, with the highest levels

on a whole weight basis being 0.47 µg/kg in a sample of red deer liver, 0.32 µg/kg in sprats and 0.23 µg/kg in chicken livers. Since the samples in the former surveys were all substantial composites, it may be the case that the results were influenced by a high contribution from certain individual samples containing a high level of BDE 209 included in the composites.

Dietary intake

This was a relatively limited survey in terms of sample numbers. Apart from fish and offal, the numbers of samples of different foods from the various food groups were low and therefore not fully representative of foods on sale in the UK. Consequently, these results cannot be used to generate a robust estimate of UK dietary exposure to PBDEs. Accordingly, the results have not been used to estimate dietary intakes except for those samples in which relatively high concentrations of PBDEs were positively detected. Samples in which high *upper bound* concentrations resulted from unusually high limits of detection were excluded. The estimated dietary intakes are

Table 3. Estimated daily dietary intakes

Most contaminated	Amount consumed	Sum PBDEs, ng/kg bodyweight	
		<i>lower bound</i>	<i>upper bound</i>
(Rest of diet)		5.5	5.6
Smoked Eel (9.4 µg/kg)	single portion ²	1.6	1.6
	1 weekly portion ³	7.1	7.2
	2 weekly portions ⁴	8.7	8.8
Herring (15.0 µg/kg)	single portion ²	5.0	5.0
	1 weekly portion ³	10.5	10.5
	2 weekly portions ⁴	15.5	15.6
Whitebait (7.2 µg/kg)	single portion ²	1.2	1.2
	1 weekly portion ³	6.7	6.8
	2 weekly portions ⁴	7.9	8.0

shown in Table 3. These are based on the estimated daily dietary exposures from the 2006 UK Total Diet

Study, excluding the contribution from the fish group but instead assuming consumption of one or two weekly portions of smoked eel (70g) or herring or whitebait (140g).

Interpretation

The UK independent expert Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) has previously concluded that, because only limited toxicological data are available, no Tolerable Daily Intakes (TDIs) could be set for PBDEs, although the toxicity of PBDFs is currently under review by the European Food Safety Authority. Nevertheless, the COT reviewed the results of the previous survey for brominated compounds in fish, which included the estimated exposure from the rest of the diet using the data from the Total Diet Study. The COT concluded that the concentrations of PBDEs detected in those two surveys did not raise toxicological concerns. The fresh results generated in the current survey do not raise any new concerns.

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