PBDEs, PBDD/Fs and PBBs IN CARCASS FAT, LIVER, EGGS AND MILK PRODUCED IN IRELAND

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Background

The Food Safety Authority of Ireland (FSAI) in collaboration with the Department of Agriculture, Fisheries and Food conducted a surveillance study on levels of chlorinated dioxins (PCDDs) and furans (PCDFs), brominated dioxins (PBDDs) and furans (PBDFs), polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), polybrominated diphenyl esters (PBDEs), hexabromocyclododecane enantiomers (HBCD Enantiomers), Decabromodiphenyl ethane, Hexabromobenzene, Bis(2,4,6-tribromophenoxy)ethane and Tetrabromo-bisphenol A (TBBP-A) in carcass fat, offal, eggs and milk produced in Ireland. This paper presents findings for PBDEs, PBBD/Fs and PBBs only and reflects increasing international awareness as to their potential persistent and bio-accumulating properties. Monitoring of these compounds was also recently recommended by the European Food Safety Authority[1]. Very little occurrence data in food exists for PBDD/Fs and PBBs and this survey was conducted with a view to establish background levels in Ireland and to also aid ongoing global efforts in assessing potential risks to human health from these compounds.

Introduction

PBDEs and PBBs belong to the group of brominated flame retardant additives, chemicals which are added to many household products for the purpose of fire prevention, which has undoubtedly resulted in a reduction in human injury and fatality as a result of fires. The types of products containing these chemicals include household appliances, furniture, clothing, computers and TVs. The unrestricted application of these materials in the past however, has allowed diffusion of the contaminants into the environment during manufacture, use and disposal and this continues to happen. This release is evident from the occurrence of PBDEs in environmental compartments such as water, sediments and biota[2] and accompanies an increasing amount of evidence on potential detrimental human health effects[2,3,4].

PBDDs/PBDFs are not intentionally produced (except for scientific purposes) but are generated as undesired by-products in various processes. They can be formed by chemical, photochemical, or thermal reactions from precursors and by so-called de novo synthesis. PBDDs/PBDFs have been found as contaminants in brominated organic chemicals, in particular in flame retardants, such as PBDEs. PBDFs and, to a lesser extent, PBDDs have been detected as photochemical degradation products of brominated organic chemicals, such as PBDEs and bromophenols[5]. As the utilisation of BFRs continues to increase, a corresponding increase in PBDD/Fs levels can be expected. Studies on the toxicity of PBDD/Fs are limited but both, in vivo and in vitro studies demonstrate AhR agonist properties and dioxin-like effects[6,7]. Although there are a number of methods reported for the analysis of PBDEs, very few methods exist for the determination of PBDD/Fs[3,8,9].

Materials and Methods

For this survey, avian, bovine, porcine and ovine carcass fat and liver, bovine milk and avian egg samples were collected at production/processing stage. All samples were pooled samples (see Table 1) and due to the lipophilic nature of the compounds analysis was performed on the fat fraction of the samples.

The following analytes were measured: Polybrominated diphenylethers (PBDEs) - IUPAC numbers 17, **28**, **47**, 49, 66, 71, 77, 85, **99**, 100, 119, 126, 138, **153**, **154, 183** and **209**. PBB congeners: IUPAC numbers 15, 49, **52**, 77, 80, 101, **126**, 169, **153** and 209. Ten, 2,3,7,8-Bromo substituted PBDD/Fs – tetra to hepta substituted congeners as well as 2,3,7-TBDD and 2,3,8-TBDF. (Those for which ^{13}Carbon labelled standards were used as internal or sensitivity standards are shown in bold type and these also included 6 PBDD/F congeners). Robustly validated methodology, accredited to the ISO17025 standard, for the analysis of these contaminants has been detailed elsewhere[2,10]. Analytical measurement sets included blanks and reference materials, and data quality was ensured by continuous successful, participation[2,10,11] in international inter-calibration exercises (e.g. Dioxins in Food, Quasimeme).

Results and Discussion

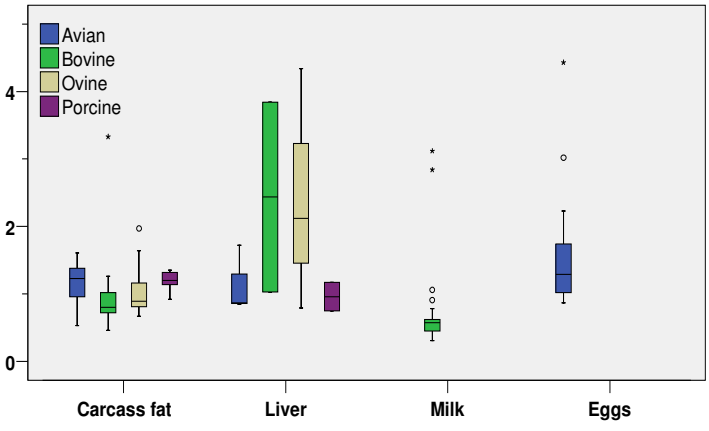
Table 1 provides an overview of frequency of occurrence of PBDD/Fs, PBDEs and PBBs >LOD in the samples tested and shows widespread occurrence of PBDEs whereas frequency of occurrence of PBDD/Fs and PBBs is somewhat lower. The Congener profiles for PBDEs are largely similar to those of commercial penta mixtures as described by Sjodin[12] and occurrence levels of BDE209 suggest use of deca mixtures (See Table 2).

Table 1 % Detected PBDE, PBDD/F and PBB occurrence

	Carcass Fat	Eggs	Liver	Milk		Carcass Fat	Eggs	Liver	Milk
N	38	19	12	30	N	38	19	12	30
Sub-N	10-40	24	10-40	Herd	Sub-N	10-40	24	10-40	Herd
	% Detected Occurrence					% Detected Occurrence			
BDE-99	100	89	100	30	237-TriBDD	18	0	17	0
BDE153	100	89	83	27	2378-TetraBDD	18	5	17	0
BDE-47	97	95	100	37	12378-PentaBDD	0	0	0	0
BDE-100	97	100	75	27	123(4/6)78-HexaBDD	0	0	0	0
BDE 154	92	68	58	17	123789-HexaBDD	0	0	0	0
BDE-183	74	100	100	0	238-TriBDF	18	5	58	20
BDE-49	61	89	25	3	2378-TetraBDF	66	95	83	60
BDE-66	50	68	67	7	12378-PentaBDF	0	16	17	7
BDE-209	32	100	83	0	23478-PentaBDF	32	37	75	57
BDE138	18	5	17	0	123478-HexaBDF	0	0	42	3
BDE-85	13	5	17	3	1234678-HeptaBDF	26	53	33	10
BDE-28	3	16	50	0	PBB-153	0	0	8	0
BDE-17	0	0	17	0	PBB-209	13	100	75	0
BDE-119	0	5	0	0	PBB77	13	21	8	0
BDE-77, 126, 71	0	0	0	0	PBB126	0	0	58	0
					PBB-15, 49, 52, 80, 101, 169	0	0	0	0

Figure 1 shows comparable levels of Total Sum BDE 17 in carcass fat for all species, whereas ovine and bovine liver show higher levels than avian and porcine liver. Milk overall shows the lowest BDE concentrations in tandem with the lowest frequency of BDE occurrence. Taking into account lower analytical sensitivity in this study, levels for PBDEs are comparable to levels found in a similar study conducted in 2003[13]. This is expected, as the EU wide ban of penta- and octaBDE will take time to result in a decline of occurrence in food. In recent years the EU has carried out a comprehensive risk assessment under the Existing Substances Regulation (793/93/EEC) of commercial PBDE products. The outcome was a ban on the use of Penta-and OctaBDE since 2004, whilst deca-BDE remained under review until additional toxicological and occurrence data are finalised.

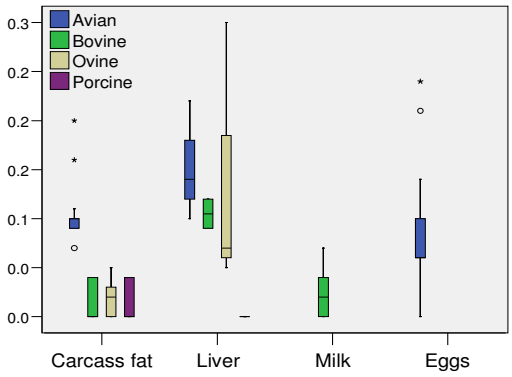
Figure 1 Sum of 17 BDE congeners (ng/kg fat weight) per Food Category and Species (upperbound)



However, The European Court of Justice on 1st April annulled the exemption granted in 2005 for Deca-BDE to the EU RoHS Directive. In 2007, the European Commission commissioned a *"Review on production processes of Decabromodiphenyl Ether (DecaBDE) used in polymeric applications in electrical and electronic equipment, and assessment of the availability of potential alternatives to DecaBDE"*[14], and identified 27 alternative substances, some of which were included in this project and are currently subject to analysis.

With the exception of penta- and hexa-brominated compounds PBDD/Fs were detectable in the majority of samples and overall brominated furans occurred at a higher frequency than brominated dioxins. Similar observations in shellfish are reported in a recent paper by Fernandes et al[15]. Similar to BDE occurrence, PBDD/F occurrence was matrix-dependant with liver showing the highest levels, which is expected due to the metabolic function of this organ (Figure 2). Whereas Tetra BDF was the most frequently occurring congener, Hepta and 23478 Penta BDF showed the highest concentrations. However, TBDF has a higher binding affinity to the AhR, whilst also more resilient to metabolism than its chlorinated analogue.
Birnbaum et al.[6] further outline differences between chlorinated and brominated compounds and more research is needed before robust TEFs can be developed for calculation of overall additive burden from these contaminants to the total TEQ. In particular, the contribution from the tri-brominated compounds needs consideration, as they show a higher level of AhR activity compared to their chlorinated analogues.

Figure 2 TBDF (ng/kg fat weight) per Food Category and Species



PBBs were only detected in carcass fat, liver and eggs. The predominant congener was PBB-209, which occurred in all egg samples (0.1-2.84 µg/kg fat), half of all avian fat samples (0.03-0.26 µg/kg fat) and in all avian, ovine and porcine liver samples (0.15-0.30 µg/kg fat). PBB-126 occurred in bovine and ovine liver only (0.16-0.78 ng/kg fat). PBB-77 was detected in 5 samples close to the LOD (0.05-0.08 ng/kg fat) and PBB-153 was detected in one ovine liver. All remaining PBB congeners were not detected.
The currently limited data available on the health effects of PBDD/Fs and PBBs supports the hypotheses that these compounds have similar biological properties to their chlorinated relatives [6,16]. However, the general lack of occurrence data does not allow for comparison or observations on the trend in occurrence of these compounds in food. PBDD/Fs, PBBs and certain other individual and groups of compounds were identified for possible future inclusion in the TEF concept. However, more relative effect potency studies are needed, before a TEF system for these compounds can be established[17]. It is however, likely that their presence will incrementally add to the total dioxin body burden, which currently is predicted to be below the European Average in Ireland due to lower occurrence levels of PCDD/Fs and PCBs compared to other European countries.

Overall, the findings of this survey add to the limited existing evidence that these compounds are entering the food-chain and further stress the need for more research into their toxicological properties.

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Table 2 PBDE and PBB Occurrence levels in Carcass Fat, Liver, Milk and Eggs expressed on a µg/kg fat basis, except PBBs 126 and 77, which are expressed on a ng/kg fat basis (lowerbound-upperbound)

		BDE-154	BDE-100	BDE153	BDE-183	BDE-209	BDE-47	BDE-99	ΣBDE17	PBB126	PBB77	PBB-153	PBB-209
Carcass fat	Mean	0.05-0.05	0.05-0.05	0.20-0.20	0.58-0.58	0.10-0.43	0.15-0.15	0.18-0.18	1.33-1.75	0.00-0.05	0.01-0.06	0.00-0.01	0.01-0.04
	Med	0.03-0.03	0.04-0.04	0.08-0.08	0.02-0.02	0.00-0.44	0.12-0.12	0.15-0.15	0.67-0.99	0.00-0.04	0.00-0.06	0.00-0.01	0.00-0.01
	Min	0.00-0.01	0.00-0.01	0.02-0.02	0.00-0.01	0.00-0.09	0.00-0.06	0.06-0.06	0.16-0.46	0.00-0.02	0.00-0.05	0.00-0.01	0.00-0.01
	Max	0.61-0.61	0.15-0.15	3.45-3.45	19.3-19.3	0.83-0.83	0.48-0.48	0.66-0.66	24.8-25.3	0.00-0.09	0.07-0.07	0.00-0.01	0.26-0.46
Liver	Mean	0.02-0.03	0.07-0.08	0.11-0.12	0.04-0.04	0.80-0.86	0.20-0.20	0.27-0.27	1.55-1.75	0.18-0.22	0.00-0.08	0.01-0.03	0.34-0.36
	Med	0.01-0.02	0.04-0.05	0.06-0.07	0.03-0.03	0.52-0.52	0.18-0.18	0.13-0.13	0.92-1.10	0.08-0.13	0.00-0.08	0.00-0.01	0.23-0.23
	Min	0.00-0.01	0.00-0.03	0.00-0.04	0.01-0.01	0.00-0.14	0.10-0.10	0.11-0.11	0.38-0.75	0.00-0.06	0.00-0.05	0.00-0.01	0.00-0.05
	Max	0.09-0.09	0.26-0.26	0.61-0.61	0.11-0.11	3.12-3.12	0.39-0.39	1.33-1.33	4.25-4.34	0.78-0.78	0.00-0.12	0.06-0.06	1.30-1.30
Milk	Mean	0.01-0.02	0.02-0.03	0.02-0.04	0.00-0.01	0.00-0.22	0.10-0.14	0.09-0.13	0.24-0.71	0.00-0.05	0.00-0.05	0.00-0.01	0.00-0.00
	Med	0.00-0.01	0.00-0.02	0.00-0.02	0.00-0.01	0.00-0.17	0.00-0.07	0.00-0.07	0.00-0.58	0.00-0.05	0.00-0.05	0.00-0.01	0.00-0.00
	Min	0.00-0.01	0.00-0.01	0.00-0.01	0.00-0.01	0.00-0.09	0.00-0.04	0.00-0.04	0.00-0.31	0.00-0.03	0.00-0.05	0.00-0.01	0.00-0.00
	Max	0.11-0.11	0.22-0.22	0.34-0.34	0.00-0.05	0.00-0.62	1.12-1.12	1.06-1.06	2.93-3.12	0.00-0.11	0.00-0.10	0.00-0.01	0.00-0.00
Eggs	Mean	0.03-0.04	0.07-0.07	0.09-0.10	0.03-0.03	0.75-0.75	0.18-0.19	0.20-0.27	1.39-1.60	0.00-0.10	0.02-0.09	0.00-0.01	0.72-0.72
	Med	0.02-0.03	0.05-0.05	0.06-0.06	0.03-0.03	0.47-0.47	0.17-0.17	0.19-0.20	1.05-1.29	0.00-0.11	0.00-0.09	0.00-0.01	0.15-0.15
	Min	0.00-0.02	0.03-0.03	0.00-0.04	0.02-0.02	0.27-0.27	0.00-0.11	0.00-0.11	0.58-0.87	0.00-0.04	0.00-0.07	0.00-0.01	0.08-0.08
	Max	0.16-0.16	0.19-0.19	0.67-0.67	0.05-0.05	3.85-3.85	0.35-0.35	0.49-0.67	4.34-4.43	0.00-0.17	0.10-0.11	0.00-0.01	2.84-2.84

Table 3 PBDD/F Occurrence levels in Carcass Fat, Liver, Milk and Eggs expressed on a ng/kg fat basis (lowerbound-upperbound)

	Stats	237-TriBDD	TBDD	12378-Br_5BDD	123(4/6)78-Br_6BDD	123789-Br_6BDD	238-TriBDF	TBDF	12378-Br_5BDF	23478-Br_5BDF	123478-Br_6BDF	1234678-Br_7BDF
Carcass fat	Mean	0.03-0.04	0.00-0.02	0.00-0.09	0.00-0.11	0.00-0.10	0.01-0.04	0.05-0.06	0.00-0.05	0.04-0.08	0.00-0.10	0.18-0.64
	Med	0.00-0.02	0.00-0.02	0.00-0.08	0.00-0.11	0.00-0.10	0.00-0.04	0.04-0.04	0.00-0.05	0.00-0.07	0.00-0.09	0.00-0.55
	Min	0.00-0.01	0.00-0.01	0.00-0.07	0.00-0.07	0.00-0.05	0.00-0.03	0.00-0.02	0.00-0.01	0.00-0.05	0.00-0.05	0.00-0.24
	Max	0.47-0.47	0.03-0.03	0.00-0.13	0.00-0.20	0.00-0.19	0.06-0.06	0.20-0.20	0.00-0.10	0.42-0.42	0.00-0.18	1.08-1.08
Liver	Mean	0.01-0.03	0.00-0.02	0.00-0.11	0.00-0.16	0.00-0.19	0.03-0.05	0.11-0.12	0.00-0.07	1.04-1.07	0.23-0.32	1.54-2.17
	Med	0.00-0.03	0.00-0.02	0.00-0.10	0.00-0.16	0.00-0.20	0.03-0.04	0.10-0.10	0.00-0.07	0.64-0.64	0.00-0.19	0.00-0.96
	Min	0.00-0.02	0.00-0.01	0.00-0.07	0.00-0.11	0.00-0.12	0.00-0.03	0.00-0.05	0.00-0.03	0.00-0.07	0.00-0.09	0.00-0.66
	Max	0.07-0.07	0.00-0.05	0.00-0.15	0.00-0.23	0.00-0.31	0.07-0.07	0.30-0.30	0.00-0.16	6.15-6.15	1.27-1.27	11.77-11.77
Milk	Mean	0.00-0.02	0.00-0.02	0.00-0.07	0.00-0.11	0.00-0.08	0.01-0.03	0.02-0.03	0.00-0.05	0.05-0.07	0.01-0.14	0.12-0.69
	Med	0.00-0.02	0.00-0.02	0.00-0.06	0.00-0.11	0.00-0.08	0.00-0.03	0.02-0.04	0.00-0.05	0.06-0.06	0.00-0.08	0.00-0.55
	Min	0.00-0.01	0.00-0.01	0.00-0.02	0.00-0.07	0.00-0.06	0.00-0.01	0.00-0.01	0.00-0.02	0.00-0.04	0.00-0.04	0.00-0.08
	Max	0.00-0.05	0.00-0.05	0.00-0.12	0.00-0.24	0.00-0.15	0.06-0.08	0.07-0.07	0.05-0.10	0.22-0.22	0.25-0.43	2.78-2.78
Eggs	Mean	0.00-0.04	0.00-0.02	0.00-0.13	0.00-0.18	0.00-0.21	0.00-0.07	0.09-0.09	0.02-0.10	0.06-0.12	0.00-0.19	1.32-1.68
	Med	0.00-0.03	0.00-0.02	0.00-0.13	0.00-0.19	0.00-0.22	0.00-0.08	0.06-0.06	0.00-0.10	0.00-0.10	0.00-0.19	0.88-0.88
	Min	0.00-0.02	0.00-0.01	0.00-0.12	0.00-0.13	0.00-0.17	0.00-0.05	0.00-0.04	0.00-0.08	0.00-0.05	0.00-0.16	0.00-0.72
	Max	0.00-0.07	0.03-0.03	0.00-0.15	0.00-0.23	0.00-0.27	0.08-0.09	0.24-0.24	0.18-0.18	0.30-0.30	0.00-0.26	8.75-8.75