Investigation into levels of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane diastereomers (HCBD) in fishery produce available on the Irish market

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Introduction

The Food Safety Authority of Ireland (FSAI) has a statutory responsibility to ensure the safety of food consumed, distributed, produced and sold on the Irish market. The results of a targeted surveillance study planned and executed in collaboration with the Marine Institute and Board Iascaigh Mhara (Irish Sea Fisheries Board) on levels of polybrominated diphenyl ethers (PBDEs) and total hexabromocyclododecane diastereomers (HBCD) in various fish species available on the Irish market are presented here.

This study was undertaken against the background of increased awareness in the European Union of the possible health risks posed by PBDEs in the food chain, and builds upon previous studies undertaken by the FSAI into levels of these contaminants in eggs[1], meat, dairy and other food-groups[2].

Materials and Methods

For this survey a total of 70 samples were collected comprising the following species and retail groupings: (1) Farmed Atlantic salmon, (2) Wild Atlantic salmon, (3) Fresh herring,(4) Fresh mackerel, (5) Fresh tuna, (6) Fresh Shellfish, (7) Smoked farmed salmon, (8) Canned salmon, (9) Canned tuna, (10) Canned herring, (11) Canned sardines and (12) Canned mackerel.

Groups 1 to 6 were provided by staff of the Marine Institute at landing from Irish waters and production level (farmed salmon), group 7 was provided by Board Iascaigh Mhara and the remainder were sampled by officers of the Food Safety Authority of Ireland at retail level. Fresh tuna and wild salmon samples were analysed individually, all other groupings composed a number of pooled sub-samples. Capture locations and retail batch origin details were collected as appropriate.

Muscle tissue samples were homogenised by Marine Institute personnel and sub-samples were analysed for a total of 16 PBDE congeners, namely BDE 47, 49, 99, 100, 66, 28, 154, 17, 153, 119, 71, 85, 77, 126, 138, 183 and for total α-, β-, γ-HBCD diastereomers by Eurofins Europe under contract to FSAI.

Analytical methodology included lipid extraction, addition of radio-labelled PBDEs, sulphuric acid clean-up procedures followed by analysis utilising LR- and HR-MS on a HP5 GC column. Quality assurance procedures included duplicate analyses and use of appropriate reference materials. Total lipid content was determined by the Marine Institute using the Smedes method[3].

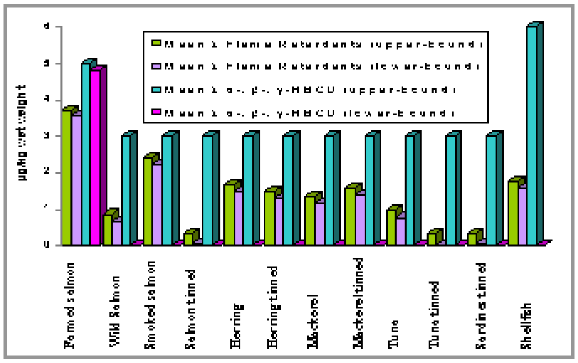
Results and Discussion

Figure 1 provides an overview of upper-bound and lower-bound concentrations of the sum (Σ) of all PBDE congeners analysed in addition to the upper-bound and lower-bound concentrations for Σ of α, β and γ HBCD.

The most abundant congeners determined in all samples were BDEs-47, 49, 99, 100, 66, 28 and 154 (see Table 1). BDEs-17, 153 and 119 were frequently below or close to the Limit of Quantitation (LOQ) (0.01, 0.03, 0.02 µg/kg wet weight respectively) except for farmed and smoked salmon with average BDE-153 levels of 0.07 and 0.05 µg/kg wet weight respectively. No sample showed levels of BDE-71, BDE-85, BDE-77, BDE-126, BDE-138, BDE-183 above the LOQ (0.01, 0.02, 0.01, 0.02, 0.03, 0.05 µg/kg wet weight respectively), with the exception of one shellfish sample.

Figure 1 Mean upper (

concentrations of Σ PBDE and Σ HBCD (µg/kg wet weight)



Levels of the three HBCD diasteromers above the LOQ were only found in farmed salmon, with a mean level of 5 µg/kg and a range of 3.23-7.41 µg/kg wet weight. Table 1 presents mean and median occurrence levels for BDEs 47, 49, 99, 100, 66, 28 and 154, which were present above their respective LOQs in all samples tested except for canned salmon, canned tuna and canned sardines. The mean upper-bound sums as well as the range of sums of all congeners tested are also presented.

Table 1 Mean and (median) concentration of the most abundant BDE congeners (µg/kg wet weight), values prefixed with "<" indicate detection below respective LOQs

	N (Sub-N)[a]	% lipid ***	BDE congeners (µg/kg wet weight)							Mean sum (UB)		Range (UB)
			47	49	99	100	66	28	154	Most abundant	16 congeners tested	
Wild Salmon	10 (1)	10.4 (11.5)	0.34 (0.34)	0.04 (0.04)	0.11 (0.12)	0.06 (0.06)	0.02 (0.02)	0.02 (0.02)	0.07 (0.07)	0.66	0.86	0.7-1.01
Farmed Salmon	15 (5)	14.4 (14.2)	1.74 (1.78)	0.46 (0.45)	0.58 (0.48)	0.35 (0.37)	0.11 (0.12)	0.08 (0.08)	0.16 (0.16)	3.47	3.71	2.42-5.05
Smoked Salmon	11 (5)	9.9 (10.0)	1.07 (1.12)	0.3 (0.3)	0.37 (0.33)	0.21 (0.22)	0.06 (0.06)	0.05 (0.05)	0.1 (0.1)	2.17	2.39	1.69-3.58
Canned Salmon	5 (5)	6.2 (7.1)	0.04 (0.03)	< 0.01	<0.02	<0.02	< 0.01	< 0.01	<0.03	0.14	0.34	0.33-0.35
Herring	4 (10) * 2 (5)**	12.4 (12.4)	0.69 (0.71)	0.35 (0.35)	0.11 (0.11)	0.15 (0.16)	0.03 (0.03)	0.03 (0.03)	0.05 (0.05)	1.41	1.61	1.46-1.77
Mackerel	7 (10) * 2 (5)**	14.2 (9.8)	0.54 (0.53)	0.18 (0.18)	0.22 (0.21)	0.13 (0.11)	0.05 (0.05)	0.04 (0.04)	0.05 (0.05)	1.21	1.41	0.93-1.86
Tuna	5 (1)	11.5 (8.7)	0.36 (0.35)	0.08 (0.08)	0.05 (0.05)	0.11 (0.11)	0.05 (0.05)	0.02 (0.03)	0.1 (0.1)	0.76	0.96	0.57-1.36
Canned Tuna	5 (5)	5.3 (1.4)	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01	< 0.03	0.11	0.31	0.31-0.31
Canned Sardines	1 (5)	21.4	0.04	0.01	< 0.02	< 0.02	< 0.01	< 0.01	< 0.03	0.34	0.05	-
Shellfish	5	1.7 (1.4)	0.6 (0.4)	0.14 (0.11)	0.39 (0.29)	0.23 (0.14)	0.04 (0.03)	0.03 (0.02)	0.11 (0.11)	1.51	1.75	0.69-4.21

* fresh ** canned *** extractable lipid

[a] Sub-N denotes the number of individual samples aggregated to provide a single analytical sample

The upper-bound sum of the most abundant congeners was 0.14 wet weight in canned salmon and 3.47 ug/kg in farmed salmon, with wild salmon having levels approximately 20% those of farmed salmon.

No difference in contaminant occurrence could be observed between canned and fresh samples for either Herring and Mackerel. Levels in canned tuna were all below the limit of quantification in contrast to fresh tuna. This difference may in part be due to differences in types of species used, i.e. skipjack tuna being the dominant species used for canning and Albacore tuna being the most widely species marketed fresh in Ireland or due to retail processing practices. The size/age, diet, lipid content and trophic status of the fish are also likely to be contributing factors. Furthermore, the majority of canned samples available on the Irish market differ in geographic origin from the fresh samples analysed, with canned samples mainly being imported/originating from countries bordering the Indian Ocean. A similar observation could be made with respect to canned red and pink salmon, which also showed low contaminant levels. Again the latter may be attributable to the origin of the fish, namely Alaska and Canada or to size, trophic status and differences in diet between the fish. Results for canned sardines were also comparably low.

Differences in contaminant occurrence above the limit of quantification could be observed with regard to species, origin (farmed vs. wild) and processing methodology (see Figure 2). Data below respective LOQs are not displayed (e.g. canned tuna, canned salmon).

Figure 2: Comparison of BDE congener occurrences between fish species (µg/kg wet weight)

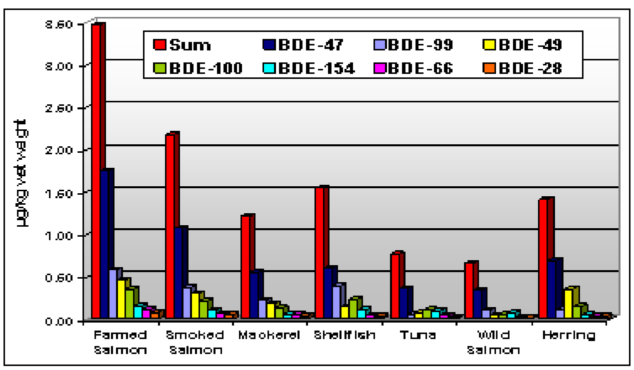
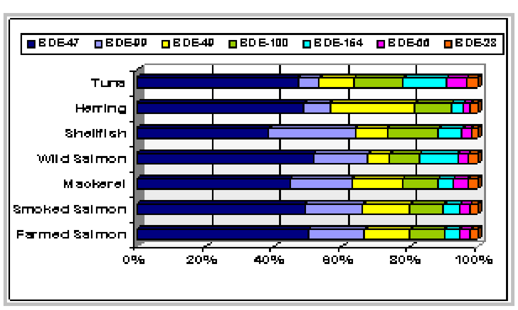


Figure 2 shows a relatively higher contaminant occurrence on a wet weight basis in farmed salmon compared to all other species tested in this survey. Smoked salmon, (also farmed), shows a slightly lower concentration than its unprocessed counterpart, which may in part be attributed to the absence of skin (and associated fat layer) in this product or possibly related to diet variances and processing factors. Lowest concentrations can be observed in wild salmon, with levels broadly similar to those previously reported by Hites and co-workers for pacific salmon[4]. Hites also reported similar levels for PBDEs in farmed Atlantic salmon from Europe.

While farmed salmon, smoked salmon, and mackerel showed a similar congener occurrence pattern (see Figure 3), this pattern was somewhat different for the remaining samples. With the exception of shellfish (39%), BDE 47 on average contributes to almost half of the total sum of the most abundant BDEs. BDEs 66 and 28 contribute the least (2.5 % and 3.5% respectively) for all species displayed. For BDEs 99, 49, 100 and 154 a species-dependent variation can be observed, showing a range of 19.1 % for BDE 99 (6.3 -25.5%), 18. 5 % for BDE 49 (6.4 – 24.9%) 6. 5 % for BDE 100 (8.6 – 15.1 %) and 9.2 % for BDE 154 (3.4 – 12.6%).

Figure 3: Congener pattern (% contribution)



Conclusions

The findings of this survey are generally comparable to studies on PBDE occurrence in fish reported in the literature. Of the 16 PBDE congeners analysed, only 7 congeners (BDEs 47, 99, 100, 154, 66 and 28) were found to be prevalent.

The highest concentrations of total PBDE (sum 16) were observed in farmed and smoked (farmed) Atlantic salmon (3.71 and 2.39 µg/kg ww respectively), fresh Mackerel, fresh Herring and Shellfish showed lower levels (1.41, 1.61 and 1.51 µg/kg ww respectively) as did fresh Tuna and wild salmon (0.96 and 0.86 µg/kg ww respectively) which showed the lowest levels in all fresh fish included in this survey. The higher concentrations observed in farmed Atlantic salmon versus wild Atlantic salmon may be attributable to the feed regime and source. Differences observed in fresh salmon and fresh tuna versus canned salmon and canned tuna may be attributable to the, age, sex, trophic status and origin of the fish, the latter being imported from North America and the Indian Ocean region. The latter mentioned factors are currently outside the scope of this paper and no firm conclusions can be drawn as to their influence on the findings.

Acknowledgements

The authors wish to thank all participating staff of the Marine Institute for their input and support in this survey.

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