GEOGRAPHICAL INVESTIGATION OF BFRs, BROMINATED AND MIXED HALOGENATED DIOXINS AND FURANS, AND POLYCHLOINATED NAPHTHALENES IN FISH COLLECTED FROM UK AND PROXIMATE MARINE WATERS

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Introduction

The fish collected and measured for dioxins and PCBs and described in an accompanying abstract: 'Geographical investigation for PCDD/F and PCB in fish collected from UK and proximate marine waters'[1] were also analysed for other contaminants that are under review by the European Commission Expert Committee on POPs in Food, or are candidate compounds for listing under the Stockholm Convention and chemicals identified under the UK Food Standards Agency's (FSA) own emerging risks programmes. This abstract summarises the data for PBDEs from all the fish that were collected, and results from selected fish that were analysed for PBBs, brominated and mixed halogenated dioxins and furans, and polychlorinated naphthalenes.

PBDEs are mass-produced brominated flame retardants (BFRs) that were incorporated into a number of commonly used commercial materials such as plastics, rubbers, textiles and electronic components. As these are open-ended applications, the BFRs are available to diffuse out of materials into the environment, and this can occur during manufacture, use and disposal of the product. Emerging toxicological data shows that PBDEs can cause liver and neurodevelopmental toxicity and affect thyroid hormone levels. Additionally, they may be particularly harmful during a critical window of brain development during pregnancy and early childhood[2]. Their occurrence in food has been investigated in studies that also target PBDD/Fs and PBBs[3] but, unlike these contaminants, they show more frequent and abundant occurrence. Fish, and in particular oily fish species, generally tend to show higher levels of contamination than other food types.

Polychlorinated naphthalenes (PCNs) also show properties of stability, high bio-accumulative potential and persistence, coupled with a similarity in structural configuration to planar PCDD/Fs. Some congeners can contribute to dioxin-like toxicity and have shown a combination of toxic responses such as mortality, embryotoxicity, hepatotoxicity, immunotoxicity, dermal lesions, teratogenicity and carcinogenicity[4,5]. There have been a few recent studies confirming occurrence in food and human exposure, and in particular fish[6,7].

Brominated dioxins and biphenyls - PBDD/Fs and PBBs - have physico-chemical and toxicological properties that are similar to their chlorinated analogues. The PBDD/Fs originate from similar anthropogenic sources as chlorinated dioxins, such as incineration, particularly of bromine containing waste, or chemical manufacture, whereas PBBs were produced commercially as flame retardants chemicals long before the large volume production of the more familiar BFRs such as PBDEs and HBCD. Their occurrence in food in the UK has been confirmed in earlier studies funded by the FSA, including an investigation on fish carried out in 2005[8]. The study showed a greater frequency of occurrence of PBDFs, whilst PBBs generally showed very low occurrence. A later study on individual foods including fish and shellfish confirmed these findings.[9]

PXDD/F and PXBs are mixed bromo/chloro analogues of PCDD/F and PCBs and share the same sources and toxicological properties as the other analogues, except that PXBs were never intentionally produced. Analysis of these is complex due to the large numbers of possible compounds (4600 PXDD/Fs and 9180 PXBs) and the potential for false positive detection during mass spectrometric measurement, as these compounds share ions with other more abundant and less toxic contaminants. Toxicologically, some PXDD/F congeners show Ah receptor binding potency similar to the most toxic PCDD/Fs and, for some congeners, may even be more potent. There have been only a few studies carried out to date on the occurrence of these contaminants in foods [10,11,12] and the current study has provided a baseline for the occurrence of these contaminants in fish.

Materials and methods
Details of the samples collected are described in the accompanying abstract[1] and analytical methodology has been described previously[6,11].

Results and discussion:
All samples were analysed for PBDEs, while smaller sub-sets of samples (covering the more susceptible species - sardines, mackerel, herring, grey mullet, sprat, sea bass and turbot) were analysed for the other contaminants.

PBDEs were observed in all samples with all measured congeners being detected apart from BDE-126 (Table 1). There are only minor differences between the average values for both the sum of the 17 congeners and those regulated in the EU, which confirms an informed choice of congeners for the EU list. The concentrations range from 0.04 µg/kg to 8.87 µg/kg whole weight for the sum of all measured PBDE congeners (0.04 µg/kg to 8.63 µg/kg for the EU listed PBDEs). The highest average values were observed for herring, sea bass, mackerel and sprat (2.08, 2.0, 1.45 and 1.27 µg/kg respectively). PBBs were detected less frequently and at lower concentrations (not tabulated due to space restraints and infrequency of detection), confirming a trend observed in other studies[13,14] The highest value observed was 0.65 µg/kg for BB-52 in grey mullet from France. In general, most of the higher positive values for PBBs were observed for samples taken from French waters and from the southern coast of England. This may reflect a higher utilisation of PBBs in France relative to the UK where PBBs are generally not detected or occur at very low concentrations in foods.

PCNs were measured in 76 samples covering 7 species (Table 1). The sum of the 12 reported PCNs ranged from 0.7 ng/kg whole weight for a sample of turbot to 265 ng/kg whole weight for a sample of sprats. Mackerel and sprats showed the highest concentrations with average values of 68 ng/kg and 67 ng/kg whole weight respectively. An earlier study on individual UK foods[6] showed an average of 20 ng/kg whole for individual fish samples (salmon, herring, sprats, eels, trout, etc.), and the concentration in the fish group in the last total diet study (TDS)[14] was 6.6 ng/kg whole. The composition of the TDS fish group would include both oily and white fish as well as shellfish, as compared to the mostly oily species targeted in this study. Although a majority of the higher concentrations observed in this study arose from the Southern and Eastern UK coasts and Northern France, the highest values were seen in samples received from Northern Ireland and taken from the Irish Sea.

The occurrence profile for the PBDD/Fs confirms observations from earlier studies on these contaminants, with a greater frequency of detection for the PBDFs relative to the PBDDs. The penta- and hexa-brominated dioxins were not detected in any of the samples. The PBDD/Fs occur to a much lower extent than the chlorinated analogues. The PBDD/F concentration data converted to TEQs, range from 0.001 to 0.04 ng/kg TEQ whole weight (Table 1) which is comparable to the concentration in the fish group in the last TDS[12] at 0.02 ng/kg whole. As in previous studies, TEFs associated with the analogous chlorinated compounds have been used to compute these TEQs, as there is no universally recognised TEF scheme for these compounds.

PXDFs were detected more frequently than the PXDDs (Table 2). Apart from a couple of sea bass samples, at least one PXDD/F congener was detected in all of the 59 analysed samples, albeit at low concentrations relative to PCDD/Fs. PXBs were detected in all samples with highest concentrations being observed in mackerel, sprats and sea-bass. In general, the frequency of detection was similar to that observed in an earlier study on foods[7] and followed the order PXBs>PXDFs>PXDDs. The concentration range reported in the earlier study for a set of 40 fish was <0.005 to 1.12 ng/kg fat for PXDD/Fs and <0.005 to 14.7 for the PXBs. The range in the current study was similar for PXDD/Fs (<0.005 to 1.62 ng/kg fat), but the upper end of the range for PXBs (<0.005 to 42 ng/kg fat) was approximately a factor of 3 higher than the earlier study. The higher concentrations for the PXBs were generally associated with samples from Northern France/Southern UK waters and the Irish Sea.

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Table 1. Results for PBDEs, PCNs and PBDD/Fs.

		Min	Max	Mean (Sardines)	Mean (Mackerel)	Mean (Herring)	Mean (Grey Mullet)	Mean (Sprat)	Mean (Sea Bass)	Mean (Turbot)	Mean (Shark – various spp)
PBDE µg/kg	Sum of all measured	0.04	8.87	0.50	1.45	2.08	1.10	1.27	2.00	0.37	0.54
whole wt	Sum of EU regulated	0.04	8.63	0.49	1.35	2.00	1.08	1.23	1.97	0.35	0.51
Sum PCN ng/kg	whole wt; lower bound	0.7	264.5	19.7	67.9	38.5	14.6	66.4	29.3	5.3	n/a
	whole wt; upper bound	0.7	264.8	19.8	68.0	38.7	14.7	66.5	29.4	5.3	n/a
	fat wt; lower bound	21	301	289	647	429	1291	680	995	338	n/a
	fat wt; upper bound	22	7572	291	648	431	1293	680	999	343	n/a
PBDD/F TEQ	whole wt; lower bound	<0.001	0.021	0.006	0.004	0.005	0.005	0.004	0.003	0.002	n/a
ng/kg	whole wt; upper bound	0.001	0.042	0.022	0.015	0.019	0.013	0.016	0.014	0.008	n/a
	fat wt; lower bound	<0.001	0.579	0.063	0.076	0.034	0.103	0.077	0.116	0.097	n/a
	fat wt; upper bound	0.072	2.138	0.265	0.332	0.153	0.304	0.234	0.510	1.056	n/a

The number of fish analysed was between 6 and 41 individual samples per species reported.

Table 2: Range of PXDD/F and PXB concentrations for selected congeners

PXDD/Fs ng/kg fat wt	Min	Max
2-B-7,8-CDD	<0.005	0.199
2-B-3,7,8-CDD	<0.005	0.134
2,3-B-7,8-CDD	<0.005	0.101
1-B-2,3,7,8-CDD	<0.005	<0.111
2-B-1,3,7,8-CDD	<0.005	<0.097
2-B-3,6,7,8,9-CDD	<0.005	<0.191
2-B-7,8-CDF	<0.007	0.231
3-B-2,7,8-CDF	<0.005	0.134
2-B-6,7,8-CDF	<0.005	1.627
2,3-B-7,8-CDF	<0.005	1.267
1-B-2,3,7,8-CDF	<0.005	<0.134
4-B-2,3,7,8-CDF	<0.005	0.257
1,3-B-2,7,8-CDF	<0.005	<0.185
PXBs		
4'-B-3,3',4,5-CB (PXB126)	0.008	0.532
3,4-B-3',4',5'-CB (PXB126 di-Br)	<0.005	0.084
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.005	0.225
4'-B-2,3',4,5-CB (PXB 118)	0.567	42.032
4'-B-2,3,3',4-CB (PXB 105)	0.201	9.705
4'-B-2,3,3',4,5-CB (PXB 156)	0.101	6.567

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