Brominated dioxins (PBDD/Fs) and flame retardants (BFRs) in Scottish Shellfish

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Introduction

Shellfish are an economically important produce for Scotland, both for national consumption as well as export, and mussels (*Mytilus edulis*), oysters (*Crassostrea gigas, Ostrea edulis*) and scallops (*Pecten maximus*) are among the most popular bivalve species produced. Marine shellfish have a recognised potential for bio-accumulating contaminants and some species, such as mussels, are commonly used as early indicators of local pollution. This is because bivalve shellfish feed by filtering nutrients from seawater and are unable to metabolise some contaminants that they ingest at the same time. The resulting bio-accumulation of persistent environmental contaminants such as brominated dioxins (PBDD/Fs) and BFRs is also particularly relevant when species are used for food. There is very little information on the occurrence of these contaminants in marine species (1). This is perhaps unsurprising given the relatively recent recognition of the global environmental distribution of these pollutants, and the difficulties in analytical accessibility (2).

Polybrominated diphenylethers (PBDEs), hexabromocyclododecane (HBCD), & tetrabromobisphenol A (TBBPA) and are mass-produced BFRs. These chemicals are incorporated into commercial materials and used specifically to slow down or inhibit the initial phase of a developing fire. (Polybrominated biphenyls (PBBs) were previously used for the same purpose but have been banned since the 1970s.) Their use has undoubtedly resulted in a reduction in human injury and fatality as a result of fires. However, the unrestricted application of these materials has allowed diffusion of the contaminants into the environment during manufacture, use and disposal and continues to do so. This release is evident from the occurrence of BFRs in environmental compartments such as water, sediments and biota (2) and accompanies an increasing amount of evidence on potential detrimental human health effects (2-4).

PBDD/Fs are unintentional by-products of combustion processes and have physico-chemical properties that are similar to their chlorinated analogues. They originate from similar anthropogenic sources as chlorinated dioxins. For example, there are studies (2,5) to show that the incineration of items containing BFRs, as well as thermolysis of BFR products such as PBDEs, is an important source of PBDD/Fs. They can also be formed from PBDEs during thermal processing procedures such as extrusion, moulding and recycling, and degradation (2).

A recent study in the UK (1) investigated the occurrence of brominated dioxins and BFRs (PBBs, PBDEs, HBCDs and TBBP-A) in composite samples of fish and shellfish in England and Wales. Certain PBDE congeners were present in most or all of the samples analysed, the most abundant being PBDEs 28, 47, 49, 66, 99, 100, 153 and 154. HBCDs and PBBs were detected less frequently (α-HBCD being the most abundant) and more PBDF congeners were detected than PBDDs. TBBP-A was not found above the limit of detection in any samples. The data presented here complements the above study for the UK as a whole. This data is unique as it is the first study that investigates the range of brominated contaminants in shellfish in such a comprehensive manner.

Sampling and Analysis

Individual sub-samples of mussels, oysters and scallops were collected in Scottish in-shore and off-shore areas between January and March 2006. The sampling interval was selected to capture the pre-spawning period for the selected species, and also coincides with the time when fat levels are highest and the shellfish are most suitable for consumption. The samples were representatively pooled and homogenised to yield 35 composite analytical samples. As scallops partition chemicals differently in the adductor and gonad tissue, these were divided into separate adductor and gonad portions prior to pooling. 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**. **TBBPA** and **HBCD**: **α**, **β**, and **γ** enantiomers. PBB congeners: IUPAC numbers 15, 49, **52**, **77**, 80, 101, **126**, 169, **153** and 209. 2,3,7,8-Bromo substituted PBDD/Fs – tetra to hexa substituted congeners as well as 2,3,7-TBDD and 2,3,8-TBDF. Those for which ^{13}Carbon labeled standards were used as internal or sensitivity standards are shown in bold type and these also included 6 PBDD/F congeners). Robustly validated methodology for the analysis of chlorinated and brominated contaminants in food has been reported elsewhere (6,7). Additionally, methodology for PBDD/Fs, PBDEs and PBBs has been accredited to the ISO17025 standard. Sample batches included a blank and a BCR reference material and data quality was ensured by continuous successful participation in international inter-calibration exercises (e.g. Dioxins in Food, Quasimeme).

Results and Discussion

Due to the large volume of data produced in this work, only a summarised version of the results for each of the 3 shellfish species is presented in this paper (Table 1). Data for the PBDD/Fs and non-ortho-substituted PBBs (PBBs 77,126,169) have been presented as WHO-TEQs. The use of analogous chlorinated dioxin and PCB TEFs to estimate toxicity arising from PBDD/Fs and non-ortho PBBs is an interim measure (8) until reliable TEF values that cover all the congeners that show dioxin-like toxicity become available in the literature. However it provides data to allow comparisons with other studies that have used this approach (1,9). Table 1 also includes the results for PBDEs as a sum of 17 congeners, together with the data for HBCD. Data for ortho-substituted PBBs is not presented here as values were very low (0.005µg/kg on average). All data is presented as upper bound whole weight concentrations. All of the samples were found to contain all of the contaminant groups under investigation, with the exception of TBBPA and some PBDD and PBB congener groups (notably penta and hexa-brominated compounds) for which no positive identifications were made.

PBDD/Fs were observed in all samples, with marginally higher values on average observed in scallop gonad tissue than in oysters and mussels (0.083 ng/kg WHO-TEQ compared to 0.053 and 0.058 ng/kg for oysters and mussels respectively). However, mussels generally showed a more complete range of detectable congeners, particularly the PBDFs (Figure 1). The toxicology of the tri-brominated dioxins/furans is particularly relevant in the context of the data presented here (especially for oysters) and in other studies (1,10) where significant concentrations of these congeners have been detected (up to 0.27 and 0.51 ng/kg whole weight for 2,3,7-TBDD and 2,3,8-TBDF respectively). It should particularly be noted that the concentrations of tri-bromo substituted PBDD/F congeners have not been included in the summed TEQs, as there are no recognised analogous WHO-TEF values for tri-chloro substituted PCDD/Fs. In general, the occurrence of PBDFs predominates that of PBDDs (Figure 1), reflecting the environmental distribution and source emission profiles of these contaminants. Similarly, the relative concentrations of the flame retardants – PBBs (low levels) and PBDEs (higher levels) is consistent with the greater and more recent usage of PBDEs in the UK. The low levels of PBBs observed are likely to arise from long-range marine and aerial transport as observed in the detection of this contaminant in Arctic polar bear tissue. On average, higher concentrations of PBDEs were observed in mussels compared to the other species, with the lowest levels being observed in scallop adductor tissue. The predominance of BDEs 47, 99, 100 and, to a lesser extent, 154 and 209 is similar to that observed in other studies (1,2,9,11) and reflects the use of commercial PBDE formulations (2) such as "penta". The levels of BDE 47 correlate well (R= 0.98) with the total PBDE levels for all species and this accords well with commercial "penta" as a source, as BDE 47 is the major component. BDE 209 was detected in most of the shellfish samples. The detected concentrations of this congener do not correlate well (R= 0.53) with levels of total PBDE probably because they arise from the use of a different commercial mixture ("deca"). The occurrence of BDE 209 appears to be species selective with the highest values occurring almost exclusively in mussels.

Of the other BFRs studied, TBBPA was not detected in any of the shellfish species. This is consistent with the results of other recent studies (1,9,11) in which either low or undetectable levels were reported. For the HBCDs, the predominance of the alpha-enantiomer relative to the beta- and gamma-forms is observed in all the shellfish species studied here with the highest levels observed for mussels. Although commercial formulations and sediments contain mainly gamma-HBCD, the predominance of the alpha-form has previously been documented in fish and other mammalian species and probably arises as a result of selective metabolism and biotransformation mechanisms (12). The HBCD levels recorded in this work are similar to those for other shellfish and fish species (1,11).

The human dietary exposure to all of these contaminants, through shellfish consumption is currently under evaluation although on the basis of comparable data for UK composite samples, the UK COT concluded that no toxicological concerns were raised.

Figure 1: Typical profile for PBDD/Fs in mussels

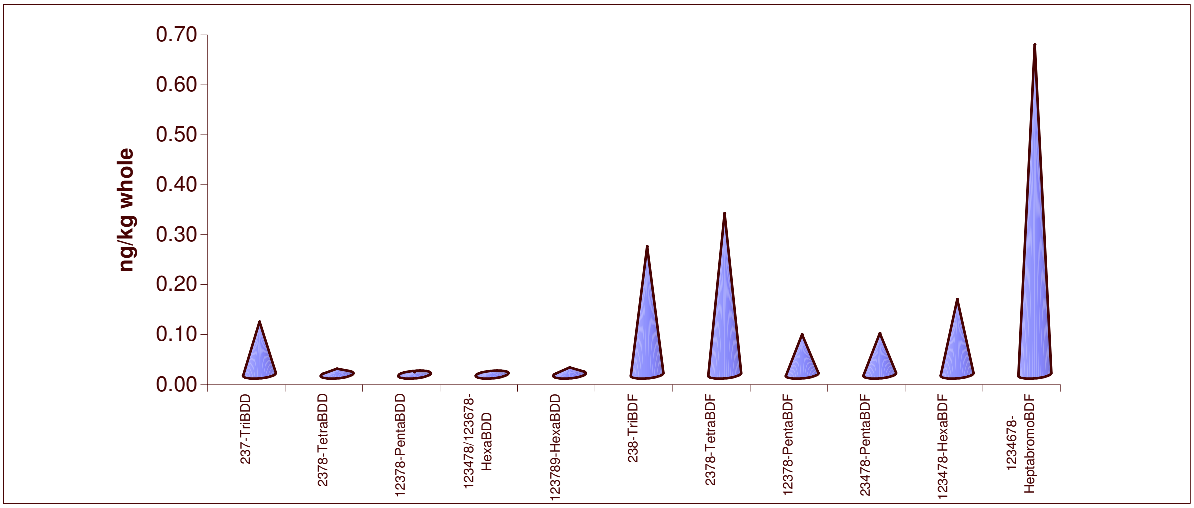

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Table 1: Summary of contaminant concentrations in shellfish species

Summary of Contaminant Concentration values in shellfish Species

	ng/kg WHO-TEQ		**PBDD/F WHO-TEQ**	**PBDD/F & PBB WHO-TEQ**	
	Min		0.031	0.032	
	Mean		0.053	0.054	
	Median		0.037	0.038	
	Max		0.121	0.122	
Oysters	**µg/kg**	**α HBCD**	**β HBCD**	**γ HBCD**	**Sum PBDEs**
	Min	0.30	0.04	0.03	0.17
	Mean	0.52	0.13	0.08	0.44
	Median	0.42	0.15	0.07	0.33
	Max	0.98	0.21	0.15	0.89
	ng/kg WHO-TEQ		**PBDD/F TEQ**	**PBDD/F & PBB WHO-TEQ**	
	Min		0.028	0.029	
	Mean		0.058	0.059	
	Median		0.049	0.050	
	Max		0.118	0.119	
Mussels	**µg/kg**	**α HBCD**	**β HBCD**	**γ HBCD**	**Sum PBDEs**
	Min	0.13	0.01	0.03	0.18
	Mean	1.36	0.26	0.24	0.66
	Median	0.43	0.09	0.09	0.35
	Max	8.93	1.60	1.52	2.74
	ng/kg WHO-TEQ		**PBDD/F TEQ**	**PBDD/F & PBB WHO-TEQ**	
	Min		0.040 (0.022)	0.041 (0.023)	
	Mean		0.083 (0.032)	0.085 (0.034)	
	Median		0.056 (0.033)	0.058 (0.034)	
	Max		0.233 (0.041)	0.235 (0.043)	
Scallops Gonad (Adductor)	**µg/kg**	**α HBCD**	**β HBCD**	**γ HBCD**	**Sum PBDEs**
	Min	0.06 (0.01)	0.01(0.01)	0.01 (0.01)	0.12 (0.04)
	Mean	0.46 (0.04)	0.05 (0.03)	0.04 (0.02)	0.42 (0.08)
	Median	0.26 (0.04)	0.02 (0.02)	0.03 (0.02)	0.27 (0.07)