Organohalogen Compounds, Volume 61, Pages 41-44 (2003)

HEXABROMOCYCLODODECANE (HBCD) DIASTEREOISOMERS AND BROMINATED DIPHENYL ETHER CONGENER (BDE) RESIDUES IN EDIBLE FISH FROM THE RIVERS SKERNE AND TEES, U.K.

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Introduction

Hexabromocyclododecane (HBCD) is a high volume, additive brominated flame retardant that has been in use for about 20 years[1]. Its major application (~ 80%) in the UK is as a flame retardant for extruded or expanded polystyrene foam, the balance is used in textile backcoatings. HBCD is manufactured in the UK by Great Lakes Chemicals at Newton Aycliffe, Co. Durham but is also imported from the Netherlands and the USA. Production figures for the Great Lakes plant are unavailable due to commercial considerations, but total sales in the UK were reported to be 570 tonnes in 2000, and European consumption was 8,900 tonnes in 1999 [2].

The UK production facility has been the source of significant emissions to the river Skerne (1098 Kg/yr in 2000) but procedures have been put in place to reduce these emissions, to 75Kg/yr in 2002 and to <10Kg/yr in 2004[2]. HBCD is currently undergoing a risk assessment within the EU, and HBCD has also been identified by the UK Chemical Stakeholders Forum as persistent, bioaccumulative and toxic. Despite its high level of use, few environmental data are available for HBCD and until now no data for the individual diastereoisomers has been reported for the UK.

Polybrominated diphenyl ethers (PBDEs) have, in contrast, been quite widely studied and numerous data exist for England and Wales[3-9]. PBDEs were also manufactured at the Great Lakes plant at Newton Aycliffe, but production was reported to have ceased in 1998 and PBDE usage in the UK has recently been curtailed as a result of EU legislation.

Technical HBCD is a mixture of three diastereoisomers. A gas chromatographic (GC) separation of the three HBCD diastereoisomers is currently not achievable and, given the thermal instability of HBCD at temperatures above 160^0C, GC is not an appropriate methodology, therefore a sensitive and robust LC-MS method was developed. The aims of this study were to apply this recently developed LC-MS methodology [10] to determine current concentrations of HBCD diastereoisomers in two species of edible fish at several locations on the rivers Skerne and Tees and also to build on existing knowledge of the occurrence of PBDEs in the Skerne/Tees system.

Methods and materials

Brown trout (Salmo trutta L. 1758) and eel (Anguilla anguilla L. 1758) were caught by electro fishing techniques or by the use of baited Fyke nets at 8 locations on the river Skerne and Tees, for locations see fig 1. The fish were killed, wrapped in pre-cleaned aluminium foil and shipped on dry ice to the Burnham Laboratory. BDE congeners (BDE28, 47, 99, 100, 153 & 154) were determined in muscle using established methodology [11]. HBCD diastereoisomers were determined

by LC-MS using gradient elution liquid chromatography techniques coupled with electrospray ionisation MS [10].

Results and Discussion

Summary results are presented in Tables 1 & 2

BDEs were detected in fish from all sites. The lowest concentrations were detected in trout from the two upstream Tees sites at Middleton in Teesdale and Low Coniscliffe with mean values for the sum of the six BDE congeners (∑BDE) of 4.9 and 5.3µg/kg wet weight respectively. The highest concentrations for ∑BDE in trout were seen at Haughton Road on the Skerne, downstream of the former manufacturing plant, with mean values of 118µg/kg wet weight. Individual values for ∑BDE at this site were close to 200µg/kg wet weight. ∑BDE concentrations declined downstream but mean values of 23µg/kg were still recorded in trout from Croft on Tees, the lowest point from which trout were available.

Eel samples were not available at Haughton Road but were available from the next nearest downstream site at Oxenfield Bridge which yielded the highest ∑BDE concentration in eels with a mean of 235µg/kg wet weight.

Concentrations also declined in eel samples downstream, but significant concentrations were still detected in samples from the Tees Barrage with a mean of 130µg/kg wet weight.

A characteristic and consistent BDE congener pattern was observed at most sites with the chromatographic profile of trout and eel being dominated by the tetrabromo-congener BDE47 followed by BDE99>BDE100>BDE154>BDE153, reflecting to a large extent exposure to the so called “penta-mix” PBDE formulations.

HBCD residues were also detected in all samples with a similar distribution pattern to the BDEs. HBCD concentrations were generally higher than the BDEs, with mean values of 20 and 26µg/kg wet weight for the sum of the three diastereoisomers (∑HBCD) in trout from Middleton in Teesdale and Low Coniscliffe respectively. Very high concentrations were detected at Haughton Road, downstream of the HBCD manufacturing plant, with a mean in excess of 2300µg/kg and individual values in excess of 6700µg/kg wet weight. Concentrations in eels were even higher, with mean values in excess of 3200 µg/kg wet weight for ∑HBCD at Oxenfield Bridge and individual values in excess of 10,000 µg/kg wet weight for ∑HBCD. Again concentrations declined downstream, but mean ∑HBCD values for trout of 117 µg/kg wet weight were still recorded at Croft on Tees and 430 µg/kg wet weight in eel at the Tees Barrage.

The chromatographic profile was dominated by the alpha diastereoisomer, with lower amounts of the gamma and then the beta diastereoisomer. This profile is consistent with other recent studies we have recently undertaken [12] and is in contrast to the profile seen in sediment where the gamma diastereoisomer is generally dominant. It is unclear if the differing profiles seen in sediment and biota is due to differences in bioavailability, preferential uptake, depuration or metabolism.

It seems clear that the primary source of HBCD and BDEs to the Skerne and Tees rivers is from the Newton Aycliffe sewage treatment works (into which Great Lakes Chemicals discharge) to the River Skerne. There may also be some contamination from surface drains that feed into Demons

and Howden Becks which bypass the sewage treatment works. Tissue residue concentrations reach maximum levels immediately below this point. Significant concentrations of both HBCD and BDEs were still detected at the lowest point sampled, just above the tidal limit at the Tees barrage. This is entirely consistent with previous work conducted on BDEs, on sediment and marine biota, which indicated widespread contamination of the River Skerne, River Tees, Tees Bay and the western North Sea[3,4,5,9].

Despite cessation of production in the late 1990s, BDE concentrations remain high in edible fish tissue from the Skerne and Tees. High and, in some cases, extremely high concentrations of HBCD were also found. Although measures are being put in place to reduce emissions of HBCD which may in turn be reflected in reduced residue levels HBCD, a persistent, bioaccumulative and toxic substance is still in production at this site and being released to the wider environment.

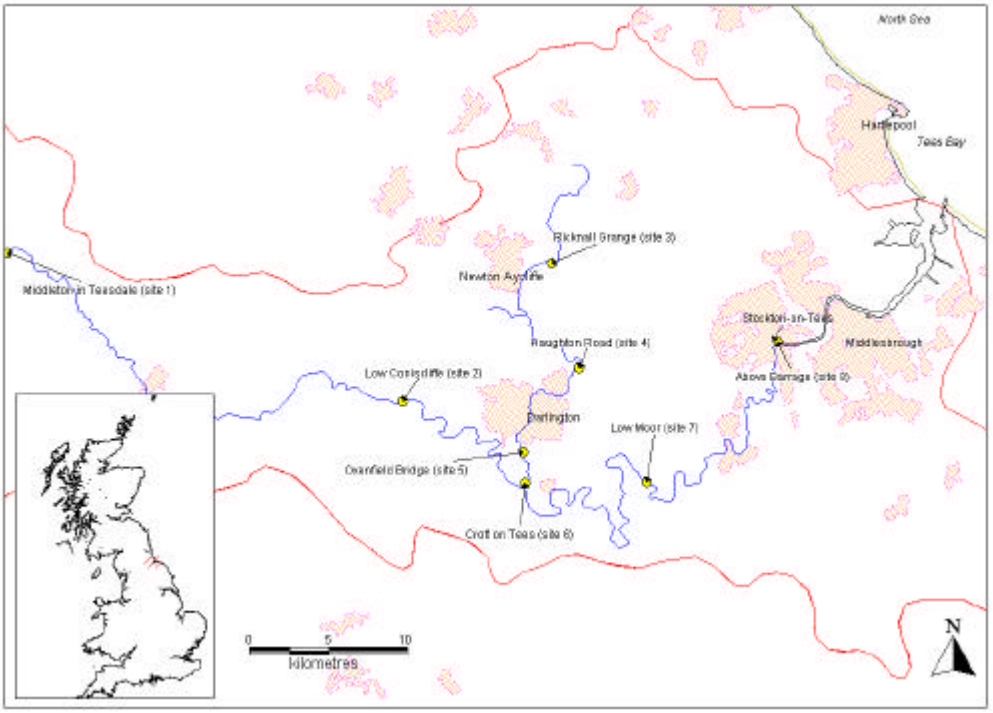
Table 1. Summed BDE congener concentrations in eel and trout muscle (µg/kg wet weight).

Site	**Eels**			**Trout**		
Sum BDEs	**Mean**	**SD**	**Range**	**Mean**	**SD**	**Range**
Site 1	-	-	-	4.9	9.2	1.34 - 17.67
Site 2	-	-	-	5.3	3.3	2.95 - 7.55
Site 3	-	-	-	12.66	0.8	12.08 - 14.02
Site 4	-	-	-	117.6	55.9	59.14 – 196.5
Site 5	235.0	57.2	163.8 - 294.5	59.9	54.9	26.65-123.3
Site 6	144.4	86.4	50.3 - 220.2	22.8	24.1	1 - 57.1
Site 7	157.6	80.4	36.4 - 263.1	-	-	-
Site 8	129.9	100.3	50.8 - 242.7	-	-	-

Table 2. Summed HBCD concentrations in eel and trout muscle (µg/kg wet weight).

Site	**Eels**			**Trout**		
Sum HBCDs	**Mean**	**SD**	**Range**	**Mean**	**SD**	**Range**
Site 1	-	-	-	20.3	27.0	<1.2 - 52.5
Site 2	-	-	-	25.9	-	<1.2 - 25.9
Site 3	-	-	-	81.7	36.9	21.24 – 119
Site 4	-	-	-	2341.2	2255.2	159 – 6758
Site 5	3216	4032.6	570 -10275	221.1	168.2	106 – 414
Site 6	465.4	275.7	173 – 720.2	117.3	63.8	25.9 – 200
Site 7	399.6	352.5	66.5 - 861.7	-	-	-
Site 8	431.1	450.9	39.9 - 977	-	-	-

Figure 1. Sample locations



Acknowledgements
The study was funded by the UK Food Standards Agency.

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