RESULTS OF A COMPREHENSIVE SURVEY FOR PBDES IN THE RIVER TEES, UK

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Introduction

The use of the additive brominated flame retardants polybrominated diphenyl ethers (PBDEs) for a wide range of domestic and commercial applications is well documented [1,2,3]. In a previous study we highlighted the occurrence of high concentrations of PBDEs in samples of sediments and biota from the Rivers Tees and Skerne, in the north east of England [4]. This earlier pilot scale study reported PBDEs on the basis of commercial formulations and a limited number of individual congeners (BDE47, 85 & 99) based on determination by gas chromatography with electron capture detection (GC-ECD). We report here the results of a further, extensive survey conducted on the River Tees for a total of 14 PBDEs determined using fully optimised and validated methodology utilising gas chromatography with mass selective detection (GC-MSD) and for BDE209, GC-ECD.

Materials and methods

Sediment samples were collected by means of a modified Day grab (for sea based sampling) or a hand held van Veen grab for land based sampling. The detailed analytical methods and validation procedures are reported elsewhere [5] but basically involve Soxhlet extraction of air dried sediment (<2000um fraction) with n-hexane and acetone (1:1 v/v) with the addition of acid washed copper turnings to remove sulphur. Suitable volume extracts were purified by absorption chromatography using gravity fed columns of partially deactivated alumina and silica. Further clean-up by sulphuric acid treatment was occasionally required for samples with a high matrix background. CBs 53, 155 and 198 were used as internal standards and BDEs 28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154 and 190 were measured by negative ion chemical ionisation mass selective detection monitoring bromine at 79 and 81 Da after separation on a 50m DB-5 column. BDE209 was measured by GC-ECD with a 15m HP-1 column. During the course of this study we took part in a total of three intercomparison exercises which effectively demonstrated the applicability of the analytical approach.

Results and discussion

For ease of data interpretation the Tees is divided into four sections. These sections are identified in Table 1 which also contains the precise positional data and results of the PBDE analysis (BDE47, 99 & 209 only) as well as total organic carbon (TOC) and particle size analysis (PSA) data. Mean BDE209 data for the four sections of the Tees are presented graphically at Figure 1.

The first section has been called the Upper Tees, this runs from the source of the river in Teesdale (effectively Cow Green reservoir) downstream to Croft on Tees (excluding the confluence with the R. Skerne). The next section has been called the Middle Tees and runs from Croft on Tees to the Tees Barrage. Tees Barrage to Tees Mouth forms the Lower Tees and finally Tees Mouth and Tees Bay have been combined and called the Tees estuary.

PBDEs were not detected in sediment samples from the Upper section of the river although a low concentration of 1 μg/kg dry weight of BDE#209 was observed at Winston Gate Bridge. These results are unsurprising given the lack of any industry in the area. There is a sewage treatment works at Barnard Castle, but this is thought to be largely dealing with domestic sewage from this very rural area.

BDE#209 and BDE#47 were both seen at the last sampling point before the confluence with the River Skerne at Croft on Tees at concentrations of 1 and 0.21 μg/kg dry weight respectively (close to the detection limits).At the first sampling point downstream of the confluence with the River Skerne BDE#209 was measured at 107 μg/kg dry weight and the Sum BDE concentration (which excludes BDE#209) rose to 73 μg/kg. Concentrations generally declined through the rest of this section although a sample taken from the River Leven, a major tributary of the Tees which joins the river south west of Middlesbrough, contained 40μg/kg Sum BDE, but interestingly BDE#209 was not detected in this sample. All samples from the Lower Tees contained detectable levels of PBDEs with values ranging from 7 – 61 μg/kg dry weight Sum BDE, with a mean of 13 μg/kg. When normalised to <63μm fraction this value rose to 22 μg/kg and to 283 μg/kg when normalised to TOC.

Although normalisation to TOC is common for marine sediments, the River Tees , in common with other rivers on the east coast of England, contains significant quantities of coal particles and these can lead to high TOC values. A typical UK estuary would be expected to have TOC levels of around 2%, in this survey values ranged from 0.38 to 10.25%

BDE#209 concentrations in the Lower Tees sediments were often (but not exclusively) higher than the Sum BDE value. The mean for BDE#209 was 140 μg/kg dry weight, tens times higher than the mean value for Sum BDE. The Tees estuary yielded the highest BDE#209 concentrations with a mean of 240 μg/kg dry weight, approximately tens times higher than the mean Sum BDE value of 26 μg/kg dry weight. An extreme value of 1400 μg/kg dry weight for BDE#209 was measured at the sampling point just off Dabholm Gut, which is probably the most significant mixed industrial and domestic sewage discharge to the Tees estuary.

The BDE#209 and Sum BDE concentrations were highly variable in the estuary probably due to a combination of diffuse and point source inputs and the varied nature of the river beds which contains areas of gravel, sand, silt and cohesive muds.

Once leaving the estuary the PBDE levels generally declined quite rapidly in the sandier sediments, although there were localised pockets of elevated levels and there was some evidence of elevated levels of PBDEs in the region of the main Tees dredge spoil disposal ground.

The sediment BDE profiles, although quite varied, were generally dominated by BDE#47, 99 and 100, the primary congeners present in the penta mix DE-71 which was known to be produced until the late nineteen nineties at a plant at Newton Aycliffe on the River Skerne. This plant apparently did not produce the DecaBDE product (BDE209, DE-83R) although it may have been handled at the site in small quantities. Sources of commercial pentabromodiphenyl ether product from other than the former manufacturing site are quite likely given the mixed industrial nature of the area and it seems quite probable that there are also multiple sources of BDE209 in the Tees catchment

Fig. 1. Spatial distribution of BDE209 in R. Tees

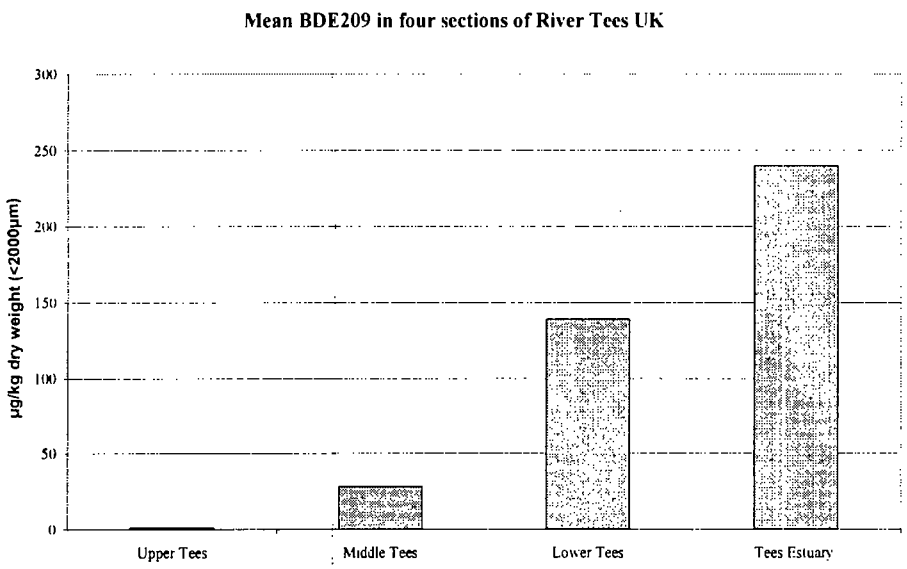

Table 1 PBDE's in sediment **µg/kg dry weight (<2000µm)**

Upper Tees (Cow Green reservoir to Croft on Tees)

LSN	Latitude	Longitude	Location	BDE#47	BDE#99	BDE#209
00/2590	54.67235	-2 231033	Langdon Beck	0.2	<0.2	<0.2
00/2591	54.62155	-2.081283	R.Tees at Middleton in Teesdale	0.2	<0.2	<0.2
00/2592	54.603683	-2.00655	R.Tees at Eggleston Bridge	<0.2	<0.2	<0.2
00/2593	54.528283	-1.892683	R.Tees at Abbey Bridge - Barnard Castle	<0.2	<0.2	0.6
00/2594	54.541433	-1.778817	R.Tees at Winston Gate Br dge	0.36	0.3	2
00/2595	54.535	-1.674183	R.Tees at Piercebridge	0.27	<0.2	<0.2

Middle Tees (Croft on Tees to Tees Barrage)

00/2596	54 486033	-1.56215	R.Tees upstream of confluence with R Skern at Croft-on-Tees	0.21	<0.2	1
00/2597	54.479533	-1.552417	R.Tees downstream of confluence with R.Skerne at Croft-on-Tees	12	25	107
00/2605	54.48435	-1.5197	R.Tees at Hurworth Bridge	2	2.5	<0 2
00/2604	54.492233	-1.409167	R.Tees at Newsham Grange	0.94	0.42	0.8
00/2603	54 512117	-1 353983	R.Tees at Yarm Bridge	2.1	2.1	4.8
00/2601	54.537083	-1 32875	R.Tees at Preston Hall	0.74	<0.2	<0.05
00/2602	54.499717	-1 31495	R.Leven at Leven Bridge	8.9	19	<0.05

Lower Tees (Tees Barrage to Tees Mouth)

00/2600	54.565383	-1.285767	R.Tees upstream of barrage (south bank)	4.2	7.2	10.3
00/2340	54.59	-1 143333	Bamlett's Wharf	13.3	17	76
00/2341	54.590667	-1 243333	Bamlett's Bight mid-channel	16.9	28	378
00/2342	54.5915	-1.242667	Bamlett's Bight North Bank	14.7	18	74
00/2343	54.5875	-1.236667	Middlesbrough Wharf mid-channel	2.9	16	13
00/2344	54.588	-1.236	Middlesbrough Wharf north bank	1.9	1.8	28
00/2345	54.584667	-1.226	Tees Transporter Bridge	8.8	14.7	164
00/2346	54.585	-1.224167	Tees Transporter Bridge	<0.2	16.4	177
00/2347	54.581333	-1.2105	Tees Storage Company	12	16	306
00/2348	54.583833	-1.1845	Cargo Fleet Wharf mid channel	2.9	4.9	119
00/2349	54.584667	-1.196167	Cargo Fleet Wharf north bank	8.4	<0.2	140
00/2350	54.5875	-1.186667	No. 25 Buoy South Bank	0.46	<0.2	165
00/2351	54.588167	-1.187667	No. 25 Buoy mid channel	6.2	2.7	55
00/2353	54.589167	-1.189667	No. 25 Buoy north bank	3.9	<0.05	55
00/2352	54.597333	-1.10068	ICI North Tees terminal mid-channel	11	0.08	327

Tees Estuary (Tees Mouth & Tees Bay)

00/2356	54.604667	-1.163333	ICI No.4 Buoy	12	21	236
00/2357	54.61	-1 155	Shell Oil jetty mid-channel	8.5	15	209
00/2358	54 6105	-1.159167	Shell Oil jetty north bank	18	29	246
00/2359	54.612667	-1.143333	Entrance to Dabholm Gut	11	17	1400
00/2360	54.6195	-1.153333	East of No.15 buoy mid channel	0.06	21	281
00/2361	54.619833	-1.15	East of No.15 buoy south bank	18	36	812
00/2332	54.626167	-1.180833	Seal sands	<0 2	<0.2	<0.2
00/2337	54.631167	-1.174167	Seaton-onTees	1.8	3.6	10.2
00/2338	54.631667	-1.155	Off Bran sands mid-channel	32.2	38	117
00/2702	54.686317	-1.150067	Tees Bay G6	0.15	0.19	2.8
00/2703	54.69405	-1.1203	Tees Bay G4	1.6	2.8	5
00/2362	54.663333	-1.171667	Tees Bay Off Seaton sands	0.3	<0.05	<0.05
00/2363	54.656333	-1.163333	Tees Bay Off Seaton sands	0 36	<0.05	<0.05
00/2704	54.6821	-1.0835	Tees Bay G1	0.23	0.19	<0.05
00/2365	54.6485	-1.140833	Tees entrance No.5 Buoy	0.85	1.2	9.6
00/2701	54.665267	-1.143217	Tees Bay G5	0.12	0.11	<0.05
00/2700	54.6568	-1.114	Tees Bay G3	0.12	0.13	<0.05
00/2705	54.6616	-1.083483	Tees Bay G2	0.37	0.46	3.7
00/2713	54.680367	-1.049783	Tees Bay Inshore disposal site C4	3.6	0.16	17
00/2367	54.636333	-1.110667	Off Coatham sands	0.14	0.13	<0.05
00/2368	54.629167	-1.093	Off Coatham sands	0.19	0.18	<0.05
00/2706	54.673567	-1.027317	Tees Inshore disposal site C6	1.1	1.2	17
00/2757	54.733183	-1.88305	NMMP 295 Off Tee's	0.54	0.63	<0.5

Conclusions

Sediment from the River Tees, below its confluence with the River Skerne to its estuary, contained higher levels of PBDEs than the Tees above the river Skerne. BDE209 was commonly, although not exclusively, the dominant congener detected. Values for BDE209 were often higher than the sum of the other congeners studied. Although considerable site to site variation exists the mean

concentrations of BDE209 increased fro the upper river to the estuary. BDE209 levels in the Upper, Middle, Lower and Tees Estuary ranged fro <0.2-2, <0.2-107, 13-378, and <0.5-1400 µg/kg dry sedi ent wt, respectively. Although detectable, levels of PBDEs declined , possibly due to dilution, in the generally sandier offshore sedi ents. The do ination of the PBDE profile by BDE209 ay be related to the varying physical/che ical properties of the PBDEs deter ined. Based on their water solubility and vapour pressures. BDE209 would be expected to partition to sedi ent and soil whereas BDE47 and 99 have less propensity to do so. The spatial variation in concentrations suggests ultiple sources to the river Tees and erits further study.

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References

1. Hedel al , P., Carlsson, P. and Pål , V. Waste fro electrical and electronic products – a survey of the contents of aterials and hazardous substances in electric and electronic co ponents. *Tema Nord* **554**, nordic council of Ministers, Copenhagen, Den ark. (1995).
2. OECD, Environ ent Directorate. Selected bro inated fla e retardants background and national experience with reducing risk. *Risk Reduction Monograph*, **3**, 152 pp. OECD Environ ent Monograph Series no. 102. OECD, Paris, France. (1994).
3. WHO/IPCS Environ ental Health Criteria 162, Bro inated Diphenyl Ethers. World Health Organisation/International Progra e on Che ical Safety, Geneva, Switzerland. ISBN 92 4 1571624 4. (1994)
4. Allchin, C.R., Law, R.J. and Morris, S. Polybro inated diphenyl ethers in sedi ents and biota downstrea of potential sources in the UK. *Environ. Pollut.*, **105**, 197-207 (1999).
5. De Boer J., Allchin, C., Law, R.J., Zegers, B., Boon, J.P. (2001) Trends Anal. Che ., sub itted.