

# POLYBROMINATED FLAME RETARDANTS - POSTERS

## POLYBROMINATED DIPHENYL ETHER RESIDUES IN CORMORANT (*Phalacrocorax carbo* L.) LIVERS FROM ENGLAND, UK.

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### Introduction

Polybrominated diphenyl ethers (PBDEs) are extensively used as additive flame retardants in polymeric materials such as acrylonitrile butadiene and high impact polystyrene and as such find many applications in both domestic and commercial situations<sup>1</sup>.

The use of flame retardants is increasing on a global scale, in 1992, 600,000 tonnes of were consumed worldwide with 150,000 tones of these being brominated compounds of which 40,000 tonnes were PBDEs, including 30,000 tonnes of the decabromodiphenyl ether (DBDE)<sup>2,3</sup>. More recent data are difficult to obtain.

PBDEs can be considered to be environmentally stable and persistent compounds, being resistant to acids, bases, and both reducing and oxidising compounds. They are hydrophobic and lipophilic and have become ubiquitous environmental contaminants being found in diverse environmental compartments and locations<sup>4,5,6,7</sup>.

PBDEs have been manufactured in England and continue to be widely used in the UK. A previous pilot scale survey reported PBDEs, quantified on a largely commercial formulation basis, but with some congener data, in samples of fish and shellfish as well as sediment<sup>8</sup>. As a result of the widespread occurrence of PBDEs demonstrated in this survey, the CEFAS Burnham Laboratory has expanded its research interests in these compounds and now has a number of studies underway. As well as investigating improvements in analytical methodology, we are conducting surveys designed to determine the distribution and fate of PBDEs in marine mammals, cormorants, sediments and fish and shellfish in waters around the UK. The latter studies are being conducted within the United Kingdom National Marine Monitoring Programme (UKNMMP) for which we are conducting a special spatial survey. The full results of these programmes will be reported elsewhere.

In this paper we report here concentrations of PBDE residues in the livers of cormorants collected from birds shot under licence during the course of investigations into the impact of piscivorous birds on fresh water fisheries.

Earlier work reported PBDEs largely on a commercial formulation basis, however more recently

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a wider range of individual PBDE congeners has become commercially available, and the synthesis and characterisation of a total of 32 polybrominated diphenyl ether congeners has been reported<sup>9</sup>. The gas chromatographic identification and quantification of PBDEs in a commercial penta mix has also recently been described<sup>10</sup>. We are currently using a mix of 14 individual PBDEs, which includes the dominant congeners found in the commercial penta mixes, as a basis on which to quantify residues. Two of these congeners (BDE47 & 99) account for 35 and 37% of the PBDE content of the penta mix, Bromkal 70-5DE<sup>10</sup>.

## Methods and Materials

PBDEs are amenable to similar preparative methodology to that employed for other organohalogens such as PCB's or DDT's, although each stage of the procedure must be optimised. We have used an extension of the methods described previously<sup>8</sup>. In essence homogenised samples are Soxhlet extracted with a 1:1 mixture by volume of *n*-hexane and acetone. Suitable sample aliquots are subjected to column chromatography over partially deactivated alumina and silica. After addition of internal standards (chlorobiphenyls CB#53, 155 & 198) PCB and OCP concentrations are determined by GC-ECD after which the extracts are treated with concentrated sulphuric acid and the PBDE content determined by GC-MS using negative ion chemical ionisation monitoring the bromide ions at *m/z* 79<sup>-</sup> and 81<sup>-</sup>. Storage of standard solutions and prepared extracts is in amber glassware and precautions are taken to reduce exposure to ambient light levels during sample manipulation.

Table 1.

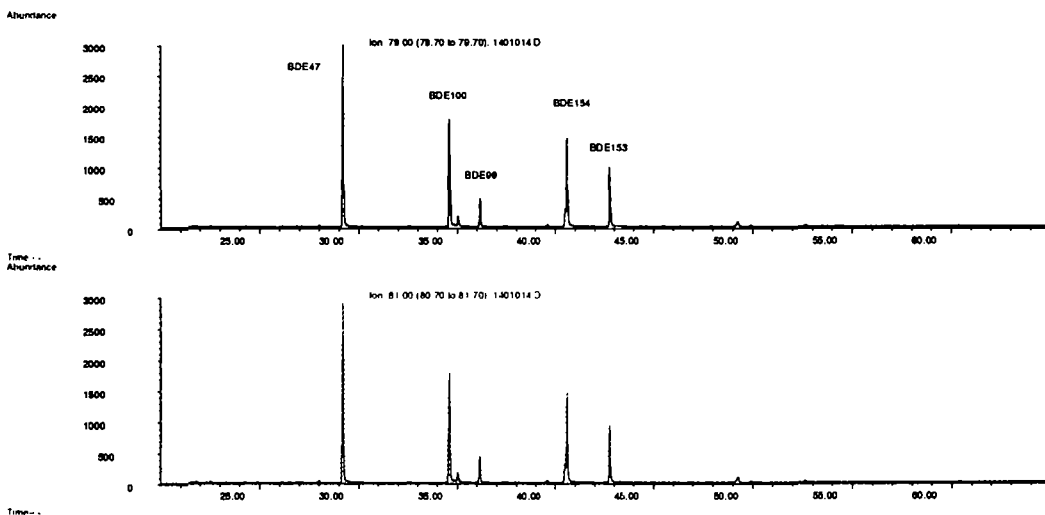
LSN	%LIPID	BDE#47	BDE#100	BDE#99	BDE#154	BDE#153	ΣBDE
99/2600	1.6	5.07	3.66	1.32	2	1.44	13.49
99/2601	<1	4.34	2.3	3.9	1.12	1.04	12.7
99/2602	<1	2.37	0.45	0.57	0.34	0.18	3.91
99/2610	1.2	4.8	2.01	1.99	1	0.72	10.52
99/2612	1.2	7.26	3.2	2.1	1.31	1.13	15
99/2613	<1	15.49	3.85	2.27	2.04	1.45	25.1
99/2614	1.6	14.08	9.1	3.39	8.46	5.38	40.41
99/2615	2	69.3	29.99	5.09	9	13.78	127.16
99/2616	<1	5.09	2.54	1.87	1.74	1.48	12.72
99/2617	1.2	2.26	1.36	0.82	0.49	0.61	5.54
99/2618	2	66.16	25.68	14.57	3.92	4.93	115.26
99/2619	2	17.42	19.61	5.98	5.03	11.77	59.81
99/2620	1.2	13.01	6.48	7.95	1.47	1.41	30.32
99/2621	1.2	4.98	1.35	0.86	0.69	0.53	8.41
99/2622	<1	1.79	0.68	0.51	0.15	0.21	3.34
99/2623	<1	1.69	0.62	0.49	0.14	0.21	3.15
99/2624	<1	4.31	1.58	2.62	0.29	0.38	9.18
99/2625	2.4	4.18	1.51	1.72	0.49	0.48	8.38
99/2626	<1	16.61	12.48	8.99	3.6	1.89	43.57
99/2627	1.6	8.93	4.47	4.51	0.93	1.58	20.42

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Table 1. gives the concentrations of BDE47, 99, 100, 153, 154 &  $\Sigma$ BDE's congeners in cormorant livers ( $\mu\text{g}/\text{kg}$  wet weight).

$\Sigma$ BDE's (the sum of 13 congeners) were detected in all samples, within the range 3-127  $\mu\text{g}/\text{kg}$  wet weight (n=20). Profiles were dominated by BDE47, 99, 100, 153 & 154. BDE47 was the most dominant congener in all samples with one exception. Other congeners were largely below the limits of detection. The predominance of BDE47 is consistent with other studies. It's relative enrichment when compared to other congeners found in the previously widely used penta mixes indicates that this congener is either more biologically available, that it is preferentially absorbed or the 2,2',4,4' configuration is the most environmentally stable. The debromination of higher brominated BDE's to the tetra-congener cannot however be ruled out.

Figure 1. Shows an example of a selected ion chromatogram of a cormorant liver extract.



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