# PERSISTENT ORGANOHALOGEN COMPOUNDS IN MARINE MAMMALS STRANDED OR BYCAUGHT IN THE UK

R.J. Law [1], C.R. Allchin [1], S. Morris [2] and P.D. Jepson [3]

1 The Centre for Environment, Fisheries and Aquaculture Science, CEFAS Burnham Laboratory, Remembrance Avenue, Burnham on Crouch, Essex CM0 8HA, UK.
2 CEFAS Weymouth Laboratory, The Nothe, Barrack Road, Weymouth, Dorset DT4 9UB, UK.
3 Institute of Zoology, Regent's Park, London NW1 4RY, UK.

***Introduction***

The UK marine mammal strandings programme is a collaborative study involving the Natural History Museum, the Institute of Zoology, SAC Veterinary Services, Inverness and CEFAS. Marine mammals are important as they are top predators in marine ecosystems, and so act as indicator organisms for bioaccumulation of POPs. Different species also exploit different prey and feeding locations, and so provide additional insights into the transport pathways and environmental distribution of contaminants. Stranded and bycaught animals are taken for post-mortem investigation, and levels of infection and parasitism, causes of death and contaminant burdens are investigated. In this paper we present data for the routinely determined POPs (organochlorine pesticides, chlorobiphenyls and brominated diphenylethers), and also some initial data for the more novel flame retardant compounds hexabromocyclododecane and tetrabromobisphenol-A. Trace elements and butyltins are also determined routinely, but those data are not considered here. The investigation of possible links between infectious disease susceptibility and contaminant burden is also discussed.

***Materials and Methods***

Selected animals, mainly those whose carcasses are considered fresh or only slightly decomposed, are taken for post-mortem study and tissues preserved for future analysis [1]. Analyses are routinely conducted for a suite of organochlorine pesticides and chlorobiphenyls (using GC-ECD), and brominated diphenyl ethers (using GC-ECNICIMS) in blubber. In this paper we also report initial data for the more novel flame retardant compounds hexabromocyclododecane (HBCD, determined on a diastereoisomer basis) and tetrabromobisphenol-A (TBBP-A) (using LC-MS). Further details of the methodology and method performance are given elsewhere [2, 3,4], as are details of the CB and BDE congeners determined [3,5].

***Results and Discussion***

*Organochlorine pesticides*

In 44 porpoises sampled in 1999-2001, concentrations were generally low. α-HCH, γ-HCH and HCB concentrations ranged from < 0.001 to 0.087, < 0.001 to 0.43, and 0.012 to 0.49 μg $kg^{-1}$ wet weight, respectively. Concentrations of dieldrin and ΣDDT (*p, p*'-DDE + *p, p*'-TDE + *p, p*'-DDT) were in the ranges 0.062 to 4.2 and 0.33 to 6.1 μg $kg^{-1}$ wet weight, respectively. The DDE/ΣDDT ratios, considered as an indication of the extent of DDT metabolism and breakdown following release [6], were generally within the range 0.5 to 0.8. A few animals showed lower ratios – in one

case as low as 0.21 – suggesting the possibility of some more recent localised inputs of DDT to UK waters.

*Chlorobiphenyls*

In the same 44 porpoises, blubber concentrations of Σ25CBs ranged from 1.3 to 48.4 mg $kg^{-1}$ wet weight. Lower concentrations were observed in 2 hooded seals found on the east coast of England in 2000, 0.37 and 0.45 mg $kg^{-1}$ wet weight, and in a fin whale, a minke whale and a humpback whale, 0.31, 0.06 and 1.2 mg $kg^{-1}$ wet weight, respectively. A single bottlenose dolphin stranded in the River Thames at Wapping had a blubber concentration of 183 mg $kg^{-1}$ wet weight, of a similar order to concentrations reported for other bottlenose dolphins from a semi-resident population in West Wales [7]. Animals from the other semi-resident bottlenose dolphin population in the Moray Firth in Scotland have much lower CB concentrations than those from West Wales [8].

*Brominated diphenylethers*

Up to 14 BDE congeners have been routinely determined in blubber samples taken during the period 1996 – 2000. Samples from 2001 & 2002 are currently being analysed. Data from 60 porpoises have been reported [5], along with 10 animals of other species, including 2 baleen whales[9]. These data are summarised in table 1, which lists concentrations for the most common congeners and the summed concentrations of all BDE congeners determined.

Table 1. Concentrations of BDE congeners in cetacean blubber (μg $kg^{-1}$ wet weight).

| **Species** | **BDE47** | **BDE99** | **BDE100** | **ΣBDE *** |
|---|---|---|---|---|
| Harbour porpoise | nd to 6110 | nd to 1290 | nd to 634 | nd to 6900 |
| White-sided dolphin | 33 | 21 | 13 | 192 |
| White-beaked dolphin | 2480 & 5780 | 622 & 1480 | 539 & 1930 | 3790 & 9410 |
| Striped dolphin | 162 | 77 | 53 | 450 |
| Common dolphin | 121 | 99 | 38 | 353 |
| Risso's dolphin | 631 | 393 | 176 | 1400 |
| Long-finned pilot whale | 163 | 51 | 20 | 319 |
| Sowerby's beaked whale | 62 | 27 | nd | 172 |
| Fin whale | 13 | 12 | 5.0 | 38 |
| Minke whale | 47 | 13 | 5.0 | 99 |

* sum of 13 or 14 congeners. nd: not detected.

In only one porpoise were BDE congeners not detected, SW1998/115 which was a 15 year old male stranded on the east coast of England. Lower concentrations were found in baleen whales than in toothed whales.

*HBCD and TBBP-A*

These compounds were determined in the blubber of 25 porpoises. TBBP-A was found in 4 samples, at concentrations between 3.9 and 376 μg $kg^{-1}$ wet weight (Table 2). HBCD residues were detected in 6 animals. α-HBCD dominated in 5, but in one animal (SW1997/111) TBBP-A and the 3 HBCD isomers were all found at concentrations around 300 μg $kg^{-1}$ wet weight. This animal was bycaught off the Yorkshire coast in July 1997, and so it is apparent that these compounds were already accumulating in North Sea foodwebs by that time. The LC-MS chromatogram obtained for this animal is shown in Figure 1.

*Possible links between contaminant burdens and infectious disease mortality*
Since the seal morbillivirus epizootic in the North Sea in 1988, there has been concern that high levels of contaminants may be suppressing the immune function of marine mammals, so making them more susceptible to infection and worsening the impact of such episodes. In earlier studies, we demonstrated an association between elevated concentrations of chlorobiphenyls in the blubber of harbour porpoises and infectious disease mortality, when compared with those animals which died due to trauma [10]. This is supporting evidence for possible suppression of the immune function in porpoises with higher burdens of a class of organic contaminants. Further analysis of data from this programme is currently underway with a larger sample size than hitherto, and will include BDEs for the first time. The potential wildlife effects of BDEs are of considerable interest and importance, and our results will feed directly into on-going risk assessments within the EU of the continued use of these compounds as fire retardants. Initial results from this data analysis confirm the association between infectious disease mortality and chlorobiphenyl concentrations, above a proposed threshold for adverse health effects (including immunosuppression) in marine mammals of 17mg/kg lipid weight in blubber, when the data are expressed as Aroclor 1254 [11]. The proposed threshold concentration was derived from dose-response relationships, based on experimental PCB-induced immunological and reproductive effects in mink, seals and otters.

Figure 1. HBCD and TBBP-A in the blubber of a one year old female harbour porpoise, reference number SW1997/111, analysed by LC-MS with electrospray ionisation.

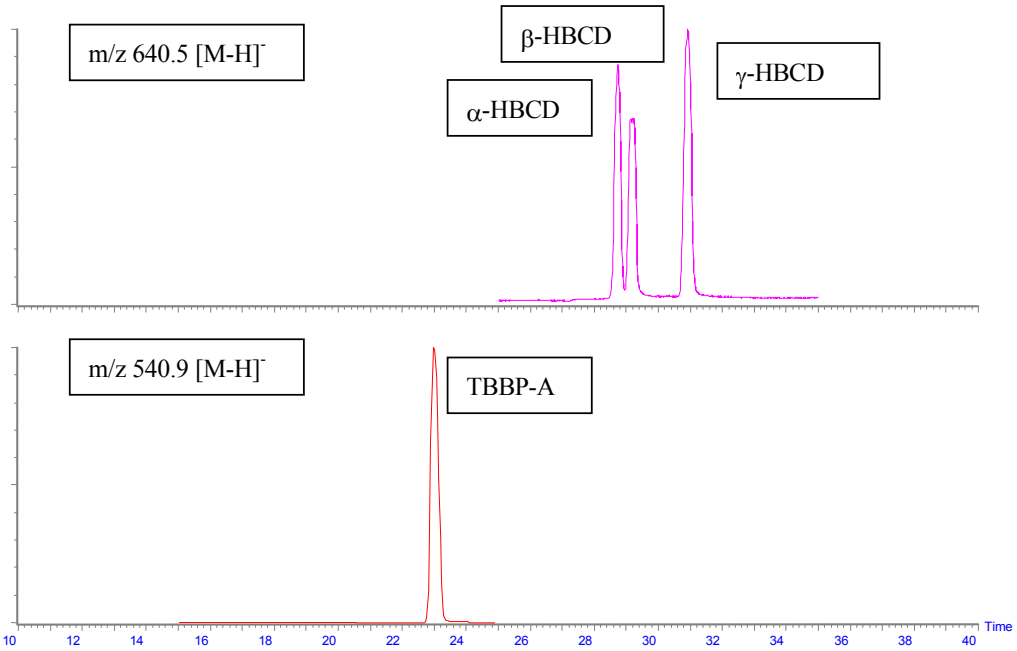

Table 2. Concentrations of HBCD and TBBP-A in porpoise blubber (μg $kg^{-1}$ wet weight).

| Reference no. | Location | TBBP-A | α-HBCD | β-HBCD | γ-HBCD |
|---|---|---|---|---|---|
| SW1996/150 | Humber | 3.9 | < 1 | < 1 | < 1 |
| SW1997/72 | Humber | < 1.1 | 89 | < 1 | < 1 |
| SW1997/80 | Tyne/Tees | < 1.1 | 315 | 2.1 | 5.1 |
| SW1997/81 | Tyne/Tees | < 1.1 | 53 | 1.2 | < 1 |
| SW1997/111 | Humber | 376 | 298 | 302 | 317 |
| SW1998/167A | E. Channel | 28 | 16 | < 1 | < 1 |
| SW1999/174B | Liverpool Bay | 8.5 | < 1 | < 1 | < 1 |
| SW2000/13 | Celtic Sea | < 1.1 | 30 | < 1 | < 1 |

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