INVESTIGATION OF TEMPORAL TRENDS OF HBCD AND BDE CONCENTRATIONS IN THE BLUBBER OF PORPOISES FROM THE UNITED KINGDOM

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Introduction

Within the UK Cetacean Strandings Programme, analysis of Brominated flame retardants began in 1999 when a suite of brominated diphenyl ether (BDE) congeners was added to the list of determinands. Although the penta-mix and octa-mix polybrominated diphenyl ether (PBDE) formulations were withdrawn from the EU market prior to August 2004, concentrations of congeners deriving from these products are still of concern. More recently, we have begun to determine hexabromocyclododecane (HBCD) within the programme, initially as a pilot study (the data presented here) but in future as part of the core programme. In this paper we report data for BDEs in blubber from 210 porpoises and for HBCD in blubber from 85 harbour porpoises (*Phocoena phocoena*) stranded or dying as a result of physical trauma (generally due to fisheries bycatch or attack by bottlenose dolphins) in the UK between 1992 and 2003. These data were also investigated for possible temporal trends in concentrations using a non-parametric significance test.

Materials and Methods

The blubber samples were collected at post-mortem from animals classified as freshly dead or only slightly decomposed at post-mortem. These protocols are given elsewhere [1]. BDE analysis was conducted using established GC-ECNIMS methodology which has been validated within an international intercomparison programme [2]. HBCD was determined on a diastereoisomer-specific basis using LC/MS. Full details of the methodologies can be found elsewhere [3,4]. Example chromatograms are given in Figures 1 & 2.

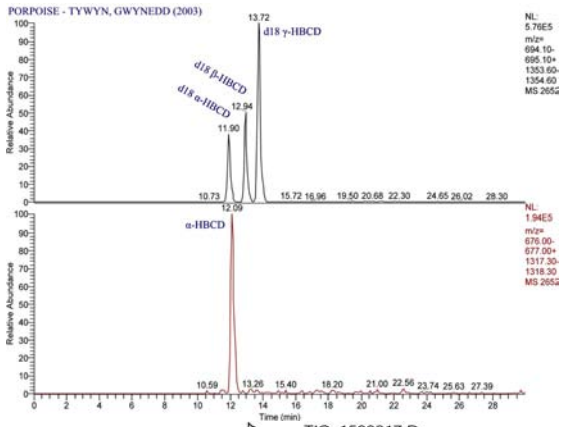

Figure 1. HBCD in porpoise blubber analysed by LC/MS. Deuterated HBCD compounds are internal standards used for quantification.

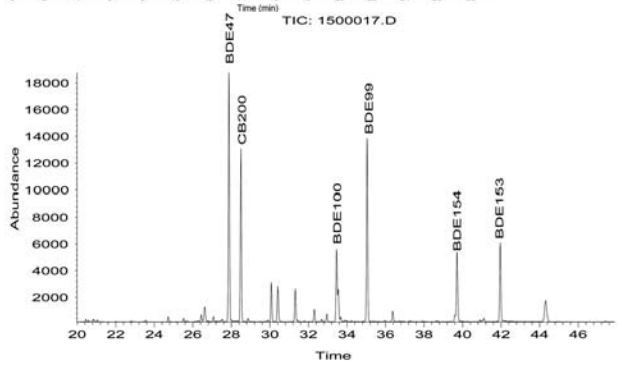

Figure 2. BDEs in porpoise blubber analysed by GC-ECNIMS. CB200 is the internal standard used for quantification.

Results and Discussion

α-HBCD dominated the HBCD profile as for other biota samples, and was detected in all 85 samples at concentrations ranging from 10 to 19,210 μgkg^{-1} wet weight (10.8 to 21,300 μgkg^{-1} on a lipid basis).

The highest concentration was observed in a juvenile male porpoise, SW2003/257C, bycaught off the coast of NE England in 2003. ΣBDE concentrations (the sum of the 10 BDE congeners determined) ranged from 14 to 13,200 μgkg^{-1} wet weight (16 to 15,700 μgkg^{-1} on a lipid basis). The highest concentration was observed in a juvenile female porpoise, SW1993/10b, stranded in Shetland (north of Scotland) in 1993. Concentrations of chlorobiphenyls (sum of 25 congeners) determined in the same animals analysed for BDEs ranged from 390 to 65,100 μgkg^{-1} wet weight- about 5 times the level of BDEs in the most contaminated animals.

Possible temporal trends in concentrations were investigated using a modified non-parametric Mann-Kendall significance test [3,4] under the null hypothesis of no trend. The null distribution of the statistic M was calculated by Monte-Carlo simulation repeated 1000 times. These values of M were compared against the observed value of M to estimate the p-value. For HBCD, the observed value was greater than all of the null values (Figure 3), giving a p-value of < 0.001. We can therefore clearly reject the null hypothesis of no trend. Observation of Figure 3 also suggests that there is an appreciable increase in levels between 2000 & 2001.

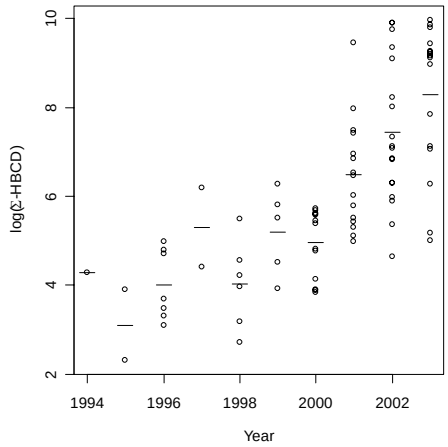

Figure 3. Plot of log(ΣHBCD concentration) values against year of stranding or bycatch. Also marked are yearly means.

In order to assess the statistical significance of such step changes between successive years, we calculated a modified version of the Mann-Kendall statistic, S. This involved calculating a value similar to M but only between points in successive years. Again, we simulated the statistic 1000 times, each time with the data randomly re-ordered within the pair of years. We then took the 25th and 975th largest points to represent a 95% randomness envelope, and the 5th and 995th largest points to represent a 99% envelope. Figure 4 shows the statistic S plotted against year, together with the 95% and 99% envelopes.

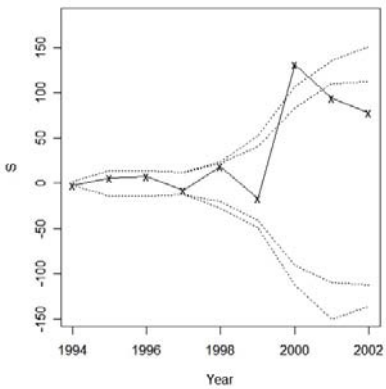

Figure 4. 95% and 99% envelope plot (dotted lines) for the statistic S comparing differences in Σ HBCD concentrations between successive years. The full line is the observed value of S. Note that points on the plot represent comparisons between that year and the next year.

The step change from 2000 to 2001 is shown up very clearly in this plot. Because the value of S is well outside the 99% envelope, the step change is strongly significant at the 1% level. Additional statistical

tests confirmed that this trend was not confounded by effects of area, sex, nutritional status (dorsal blubber thickness and blubber lipid content) or age (using body length as a surrogate).

Figure 5 shows the geographical distribution of ΣHBCD concentrations against location, up to the end of 2000 and from 2001 onwards. Again, the step change in concentrations is apparent.

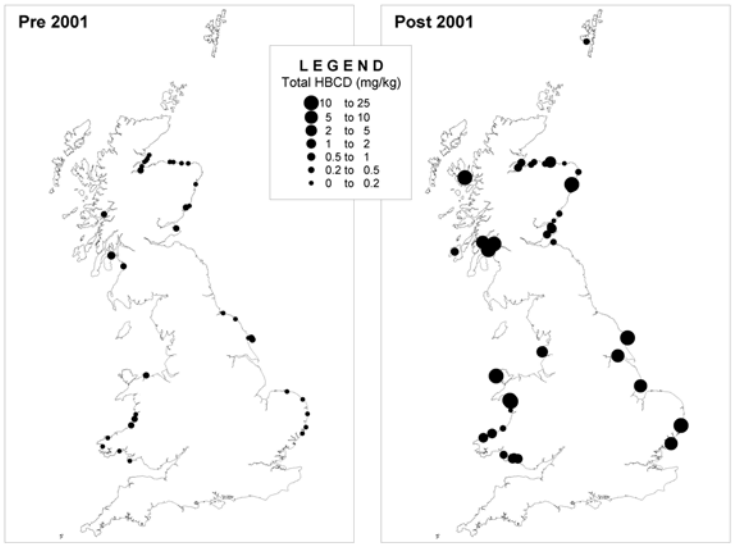

Figure 5. Spot diagrams indicating ΣHBCD concentrations in porpoise blubber against location, up to the end of 2000 and from 2001 onwards ($mgkg^{-1}$ wet weight).

A similar statistical approach was used to test for evidence of a temporal trend in BDE concentrations. In total, 270 porpoises have been analysed for BDEs within the UK Cetacean Strandings Programme [3,4]. From these, we selected adult males and juveniles of both sexes for study (n = 172) and considered only the dominant congener, BDE47, as there have been changes in the suite of congeners determined over time [3]. Figure 6 shows the BDE47 data plotted against year of stranding or bycatch.

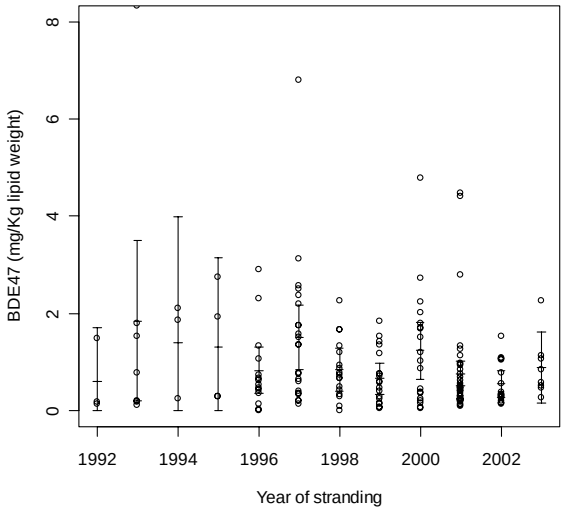

Figure 6. Plot of lipid-normalised BDE47 concentrations against year of stranding (mg kg^{-1} lipid weight). Also shown are annual means and 95% confidence intervals.

This shows no apparent trend in concentrations over the period 1992-2003. Again, we plotted the S-statistic, and Figure 7 shows the value of S plotted against year, along with the associated 95% and 99% envelopes obtained using Monte-Carlo simulation.

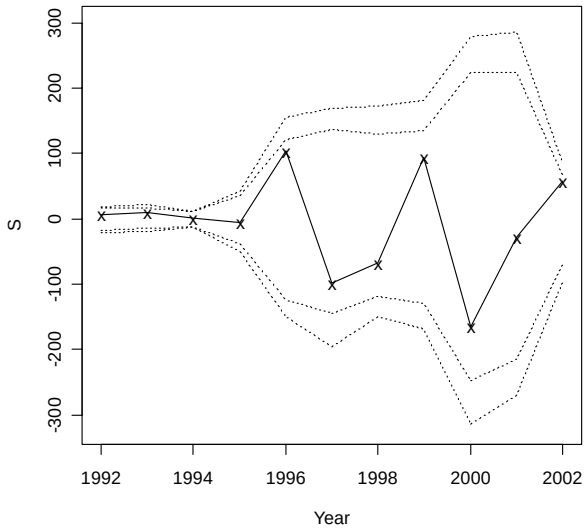

Figure 7. 95% and 99% envelope plot (dotted lines) for the statistic S comparing differences in BDE47 concentrations between successive years. The full line is the observed value of S. Note that points on the plot represent comparisons between that year and the next year.

In this case, we were unable to reject the null hypothesis of no trend. It seems, therefore, that despite the recent removal from production and use of the penta-mix and octa-mix PBDE formulations in the EU, there is as yet no downward trend in concentrations of related congeners in the blubber of UK-stranded porpoises. This suggests that the decline will be slow, at least in marine mammals.

Acknowledgements

This work was funded by the Department for Environment, Food and Rural Affairs, Marine Environment and European Wildlife Divisions.

References

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