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A Significant Downturn in Levels of Hexabromocyclododecane in the Blubber of Harbor Porpoises (*Phocoena phocoena*) Stranded or Bycaught in the UK: An Update to 2006

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In an earlier paper, we reported data indicating a sharp increase in hexabromocyclododecane concentrations in the blubber of 85 harbor porpoises from the UK, from about 2001 onward. That time trend was evaluated using data from 1994–2003, generated on a diastereoisomer basis using LC-MS. In this paper we report additional data for 138 animals collected during 2003–2006. ΣHBCD concentrations ranged from <10 to 11,500 μg kg^{-1} wet weight (up to 12,800 μg kg^{-1} lipid weight) and TBBP-A was not detected in any samples. The maximum ΣHBCD concentration observed in this study was about half that seen in the earlier study (21,400 μg kg^{-1} lipid weight) and, in both studies, the highest concentration was for an animal stranded or bycaught in 2003. Investigation of time trends confirmed a statistically significant increase between 2000 and 2001 ($p < 0.01$) and a statistically significant decrease between 2003 and 2004 ($p < 0.05$). Neither trend was confounded by age, sex, nutritional status, or location. Possible contributory factors to the observed decrease include the closure in 2003 of an HBCD manufacturing plant in NE England which had considerable emissions up to 2003, and two voluntary schemes intended to reduce emissions of HBCD to the environment from industry which, however, did not formally begin until 2006.

Introduction

Brominated flame retardants (BFRs) are a diverse group of compounds which are added to a wide range of products to prevent them catching fire. Over the past 25 years, since the polybrominated brominated diphenyl ethers (PBDEs) were first identified in environmental samples remote from sources (*1*), BFRs have become the subject of intense study (*2*). Concerns regarding certain BFRs (to date, mainly the PBDEs, hexabromocyclododecane (HBCD), and tetrabromobisphenol-A (TBBP-A)) stem from their persistence, potential for bioaccumulation, and toxicity, combined with their large scale of use. Both HBCD and TBBP-A are included in the OSPAR list of chemicals for priority action under their Hazardous Substances Strategy (*3*). All three commercial PBDE products, HBCD, and TBBP-A have been subject to full risk assessments by the EU under its Existing Substances Regulation 793/93; most have been completed and the rest are in their final stages. More information can be found on the Web site of the European Chemicals Bureau (*4*). Following controls on the production and use of the penta- and octa-mix PBDE formulations within the EU as a result of the above-mentioned risk assessments (*5*), the main focus of environmental study in Europe has switched to HBCD and TBBP-A. In other areas of the world (especially North America and Asia) PBDEs remain the major area of study, particularly in the context of e-waste "recycling" in China with potential effects on local populations (*6*). The EU risk assessment identified no significant risk from the deca-mix formulation, but concluded that further toxicological information was needed before a final conclusion could be reached. As of July 1, 2008, the deca-mix product has also been banned in Europe following a ruling by the European Court of Justice. HBCD is an additive flame retardant used primarily in expanded and extruded polystyrene for thermal insulation in buildings, with a secondary application in textiles manufacture, and TBBP-A is used primarily as a reactive flame retardant in printed circuit boards. World production of HBCD and TBBP-A in 2001 (the most recent figures available from the industry) totalled 16,700 and 119,700 t, respectively. In an earlier paper (*7*), we reported low concentrations of TBBP-A and high, and increasing, concentrations of HBCD in the blubber of 85 porpoises stranded or bycaught around the UK between 1994 and 2003. In this paper, we present data for an additional 138 porpoises which extend the timeline to 2006, comprising 16 porpoises from 2003, 31 from 2004, 63 from 2005, and 28 from 2006.

Experimental Section

Sampling, Analysis, and Analytical Quality Control. The porpoises sampled were collected within the Cetacean Strandings Investigation Program funded by the U.K. government. Animals which are found stranded, or are bycaught, and are classified as freshly dead or only slightly decomposed, are taken for postmortem study in order to establish cause of death. Contaminant analyses are conducted in tissues from selected animals with the aim of investigating possible links between contaminant burden and death due to infectious disease. The detailed protocols applied in the postmortem studies and the classification criteria are given elsewhere (*8*). Tissue samples were stored frozen at −20 °C prior to analysis and then thawed and homogenized prior to extraction. The full analytical protocol used for quantification of HBCD and TBBP-A was given in the earlier paper (*7*). Briefly, homogenized samples of blubber were extracted using a mixture of acetone/*n*-hexane in a Soxhlet apparatus for 4 h (*9*). Sample extract cleanup was performed by gel permeation chromatography (GPC) followed by a sulfuric acid treatment. For this, a suitable volume of Soxhlet extract was taken and known amounts of surrogate internal standards (d_{18}-α-HBCD, d_{18}-β-HBCD, d_{18}-γ-HBCD, and $^{13}C_{12}$ TBBP-A) were added. This was concentrated to 1.5 mL, and 900 μL was injected onto the GPC system from which fractions were collected. The fractions were evaporated just to dryness and reconstituted

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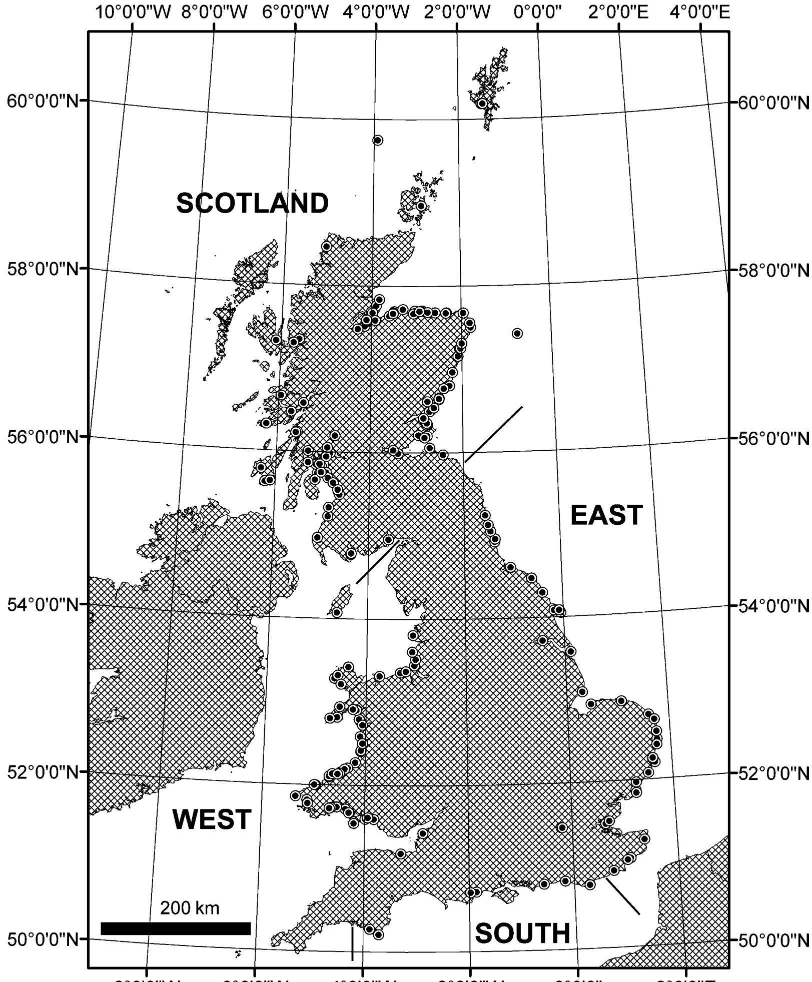

FIGURE 1. Locations from which the porpoises were collected.

to 1 mL using HPLC grade *n*-hexane prior to sulfuric acid cleanup (*10*). The final hexane extract was concentrated to dryness and reconstituted to 120 μL using methanol. The quantitative determination of HBCD and TBBP-A was conducted using LC-MS in the electrospray negative ionization mode. The limits of quantification (LOQs) for α-, β-, and γ-HBCD and TBBP-A were calculated using the lowest calibration level standard (0.010 ng μL^{-1}) for each sample. An example chromatogram is given in the earlier paper (*7*). Results obtained using LC-MS were confirmed qualitatively using LC-MS/MS by monitoring transitions from forced chlorine adducts (m/z 676.7 → 640.7) and forced dimer chlorine adducts (m/z 1318.2 → 676.7) for HBCD diastereoisomers and the transition m/z 543.1 → 447.9 for TBBP-A.

Cod muscle spiked with 24.8 $\mu g\ kg^{-1}$ Σ-HBCD and 25.0 $\mu g\ kg^{-1}$ TBBP-A was used as a laboratory reference material. Recoveries were found to average 76% (±28% RSD) for Σ-HBCD and 74% (±19% RSD) for TBBP-A (n = 9). Eight samples were analyzed in duplicate and all results but two were within 10% of the original concentrations, with one result >20%.

Statistical analysis was carried out using the software package R (*11*). The analysis included Mann−Kendall statistics to test for trend, Monte Carlo simulations, and cross-correlations.

Results

Concentrations of HBCD and TBBP-A. Supporting Information Table S1 lists the sampling dates and locations for the 138 porpoises included in the present study and gives information on sex, body length, and age (where available). See Figure 1 for the locations and areas from which samples were obtained. Ages were determined by quantification of growth-layer groups from analyses of decalcified tooth sections (*12*). Dorsal blubber thickness varied from 5 to 32 mm, and blubber lipid content varied from 56 to 97%. With the exception of 11 animals (5% of those studied), all had relatively high lipid contents (80% or greater). As in other biological samples, α-HBCD dominated the profile. In the current study, concentrations of ΣHBCD ranged from <10 to 11,500 $\mu g\ kg^{-1}$ wet weight (12,800 $\mu g\ kg^{-1}$ lipid weight) and the highest concentration was for an animal from 2003. In the earlier study, the highest concentration of ΣHBCD was 19,200 $\mu g\ kg^{-1}$ wet weight (21,400 $\mu g\ kg^{-1}$ lipid weight), again in a porpoise which died in 2003. The inclusion of HBCD data for additional animals from 2003 has changed the overall mean concentration for that year from 8,390 $\mu g\ kg^{-1}$ wet weight (as reported earlier (*7*)) to 5,450 $\mu g\ kg^{-1}$ wet weight.

In the current study, low concentrations of TBBP-A were detected using LC-MS quantification, similar to those determined previously (*7*). However, none of these positive values were confirmed by the newly developed LC-MS/MS confirmatory method so they were classified as nondetects (limit of detection using LC-MS <5 $\mu g\ kg^{-1}$ wet weight). This does call into question the positive TBBP-A data reported previously, although we cannot categorically say they were overestimates.

Investigation of Time Trends. With the 85 porpoises for which data were reported in an earlier study (*7*) and the 138 in the present study, a total of 223 data were available for

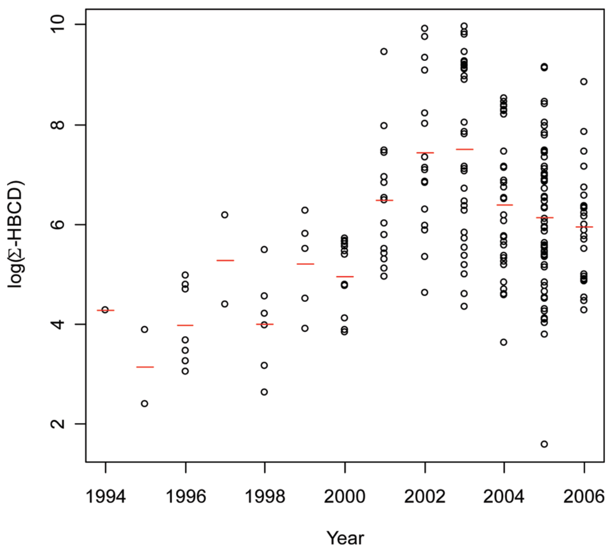

FIGURE 2. Plot of ln(ΣHBCD concentration) values against year of stranding or bycatch. Also marked are yearly means.

TABLE 1. Summary Statistics for the HBCD Data (Concentrations Are Given in μg kg^{-1} Lipid Weight; the Frequency Is the Number of Animals Sampled in Each Year)

	frequency	mean ΣHBCD concentration	median ΣHBCD concentration	mean ln(ΣHBCD) concentration
1994	1	73	73	4.29
1995	2	30	30	3.14
1996	7	71	40	3.99
1997	2	283	283	5.29
1998	6	83	61	4.01
1999	5	249	246	5.20
2000	13	178	219	4.95
2001	15	1620	649	6.49
2002	18	5140	1220	7.44
2003	32	5450	1860	7.51
2004	31	1360	487	6.40
2005	63	1180	456	6.14
2006	28	817	379	5.96

temporal trend study. The nonparametric statistical approach used to investigate possible time trends was the same as that used in the previous paper, with a null hypothesis of no trend (*7*). Effectively, this compares the number of increases and decreases in future years against what we might expect to happen assuming no trend, i.e., if the year labels for observed ln(ΣHBCD) concentrations were randomly assigned. The data are shown in Supporting Information Table S1 and Figure 2, and summary data by year are shown in Table 1. Lipid-normalized HBCD concentrations were used for the statistical calculations. The calculated value of M (the Mann–Kendall statistic) (*7*) for the period 2003–2006 indicated a negative trend that was clearly statistically significant at the 1% level ($p = 0.001$). To examine the changes further, we used the statistic S to explore differences between successive years. Using Monte Carlo simulation, as previously, we calculated the 95% and 99% envelopes of S values that could arise under the null hypothesis, and plotted the envelopes and our observed values for all years (Figure 3). Note that the points plotted refer to the change between that year and the following year. This confirms the statistically significant increase between 2000 and 2001 reported in the previous paper (*7*) ($p < 0.01$) and a statistically significant decrease between 2003 and 2004 ($p < 0.05$). The apparent decreases in later years were not sufficiently large to be confirmed by the S statistic.

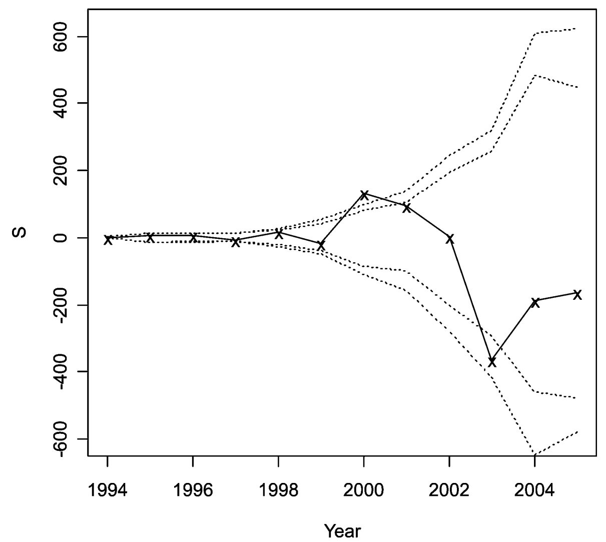

FIGURE 3. 95% and 99% envelope plot (dotted lines) for the statistic *S* comparing differences in ΣHBCD between successive years. The full line is the observed value of *S*. Note that points on the plot represent comparisons between that year and the next year. If plots fall outside the 95%/99% envelope then this is equivalent to a *p* value of <0.05/< 0.01 for the null hypothesis that there is no change between the two years.

Because our study was not balanced in terms of a range of factors, we also investigated these potentially confounding factors to see whether they might account for, in particular, the decline after 2003. A similar study of the increase between 2000 and 2001 demonstrated that these factors did not play a role (*7*). We will examine each of these factors in turn. Plots for all factors are presented in the Supporting Information (Figures S1–S5).

Area. Four areas were defined geographically: Scotland ($n = 111$), West (Cumbria to Cornwall, including North Devon: $n = 59$), East (Northumberland to Kent; $n = 44$) and South (South Devon to East Sussex; $n = 9$). When evaluating the trend from 2003, there was a statistically significant downward trend for East ($p = 0.016$) and for Scotland ($p = 0.032$). For the West, there was little evidence of a trend from 2003, although there was a large and statistically significant downward step from 2002 to 2003. See Supporting Information Figure S1.

Season. Two seasons were defined: Summer (April to September) and Winter (October to March). Note that, for winter, its "year" is taken to be that for the period January to March; this is the meaning of "adjusted" in the titles of the plots given in the Supporting Information (Figure S2). As porpoises (and other marine mammals) use their blubber for thermoregulation as well as a lipid store, they will tend to have thicker blubber layers in winter, when the water surrounding them is colder, than in the summer. This change in blubber volume could act to increase and decrease concentrations of lipophilic contaminants in the blubber. In fact, both summer and winter ln(ΣHBCD) concentrations peaked in 2003, although the 2002 summer level was very similar. There was a strongly statistically significant decrease from 2003 for summer ($p = 0.007$), although the decrease for winter was less clear-cut ($p = 0.109$) in that the main decrease occurs from 2003 to 2004 and that concentrations then remain steady. See Supporting Information Figure S2.

Bycaught or Stranded. Bycaught animals are those which are entrapped in fishing gear or die due to other trauma (boat strike, bottlenose dolphin attack, etc.) and stranded animals are those found dead on beaches. Animals found stranded are often found to have died due to infectious disease at postmortem, and again this may have affected their blubber concentrations. There were statistically sig-

TABLE 2. Blubber Concentrations of HBCD and TBBP-A Reported in Other Studies (μg kg^{-1} lipid weight (* wet weight); ND = not determined)

species	location	date	HBCD	TBBP-A	reference
Harbor seal (n = 2)	Wadden Sea	1998	63 and 2,060	<14	*13*
Harbor porpoise (n = 9)	North Sea	1998	<5–6,800	0.1–418	*13*
Harbor porpoise (n = 11)	Northern North Sea	2001–2003	393–2,590	ND	*14*
Harbor porpoise (n = 13)	Southern North Sea	2000–2003	538–2,310	ND	*14*
Harbor porpoise (n = 5)	NW Scotland	2001–2003	1,010–9,590	ND	*14*
Harbor porpoise (n = 8)	Irish Sea	2002–2003	466–8,790	ND	*14*
Harbor porpoise (n = 3)	Southern Ireland	2001–2003	710–2,270	ND	*14*
Harbor porpoise (n = 3)	NW Spain	2001–2003	79–143	ND	*14*
Common dolphin (n = 6)	Western Ireland	2001–2002	193–1,590	ND	*14*
Common dolphin (n = 31)	Northern France	2002	98–899	ND	*14*
Common dolphin (n = 24)	NW Spain	2001–2003	52–454	ND	*14*
White-sided dolphin (n = 57)	Massachusetts, U.S.	1993–2004	19–380	ND	*17*
California sea lion (n = 26)	California, U.S.	1993–2003	<0.3–12 *	ND	*16*
Ringed seal (n = 6)	Svalbard, Norway	2003	15–35	ND	*15*
Finless porpoise (n = 7)	SE China	1990	4.7–37	ND	*18*
Finless porpoise (n = 5)	Hong Kong	2000–2001	21–55	ND	*19*
Indo-Pacific humpback dolphin (n = 7)	Hong Kong	1997–2002	31–380	ND	*19*
Melon-headed whale (n = 5)	Japan	2001	330–460	ND	*19*
Striped dolphin (n = 5)	Japan	2003	580–940	ND	*19*

nificant downward trends for both bycaught (p = 0.009) and stranded (p = 0.005) porpoises. For stranded porpoises, there was a particularly large downward step between 2003 and 2004 (p < 0.01). See Supporting Information Figure S3.

Sex. There are statistically significant downward trends from 2003 for both males (p = 0.036) and females (p = 0.019). For females, the trend appeared to begin in 2002. Overall, these results support the conclusion of a downward trend from 2002 or 2003.

Age Class. Animals were generally classified as adults or juveniles at postmortem. In the very few cases where this was not recorded, an assignment was made using body length as a surrogate. The downward trend for adult females from 2003 was not statistically significant (p = 0.072), but it was from 2002 (p = 0.019). Concentrations in adult males seemed fairly static over the period 2002–2006. The downward trend in juveniles was statistically significant from 2003 onward (p = 0.001). The reason for treating adult females separately from adult males is that they download a large proportion of their burdens of lipophilic contaminants to their offspring, particularly during lactation, while males can eliminate contaminants only by excretion or metabolism. See Supporting Information Figure S4.

Blubber Thickness and Lipid Content. Blubber thickness and lipid content are factors with the potential to alter blubber concentrations of lipophilic contaminants. All of the statistical investigations were made using lipid-normalized concentration data, but in any case there was no trend in lipid concentration during the study (p = 0.43) or from 2003 onward (p = 1). Also, there was no trend in blubber thickness after 2003 (p = 0.419). See Supporting Information Figure S5.

Overall, we can conclude that none of these factors confounds the observed decline, although it suggests that the timing of the decline is not uniform. There are two slight anomalies. First, the decline observed in the East is more pronounced than that seen in the West, possibly as the result of the closure of an HBCD manufacturing plant in NE England in 2003. Second, for adult males, the concentration changes differ from those observed in adult females and juveniles. In adult males, there is a decrease from 2003 to 2004 (although it is not quite statistically significant at the 5% level) but after 2004 levels increase again. Breeding females may show rapid declines in blubber concentrations of HBCD in response to reductions in their dietary intake as they can transfer a significant proportion of their burden to their offspring, while for males the rate of reduction is limited by excretion rates and/or their ability to metabolize HBCD, so declines would be expected to be much slower.

Discussion

Comparison with Other Studies. Very few studies have included the determination of HBCD in marine mammal samples, and in only one other study has TBBP-A been determined (*13*). These studies are summarized in Table 2. Morris et al. (*13*) determined HBCD in harbor seal (*Phoca vitulina*) and harbor porpoise sampled in 1998 from the Wadden and North Seas, respectively. Maximum ΣHBCD concentrations were 2,060 and 6,800 μg kg^{-1} wet weight, respectively. TBBP-A was not detected in the two seal samples, but was found at concentrations of 0.1–418 μg kg^{-1} wet weight in the porpoises. Zegers et al. (*14*) determined HBCD in common dolphins (*Delphinus delphis*) and harbor porpoises from NW European seas collected in 2001–2003. The highest ΣHBCD concentrations were found in porpoises from the Irish Sea coasts of Scotland and Ireland (median concentration 2,900 μg kg^{-1} lipid weight; maximum concentration 9,600 μg kg^{-1} lipid weight) and the NW coast of Scotland (median concentration 5,100 μg kg^{-1} lipid weight). In other areas, the median concentrations were 1,200 μg kg^{-1} lipid weight (S. Ireland), 1,100 μg kg^{-1} lipid weight (coasts of the southern North Sea), 770 μg kg^{-1} lipid weight (E Scotland), and 100 μg kg^{-1} lipid weight (NW Spain). In common dolphins, the median concentrations were 900 μg kg^{-1} lipid weight (W. Ireland), 400 μg kg^{-1} lipid weight (Northern France), and 200 μg kg^{-1} lipid weight (NW Spain). In both cases this represents an increasing trend from south to north, with the highest concentrations in animals stranded on the coasts of the Irish Sea. In ringed seal from Svalbard, Norway, ΣHBCD concentrations were low, 15–35 μg kg^{-1} lipid weight (*15*). In California sea lions (*Zalophus californianus*), ΣHBCD concentrations were also low, <0.3–12 μg kg^{-1} wet weight (*16*). ΣHBCD concentrations in the blubber of white-sided dolphins from the Massachussetts coast of the United States from 1993–2004 ranged from 14 to 280 μg kg^{-1} wet weight (19 to 380 μg kg^{-1} lipid weight) (*17*). Relatively few data are available for Asia. In the South China Sea, ΣHBCD concentrations in finless porpoise and the Indo-Pacific humpback dolphin (*Sousa chinensis*) ranged from 4.7 to 37 μg kg^{-1} lipid weight, up to 2 orders of magnitude lower than the highest concentrations observed in NW Europe (*18*). Tanabe et al. (2008) conducted a study of spatial and temporal trends of BDEs and HBCD

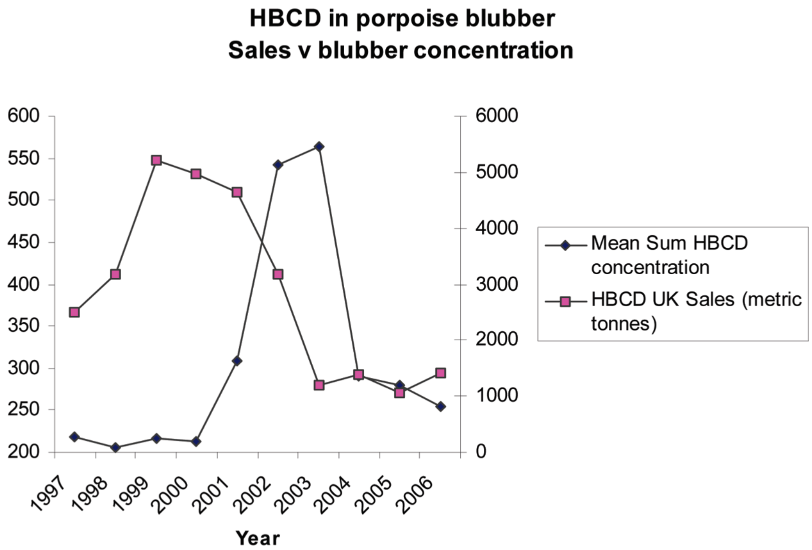

FIGURE 4. Indicative plot of mean ΣHBCD concentrations in blubber of harbor porpoises vs UK sales of HBCD in metric tonnes, 1997−2006.

in coastal and marine biota from the Asia−Pacific region (*19*) using mainly samples archived in the environmental specimen bank of Ehime University, Japan. The target BFRs were found to be ubiquitous throughout the region. HBCD was determined in the blubber of melon-headed whales and striped dolphins from Japan and of finless porpoises and Indo-Pacific humpback dolphins from Hong Kong at concentrations ranging from 330−460, 580−940, 21−55, and 31−380 μg kg^{-1} lipid weight, respectively. Since the withdrawal of some PBDE products from the Japanese market, usage of HBCD has increased although HBCD is not used as a direct substitute in or for previous PBDE applications.

HBCD Usage and Emissions. The bromine industry has provided us with UK sales data for HBCD (previously unavailable) for the years 1997−2006 (see Supporting Information Table S2). In Figure 4, these sales figures are plotted against the mean ΣHBCD concentrations in porpoise blubber. There does seem to be some correlation between the two, with a time-lag of 2−4 years. If we estimate the correlation at these lags (that is, the correlation between mean HBCD concentration at year $t+$ k and sales at year t, where k is the lag time) we get correlations of 0.55, 0.60, and 0.29, respectively. The 0.60 correlation is at the borderline of statistical significance at the 5% level. However, sales figures do not necessarily correlate with actual emissions. It is important also to note that in 2003, an HBCD manufacturing site at Newton Aycliffe, close to the NE coast of England, was closed. This site had had considerable historic emissions of HBCD to the environment during its working lifetime. According to the EU risk assessment referred to above, this was “the largest single source of emissions of HBCDD (*sic*) to the environment”, with annual emissions of more than 5 tonnes (*4*). As a consequence, HBCD emissions to the environment are likely to have decreased significantly since 2003. This may provide an explanation for the more pronounced decline seen in animals from the East region. Little or nothing is known, however, about the rates of transfer of HBCD along the porpoise food chain following discharge to the aquatic environment, so this cannot be validated. Porpoises are bottom feeders, specializing in feeding on small schooling fish such as herring or anchovy. In the Bay of Fundy (Canada), harbor porpoises are known to eat euphausiid crustaceans, so these may form a component of the diet of UK animals as well. The relatively rapid decrease in tissue concentrations from 2003 onward may suggest a relatively quick response to changes in emission levels, but continued monitoring is needed in order to determine whether this trend continues.

In recent years, the bromine industry has undertaken initiatives intended to reduce emissions from manufacture and use of HBCD and other flame retardants. Initially focused on the deca-mix PBDE formulation, the same voluntary controls are now being extended to TBBP-A and HBCD (*20*). In addition to the closure of the Newton Aycliffe site, HBCD emissions are controlled within two programs: VECAP (the Voluntary Emissions Control Action Programme for Brominated Flame Retardants) for use in textiles and plastics and SECURE (Self Enforced Control of Use to Reduce Emissions) (*21*) for use in expanded and extruded polystyrene foams. No quantitative data for reductions in HBCD emissions are available as yet, but the VECAP program for the deca-mix PBDE formulation has reduced emissions to water from the UK textile industry by 97% over the period 2002−2006. Similar reductions might therefore be expected to occur for HBCD in coming years. Both VECAP and SECURE began formally in the UK in 2006.

The downturn seen in porpoise blubber concentrations is likely to be a result of initial reductions in HBCD inputs from industrial sites to the marine environment, particularly from the Newton Aycliffe site in NE England. If this is the case, it suggests that the food chain response to such reductions is relatively fast, at ca. 2−4 years, however, further monitoring work would be necessary to confirm this. It is, of course, possible to reliably estimate point-source emissions of HBCD. In contrast, the magnitude and trend of inputs to the environment from diffuse sources such as flame retarded consumer products in use or in landfill is unknown. Any changes in emissions from such sources would be likely to occur more slowly due to the low leaching rates of BFRs from these materials. Continued monitoring is, therefore, warranted to determine whether continued emissions reduction measures are effective, and the level at which porpoise blubber levels plateau to reflect primarily diffuse inputs.

Acknowledgments

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Supporting Information Available

The full HBCD data set with associated biological information for the porpoises sampled, further detail of the outcome of statistical analyses exploring possible confounding factors, and UK sales figures for HBCD over the period 1997−2006. This material is available free of charge via the Internet at http://pubs.acs.org.

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