Screening and Time Trend Study of Decabromodiphenylether and Hexabromocyclododecane in Birds

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Introduction

With regard to the occurrence of decabromodiphenylether (decaBDE) in peregrine falcon eggs[1], and the possible implications of that observation for the EU risk assessment of decaBDE (EC Regulation No. 1488/94), it was considered necessary to study the occurrence of decaBDE in various bird species, as well as the time trends of decaBDE concentrations in selected species. The UK Environment Agency and the Bromine Science and Environmental Forum (BSEF) agreed to organise such a study. Analyses of the three HBCD diastereomers in selected samples were carried out in addition.

Materials and Methods

The Centre for Ecology and Hydrology (CEH), Monks Wood, Huntingdon, UK provided a representative cross section of bird samples from the UK feeding at a high trophic level with either a terrestrial or aquatic based food source. These samples were sent to the Netherlands Institute for Fisheries Research (RIVO) and to the Centre for Environment, Fisheries, and Aquaculture Sciences (CEFAS) for analysis. Ten peregrine falcon eggs from the Swedish study[1] were obtained for re-analysis, as well as ten peregrine egg samples from Sweden that had not been analysed yet. Cormorant samples from the Netherlands obtained through Bureau Waardenburg (Culemborg, The Netherlands) were added. Liver, muscle tissue and eggs were analysed. In total 124 samples from 13 different species were analysed. Based on the results of the screening study 48 peregrine falcon eggs (1973-2002) and 55 sparrow hawk muscle tissue samples (1975-2001) were selected for the time trend study. To ensure the comparability of the two laboratories involved, six samples were sent to both laboratories for analysis.
The methods used by the two laboratories involved have been described in de Boer et al.[2]. In summary, the samples were weighed and extracted with a Soxhlet apparatus for 6

hours with hexane:acetone. ^{13}C labelled decaBDE was added as internal standard. The extract was dried with sodium sulphate and reduced in volume by rotary evaporation. A separate aliquot was taken for the extractable lipid determination. The lipids were removed by gel permeation chromatography (GPC) or alumina columns. Sulphuric acid treatment followed by silica gel column chromatography was used for additional cleaning. The final extracts were concentrated to 200 µl, and analysed by GC/NCI-MS. A 15 m DB-5 or DB-1 column was used. More than a hundred blank analyses were carried out prior to analysis of the bird samples, to ensure that the presence of decaBDE in dust particles in the laboratory would not cause false positive results. Two blank samples, a procedural recovery standard, and one internal reference material were analysed in each series of twelve samples. Quantification of decaBDE was based on the fragments m/z 485 and 487. The limit of quantification (LOQ) was set at the lowest calibration standard. For the determination of HBCD diastereomers an aliquot of the crude extract was cleaned-up by the sequential addition of concentrated sulphuric acid, and back extracted with hexane. Following the evaporation of hexane, extracts were reconstituted in methanol. The analysis was performed by LC-MS with electrospray ionisation. Baseline separation of the three isomers was achieved with a microbore C-18 column and an aqueous-acetonitrile agent. Selective ion monitoring of m/z 640.7 was used for detection and quantitation purposes.

Results and discussion

The results of the screening study are given in Table 1. The decaBDE concentrations in Swedish peregrine egg samples reanalysed in this study were all within 30% of the concentrations originally determined in the same eggs by Lindberg et al.[1]. It has been demonstrated that the peregrine falcons from the UK as well as a number of other bird species contained decaBDE. It should, however, be stressed that a substantial number of birds did not contain decaBDE. In addition, the decaBDE concentrations found were relatively low, in many cases just above the detection limits. The decaBDE concentrations found should rather be explained as traces. A more detailed study of relevant food chains should give a better understanding of the bioaccumulation process. It is remarkable that the positive samples, apart from an occasional exception, were mainly terrestrial birds of prey. Most water birds, including all cormorants from The Netherlands (not in Table 1), showed no detectable decaBDE concentrations. The extremely low water solubility of decaBDE by aquatic organisms, the large size of the decaBDE molecule, and a possible fast metabolism in fish may be explanations for this phenomenom. DecaBDE in dust and other fine particles can apparently be taken up by small terrestrial animals, which are preys of small birds, which are in turn preys of the bird species in this study. No differentiation could be made according to the geographical

Table 1. DecaBDE concentrations in predatory birds from the UK and Sweden.

Species (Country)	Tissue type	No. of positive samples/ total No. of samples	Concentration range	
			mg/kg wet weight	mg/kg lipid weight
Peregrine falcon UK	Liver	4/6	<0.17-6.7	<5.7-181
	Muscle	5/5	1.8-9.5 (mean 4.0)	53-344 (mean 137)
	Egg	2/6	<0.08-7.5	<1.8-108
Peregrine falcon Sweden	Egg	11/20	<0.3-21	<4-412
Sparrowhawk UK	Liver	0/4	<3.2-<9.8	<82-<200
	Muscle	5/5	0.26-2.2 (mean 1.1)	13-275 (mean 101)
	Egg	3/5	<0.16-1.5	<2.1-38
Kestrel UK	Liver	2/5	<0.26-5.5	<5.8-120
	Muscle	1/5	<0.11-0.29	<4.2-10
Great crested grebe UK	Liver	1/4	<0.11-0.52	<1.5-9.1
	Muscle	1/3	<0.4-1.2	<8.1-31
Barn owl UK	Liver	3/5	<0.13-2.5	<2.6-37
	Muscle	1/5	<0.5-1.2	<6.3-14
	Egg	3/4	<2-1.7	<20-30
Heron UK	Liver	0/4	<0.08-<0.25	<2.3-<5.7
	Muscle	1/5	<0.32-4.5	<6.3-563
Gannett UK	Egg	0/12	<0.2-<2.2	<4-<57
Red Kite UK	Egg	1/4	<0.09-2.3	<2.1-29.1
Montagu's harrier UK	Egg	3/4	<0.12-1.3	<2.1-28
Marsh harrier UK	Egg	0/2	<0.09	<2-<2.4
Sea eagle UK	Egg	1/1	0.48	6.2
Osprey UK	Egg	0/3	<0.2-<1.5	<4-<27
Golden eagle UK	Egg	0/5	<0.2	<4.1
Merlin UK	Egg	1/2	<3.8-0.3	<43-4.3

origin of the samples. The highest decaBDE concentrations were found in peregrine falcon eggs followed by sparrow hawk muscle tissue.

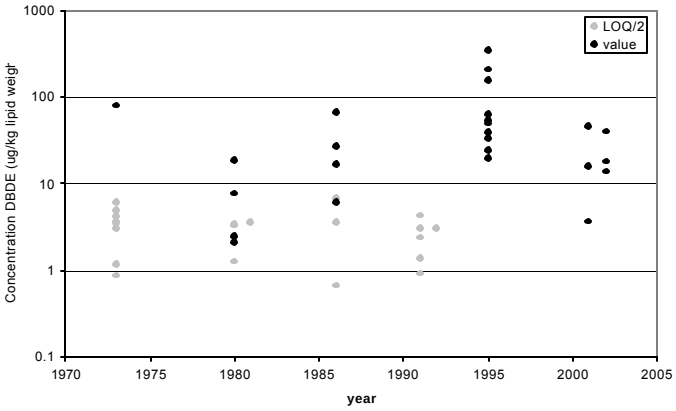

Figure 1. DecaBDE in peregrine eggs from the UK in the period 1973 to 2002. Grey points are limit of quantification (LOQ) divided by two, black points are values above LOQ.

The trend study showed a large number of non detectable data both for sparrow hawks (muscle tissue) and peregrine falcon eggs in the period before 1990 (Figure 1). No significant trends were found ($p<0.05$), but the peregrine falcon results from 1995 are significantly higher than those from other years. More data on decaBDE consumption in the UK are needed to draw conclusions.

The HBCD concentrations found in the terrestrial birds were generally very low, and no time trend could be established. HBCD was detected in 12 of the 51 samples of peregrine eggs (range: 71 to 1200 µg/kg lipid) and in 9 of the 65 samples of sparrow hawk muscle tissue (range: 84 to 19,000 µg/kg lipid). All three diastereomers of HBCD were detected in both species, although the patterns of occurrence varied from sample to sample.

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References

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