DECABROMODIPHENYLETHER IN EUROPEAN BIRDS, SEWAGE SLUDGE AND SEDIMENTS

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Abstract
DecaBDE concentrations were analysed in eggs of the sparrowhawk in the UK, eggs of the glaucous gull in an Arctic region of Norway, sewage sludge from sewage treatment plants in the UK, Ireland and the Netherlands, and in sediments from sites in the UK, Netherlands, Ireland, Germany, France and Belgium, including sites near point sources and those with diffuse sources. The decaBDE concentration in glaucous gull eggs in both 2005 and 2006 were low, ranging from <0.45 to 4.3 ng/g lipid. 42% of these eggs did not have any detectable decaBDE. Concentrations in sparrowhawk eggs were higher and ranged from 2.4 to 36 ng/g lipid. Sewage sludge showed the highest concentrations, up to 20,000 ng/g OC (216 to 843 ng/g dw) in the UK. The levels of decaBDE in sludge were not clearly related to the type of wastewater (domestic or industrial) or to the type of community it served (urban or rural). The highest decaBDE concentrations in river sediments were found in the rivers Mersey (UK) and Western Scheldt (Netherlands), 54,100 and 53,300 ng/g OC (746 and 660 ng/g dw), respectively. These concentrations were higher than in 1995, but for the Mersey lower than in 2000.

Introduction
Following a risk assessment of the European Commission[1] it was concluded that decabromodiphenylether (decaBDE) poses no risk to human health or the environment, but it was mandated to set up a monitoring programme to measure the temporal trends in decaBDE levels in the European environment. Supervised by the EU, with the UK Environmental Agency as rapporteur, the Bromine Science and Environmental Forum (BSEF) requested the Institute for Environmental Studies (IVM) to design and carry out such a study for a period of ten years. This paper gives an overview of the study results of the first two years.

Methods and materials
Sparrowhawk (*Accipiter nisus*) eggs were sampled in the UK by CEH at Monks Wood. As not to adversely affect the population, which has been threatened in the past in the UK, only failed eggs were collected. Unfortunately, in 2006 only one such egg could be collected. The glaucous gull (*Larus hyperboreus*) colony that was sampled inhabits the "top cliff" area of Bear Island or Bjørnøya off the northern coast of Norway. It consists of 50-60 nests and has been present there at least since the 1960's. A selection of sampling sites for sewage sludge was made on the basis of results of the former Dutch LOES study[2] in which decaBDE was measured in sewage sludge from sewage treatment plants (STPs) in the Netherlands and on information provided by RIZA in Lelystad (The Netherlands) and Cefas. An advantage of using these sites is that some decaBDE concentration data is already available for time points preceding the start of the monitoring programme, which is useful for comparison purposes on an even longer term. The continental sediment samples (Table 1) were taken by a mini Van Veen grab, ensuring that only the top layer (ca. 2 cm) was sampled, which represents newly deposited sediments. Four samples, each based on

nine sub-samples from an area of ca. 100 m^2, were taken per location. For the UK sites, the samples were acquired via the cruises made by the National Marine Monitoring Program (NMMP). Four samples per site were acquired consisting of one Day grab ($0.1m^2$), according to the sampling protocol used for the NMMP. The remaining sediment samples (River Mersey) were taken by Cefas personnel with a Van Veen grab in early 2007. The Irish sediment samples were acquired via the Irish national sampling program, for which 3 samples from 2006 were available and analysed.

Table 1. Sediment sampling sites (n=10) including known low and high range decaBDE sites (from DIFFCHEM study[3])

From DIFFCHEM Study	Other Sediment Locations
Mersey estuary, (Liverpool Bay) UK	Mersey River (Boillin Point), Manchester area, UK
Thames estuary, UK	Eems estuary, Germany
Humber estuary, UK	Elbe estuary, Germany
Tyne estuary (Tees Bay), UK	Seine estuary, France
Western Scheldt Schaar Ouden Doel, Netherlands	
Liffey estuary, Ireland	

Extraction, cleanup and analysis. Analyses were carried out under the specific conditions for decaBDE analysis as described in de Zegers *et al.* [4]. The extract was dried with sodium sulphate and extracted by Soxhlet with hexane:acetone 1:1 (v/v) with ^{13}C-labelled decaBDE added as internal standard. The lipids were removed by gel permeation chromatography (RIVO method) or by alumina columns (IVM and Cefas method). 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/ECNI-MS. At IVM a 15 m DB-5 column was used (internal diameter 0.2 mm, film thickness 0.1 mm). At Cefas a DB-1 column (15 m x 0.25 mm x 0.25 µm) was used. 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. The lipids of eggs were determined by either the Bligh and Dyer[5] (IVM) or Smedes[6] (Cefas). Total organic carbon was determined by the VU Sediment Analysis Laboratory using a gas chromatographic method, in which total organic carbon (including elemental carbon) is measured.

Results and Discussion

Glaucous gull eggs showed very low concentrations of decaBDE, with a high number of non-detects in 2006 (8 out of 12) compared to the first study year when there were only two non-detects (Fig.1). The average concentration of the detects was also higher in the first study year than in the second: about 2 ng/g lipid in 2005 compared to 0.2 ng/g lipid in 2006.

DecaBDE was detected in 10 of the 12 sparrowhawk eggs analysed in the first sampling year and in the single egg collected in 2006 (Fig. 1). In the 11 samples where decaBDE was detected, it was present at higher concentrations than in the glaucous gull egg samples. The decaBDE concentrations ranged from 2.4 to 36 ng/g lipid weight in sparrowhawks, (Fig. 1) whereas the glaucous gull eggs were all under 5 ng/g lw. The sparrowhawk egg from 2006 had a concentration of 2.8 ng/g lw. The average concentration found in the present study (ca. 10 ng/g lw) was about an order of magnitude lower than found by Lindberg *et al.*[7] (who found average concentrations in

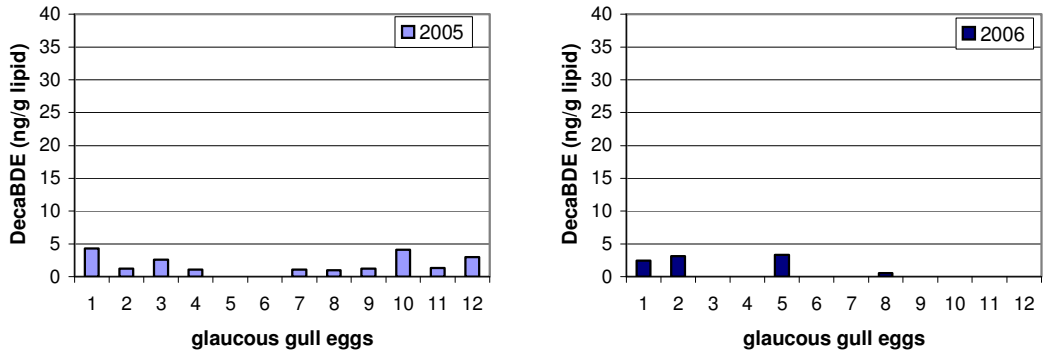

Fig 1a. DecaBDE concentrations (ng/g lipid) in glaucous gull eggs from Bear Island, Norway sampled in 2005 (left) and 2006 (right). LODs: glaucous gull egg numbers 5 and 6 in 2005 were <0.6 and <1 resp. and egg numbers 3,4,6,7,and 9-12 in 2006 were all between <0.5 and <0.6.

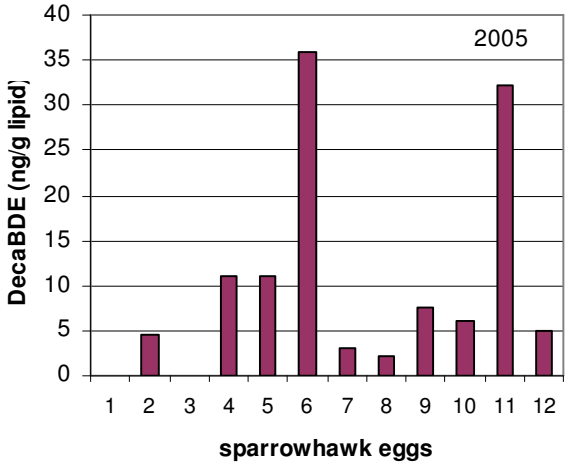

Fig 1b. Sparrowhawk eggs from the UK, sampled in 2005. Only one egg was collected and analysed in 2006 (see text, data not shown on graph). LODs: sparrowhawk egg numbers 1 and 3 both <2.

peregrine falcon eggs in S. Sweden of 130 ng/g lw (s.d. 140) and in N. Sweden, 110 ng/g lw (s.d. 76). The levels of decaBDE in sewage sludge were some of the highest of all matrices in this study. The average levels measured at the six Dutch sites were in the range of 755 to 1482 ng/g OC while in the UK and Ireland, the average levels were considerably higher, ranging from 2,388

to 20,000 ng/g OC. The much higher levels in the UK and Ireland were double-checked and confirmed by Cefas. The reason for the different pattern is unknown, although it may have to do with consumer habit differences between the countries. Possibly carpets in the UK are more heavily flame-retarded. The concentrations at Dutch STPs with substantial industrial input such as Eindhoven, Bath and Kralingseveer (including in some cases input from textile industries) were not significantly higher on a dw basis than the STPs with little to no input from such industries.
DecaBDE was detected at all sites in almost all sediment samples, covering a wide range of concentrations over the sites. The lowest levels of decaBDE were detected at the sites on the Seine, Elbe, Eems, Outer Humber and Thames, where average levels ranged from about 70 to 700 ng/g OC. Tees Bay and Dublin Harbour sediments had higher concentrations, 4,410 and 3,190 ng/g OC respectively. The highest decaBDE concentrations were measured at the sampling sites on the River Mersey (average 54,100 ng/g OC), at Liverpool Bay (40,600 ng/g OC) and the W. Scheldt (53,300 ng/g OC). DecaBDE data in sediments from some of the same sites are available from the DIFFCHEM study[7]. The organic-carbon normalized decaBDE concentrations in the Seine, Elbe, Eems and Mersey were in the same range as the concentrations reported in sediments from the same locations in the DIFFCHEM study (sampled in 1995). In the DIFFCHEM report, the mean decaBDE concentration (of 3 samples measured) in Western Scheldt sediment is 200 ng/g dw, which is considerably lower than the concentrations found in the present study. On the other hand, while the decaBDE levels in the river Mersey are in the same range as reported by DIFFCHEM, levels seemed to have increased until around the year 2000[4] but showed a decrease since then. Obviously, the monitoring period of two years until now is by far too short to make any statement on possible increasing or decreasing trend in the decaBDE levels.

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