

Monitoring of Decabromodiphenylether in the Environment: Birds' Eggs, Sewage Sludge and Sediments

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Introduction

Decabromodiphenylether (decaBDE) is a brominated flame retardant we are currently measuring in various environmental matrices in a program that covers a period of 10 years (2005-2014). The aim is to study time trends of this chemical in the eggs of sparrowhawk, glaucous gull, in sewage sludge and in sediments from various locations in Europe. Earlier studies have shown decaBDE to be present in these matrices. The first two years of sampling rounds have been completed and the majority of results are already available.

Materials and Methods

Sampling sites and matrices. The biotic sampling matrices chosen for this study were glaucous gull eggs from Bear Island, Norway (n=12 annually) provided by the Norwegian Polar Institute and (failed) sparrowhawk eggs collected by CEH in the UK (n=12 annually). Sewage sludge is being collected biennially from 6 Dutch sewage treatment plants (STPs), 5 UK STPs and 1 Irish STP. Sediments are being collected biennially from sites in continental Europe on the Seine (France), Western Scheldt (NL), Elbe and Eems (Germany), plus 4 sites in the UK (Liverpool Bay, and one site in Ireland (Liffey)). Samples are distributed between IVM and CEFAS laboratories for analysis.

Extraction, cleanup and analysis. Analyses were carried out under the specific conditions for decaBDE analysis as described in de Boer *et al.* (2001). The extract was dried with sodium sulphate and extracted by Soxhlet with hexane:acetone with ¹³C-labelled decaBDE added as internal standard. 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/ECNI-MS. A 15 m DB-5 or DB-1 column (internal diameter 0.2 mm, film thickness 0.1 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 (1959) (IVM) or Smedes method (Smedes and Thomassen, 1996) (Cefas). BDEs 28, 47, 99, 100, 126, 153 and 183 were also screened in selected samples of birds' eggs, sewage sludge and sediments.

Results and Discussion

Birds' eggs. Glaucous gull eggs (n=12) showed extremely low concentrations of decaBDE, averaging about 2 ng/g lipid weight (Fig. 1, left panel) with two non-detects in 2005 and eight in 2006. Other studies have reported decaBDE concentrations in wild predator bird eggs. De Boer *et al.* (2004) reported a large number of non-detects of decaBDE in a variety of wild bird species in different tissue types including eggs, with detectable concentrations close to detection limits. The concentrations detected in the present study fall within the same range as the study of de Boer *et al.* (2004). Lindberg *et al.* (2004) reported decaBDE concentrations in wild peregrine falcon eggs from Sweden ranging from <7 to as high as 430 ng/g lipid. All the concentrations detected in the present study were well below this maximum.

DecaBDE was detected in 10 of the 12 sparrowhawk eggs analysed from the 2005 sampling scheme (Fig. 1, right panel) at concentrations about 5 times higher than in the glaucous gull eggs (mean concentration: 10 ng/g lipid, compared to 2 ng/g lipid). In 2006, only one egg was collected due to low availability of failed sparrowhawk eggs (2.5 ng/g lipid was the decaBDE concentration in this egg). The detected decaBDE concentrations ranged from 2 to 36 ng/g lipid in all sparrowhawk eggs measured to date, whereas the glaucous gull eggs were all under 5 ng/g lipid. The sparrowhawk egg data fall in the lower end of the concentration range found by Lindberg *et al.* (2004). The mean concentration found in the present study was also about an order of magnitude lower than found by Lindberg (who found mean concentrations in peregrine falcon eggs in S. Sweden of 130 ng/g lipid (s.d. 140) and in N. Sweden, 110 ng/g lipid (s.d. 76).

Sewage sludge. The levels of decaBDE in sewage sludge from all Dutch sites were in the range of 270 to 410 ng/g dw: the highest of all matrices in this study (Fig. 2). The concentrations at STPs with substantial industrial input such as C, E and F (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.

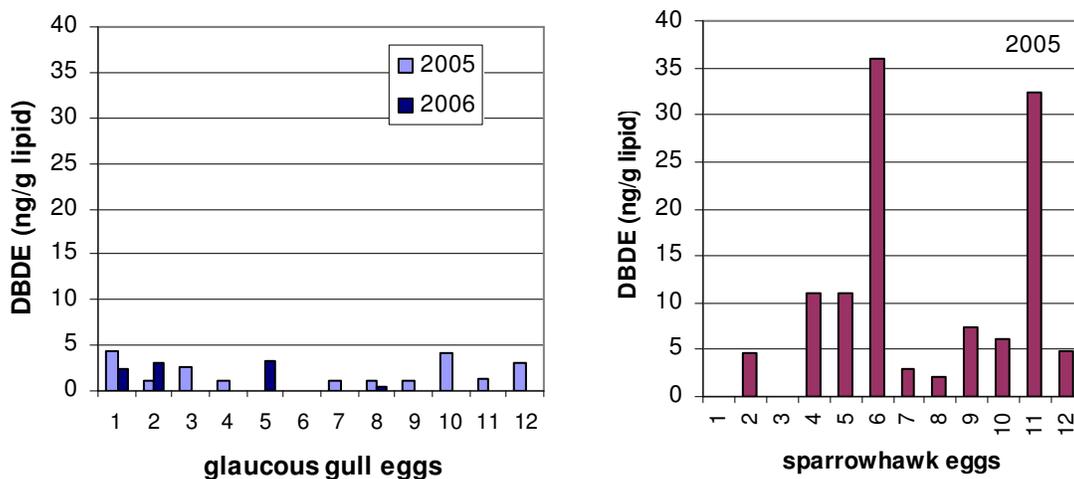


Fig 1. Right panel: DecaBDE concentrations (ng/g lipid) in glaucous gull eggs from Bear Island, Norway sampled in 2005 and 2006. Left panel: sparrowhawk eggs from the UK, sampled in 2005. Only one egg was collected and analysed in 2006 (see text, data not shown on graph). LODs for non-detects: glaucous gull egg numbers 5 and 6 in 2005 were <0.6 and <1 respectively and egg numbers 3,4,6,7,and 9-12 in 2006 were all between <0.5 and <0.6; sparrowhawk egg numbers 1 and 3 both <2.

Sediments. The decaBDE concentrations detected in sediments were generally low (Fig. 3) with the exception of the Western Scheldt and Liverpool Bay sediments. DecaBDE data in sediments collected in 1995 from some of the same sites are available from the Diffchem study report (Anon., 1997). The organic-carbon normalized decaBDE concentrations in the Seine, Elbe and Eems were very comparable to the concentrations reported in sediments from the same locations in the Diffchem study, with current average concentrations all within a factor of 2 of earlier data. The Diffchem study report presents a mean decaBDE concentration (of three <63 μm fraction samples measured) in Western Scheldt sediment (200 ng/g dw), which is lower than the concentrations reported in Fig. 3. The Diffchem study also found a mean decaBDE concentration in Mersey sediments (5-6 km from the Liverpool Bay site in this study) of 1700 ng/g dw.

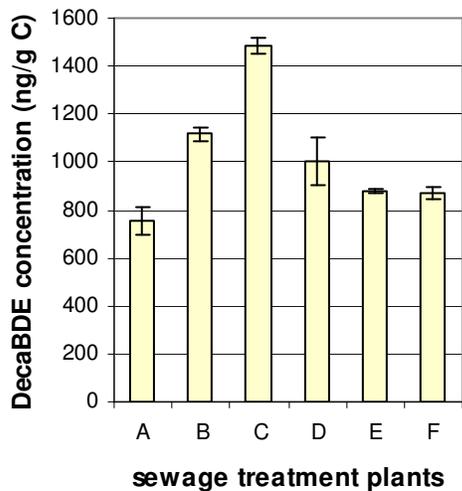


Fig. 2. Mean decaBDE concentrations in sewage sludge (average of 3 composite samples with s.e.) taken in 2006 from treatment plants in the Netherlands.

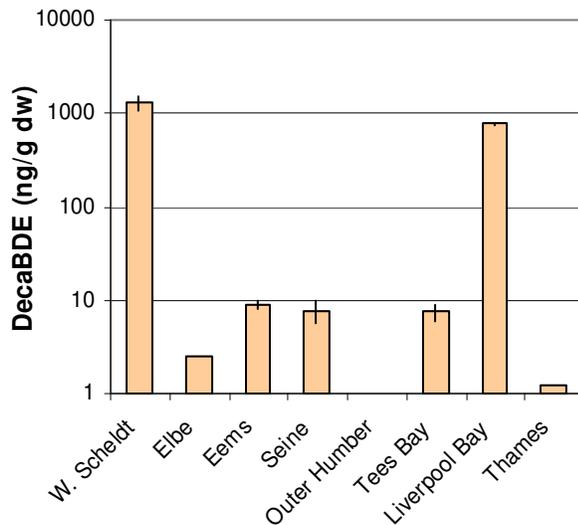


Fig. 3. Mean decaBDE concentrations in sediments sampled in 2005 from the locations in resp. NL, D (2 sites), F, and the UK (4 sites). Mean concentration of five (NL, D and F sites) or four (UK) composite samples per site plus s.d. given. (Additional data for sediments from 2 more sites will be available at a later date.)

In addition to decaBDE, some lower brominated PBDEs, particularly BDEs 47, 99, 100 and 153 were detected at relatively high levels in birds' eggs, especially in sparrowhawks (Fig. 4). In sewage sludge, the levels of these congeners were similar to levels of decaBDE at the two STPs screened (E and F). At most sediment sites these congeners were present at low levels or were undetectable, however all were detected in Western Scheldt and Liverpool Bay sediments.

BDE 126 has been indicated to a possible debromination product of decaBDE in sediments under certain conditions Keum and Li (2005), however it does not appear to be present in the estuaries screened in this study (with LODs below <0.05 ng/g dw or less), nor has it found its way through the food chain to the birds' eggs measured or to the sewage sludge screened.

The data presented here from the first sampling rounds of the DecaMonitor project represent a starting point for the ten-year monitoring period of trends of decaBDE in these environment matrices.

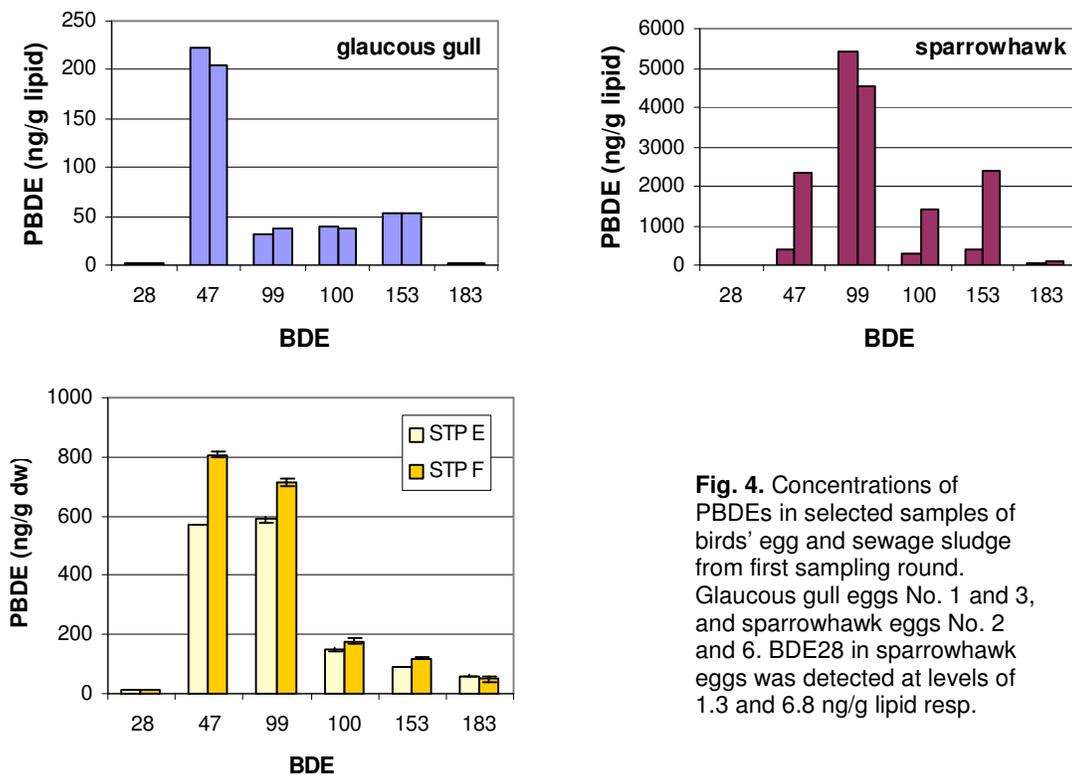


Fig. 4. Concentrations of PBDEs in selected samples of birds' egg and sewage sludge from first sampling round. Glaucous gull eggs No. 1 and 3, and sparrowhawk eggs No. 2 and 6. BDE28 in sparrowhawk eggs was detected at levels of 1.3 and 6.8 ng/g lipid resp.

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References

- Anon. 1997. Report of the one-off survey DIFFCHEM. Oslo and Paris Convention for the prevention of marine pollution, London, UK.
- Bligh EG, Dyer WJ. 1959. *Can J Biochem Physiol* 37, 911-917.
- De Boer J, Allchin CR, Law R, Zegers B, Boon JP. 2001. *Trends in Anal Chem* 20, 591-599.
- De Boer, J, Leslie HA, Leonards PEG, Bersuder P, Morris S, Allchin CR. 2004. Proceedings of the Third International Workshop on Brominated Flame Retardants. Toronto, Canada.
- Keum YS, Li QX. 2005. *Environ Sci Technol* 39, 2280-2286.
- Lindberg P., Sellstrom U, Haggberg L, de Wit CA. 2004. *Environ Sci Technol* 38, 93-96.
- Smedes F, Thomasen, TK. 1996 *Mar Pollut Bull* 32, 681-688.