

# MONITORING OF DECABROMODIPHENYLETHER IN THE EUROPEAN ENVIRONMENT: BIRD EGGS, SEWAGE SLUDGE AND SEDIMENTS – SEVEN YEARS UNDER WAY

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## Introduction

The objective of this study is to follow the concentrations of decabromodiphenylether, (BDE209) in various environmental matrices over the time period 2005-2014. The matrices selected for study include predatory birds, sewage sludge and surface sediment. The matrices were selected because it is known from previous studies that BDE209 can be present in predatory birds<sup>1</sup>, and it has a high affinity for sewage sludge and sediment<sup>2</sup>.

The monitoring has now been going on for seven years. To date, six data sets of BDE209 concentrations in birds' eggs and three data sets in sewage sludge and sediments have been generated. The statistical power for time trend analysis still requires additional time points, so only at the end of the monitoring program a proper statistical trend analysis can be carried out.

In order to monitor BDE209 in the environment, the following relevant monitoring compartments were selected: eggs of birds of prey, sewage sludge and sediment. Sparrowhawk (*Accipiter nisus*) eggs (UK) are being used to monitor diffuse sources at remote locations in the UK, while glaucous gull (*Larus hyperboreus*) eggs from the Arctic region (Norway) are sampled to provide information on exposure in areas that may be affected by long-range transport of BDE209. Eggs are sampled on an annual basis. Sewage sludge and sediments are sampled every other year. Sewage sludge sampling consists of three composite samples of secondary sludge (in some cases mixed with primary sludge) taken over a period of one week at each of the 12 sites in the Netherlands, UK and Ireland. At each of the ten sampling sites in estuaries in the Netherlands, Ireland, Germany, UK and France, four composite sediment samples were taken from the top layer.

## Materials and methods

The sampling scheme of the entire project is shown in Table 1.

**Table 1.** Sampling design summary

	Sparrowhawk egg	Glaucous gull egg	Sewage sludge	Sediment
Number of sites	2	1	12	10
Samples per site	12	12	3 composite	4
	(total all sites)	(all from Bear I.)	samples (week)	(composite)
Number of samples per sampling year	12	12	36	40
Sampling frequency	Annual	Annual	Biennial	Biennial
Total samples in 10-year program	108	108	180	200

Samples of sediments were freeze-dried and Soxhlet extracted with hexane:acetone 1:1 (v/v). The extracts were cleaned with alumina and silica columns. Egg samples were homogenized, dried with sodium sulphate and extracted by Soxhlet with hexane:acetone 3:1 (v/v). <sup>13</sup>C-labelled BDE209 was added as internal standard to all

samples prior to the extraction step. Lipids in birds' eggs were removed by acidic silica gel and silica gel column chromatography. The final extracts were concentrated to 600  $\mu\text{l}$ , and analysed by GC/ECNI-MS. A 15 m DB-5 or DB-1 column was used (internal diameter 0.25 mm, film thickness 0.25  $\mu\text{m}$ ). Two blank samples and one internal reference material were analysed in each series of samples. Quantification of BDE209 was based on the fragments  $m/z$  484.4 and 486.4. The lipid contents of eggs were determined according to Bligh and Dyer<sup>3,4</sup>. Screening for BDEs 28, 47, 99, 100, 126, 153, 183 as well as 126 was performed in selected birds' eggs samples. Total organic carbon contents were determined by a gas chromatographic method (ISO 10694) and were used to normalize concentrations of BDE209 in sediments.

## Results and discussion

Increasing or decreasing trends are not visible in the BDE209 data for biota samples over the first six years of the monitoring program (Figure 1). Throughout the program, sparrowhawk eggs have consistently contained greater BDE209 levels than glaucous gull eggs, on average, presumably due to proximity to sources. The probability of detecting time trends for these species over the ten year period will depend on the magnitude of any changes. Until now, the slight indication of a possible increasing trend of BDE209 concentrations in sparrowhawk muscle from the UK between 1975 and 2005<sup>5</sup> cannot be confirmed.

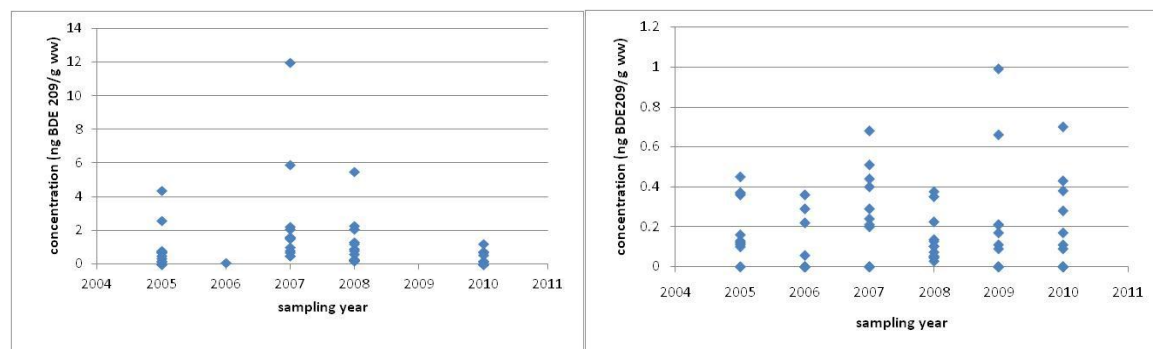


Figure 1. BDE209 concentrations in sparrowhawk eggs (left) and glaucous gull eggs (ng/g ww, non-detects plotted as zero).

BDE209 concentrations in sewage sludge in the Netherlands (500-1500 ng/g organic carbon (OC)) are lower than in the UK and Ireland, where BDE209 concentrations have been consistently higher by an order of magnitude. The most recent sewage sludge samples from sites LP and BC in the UK had approximately double the concentrations of BDE209 than in previous sampling years. Other sewage treatment sites showed neither clearly decreasing or increasing levels.

The ten sediment sampling locations range from very low ng/g OC BDE209 concentrations, e.g. Elb, Ems, Seine, Outer Humber, to high  $\mu\text{g/g}$  OC, e.g. Western Scheldt, Liverpool Bay and River Mersey (Figure 2). The concentrations in river Elb sediment were comparable to those reported by Sawal et al.<sup>6</sup>. The Dublin Harbour site appears to have higher concentrations of BDE209, however this may be partly due to the very low level of organic carbon in the sediments. In 2009, 60 ng BDE209 /g dw was measured in the Dublin sediments, but with only 0.5% organic carbon, the concentration on organic carbon basis rises to over 11600 ng BDE209/g OC. An interesting finding in the sediment data was found for the River Mersey and Liverpool Bay area. In the 2009 sampling round in the River Mersey, BDE209 concentrations were higher than in previous years, while BDE209 had decreased in measurements of samples from Liverpool Bay taken in 2010 (Fig. 2). In this case, the increased BDE209 measured upstream in the River Mersey were not reflected downstream in Liverpool Bay at a later time

point, at least not on the time scale of this study. The accuracy of the sampling location in Liverpool Bay is not expected to be a reason for this observed difference, as the correct sampling location was recorded. No metadata

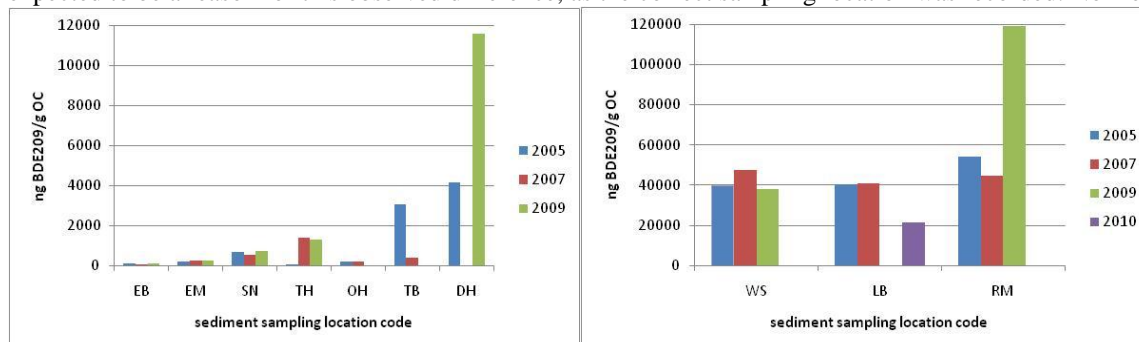


Figure 2. BDE209 concentrations in river sediments (in ng/g OC). EB: Elb, Germany, EM: Ems, Germany, SN: Seine, France, TH: Thames, UK, OH: Outer Humber, UK, TB: Tyne Bay, UK, DH: Dublin Harbour, Ireland, WS: Western Scheldt, Netherlands, LB: Liverpool Bay, UK, RM: Mersey, UK. BDE209 in Outer Humber sediments <LOQ. Tees Bay 2009 data not plotted because no samples were available from the UK national monitoring program. Concentrations are an average of four sediment samples in the sampling year.

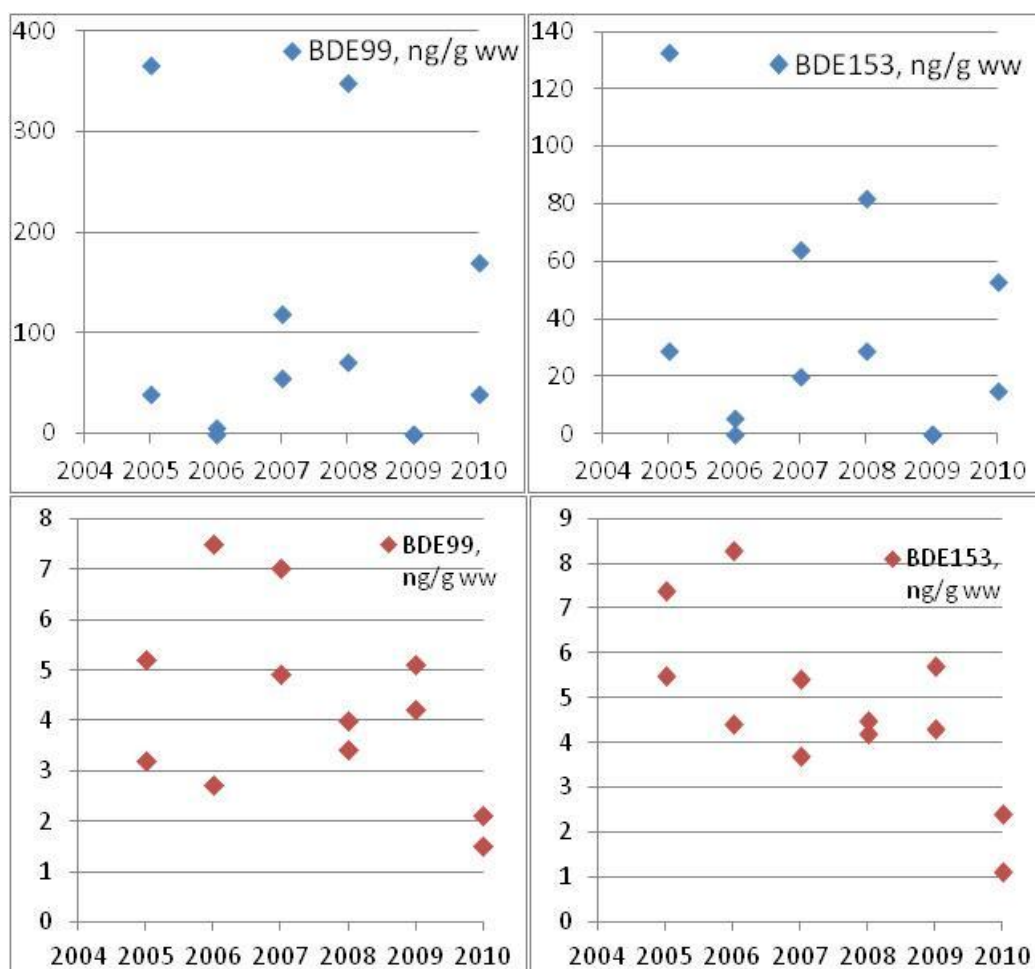


Fig. 3 BDE99 and 153 concentrations in sparrowhawk eggs (top) and glaucous gull eggs (ng/g ww).  
on the sediment dynamics is currently available for in depth interpretation of this data.

Throughout the first six years of the study, lower brominated BDEs have been detected in all sparrowhawk and glaucous gull eggs (Figure 3) screened, with occasional non-detects of certain congeners. As expected for biota samples, the data for individual eggs is more scattered than for other matrices. No clear increasing or decreasing trends can be calculated from the data to date, except in the case of BDE153 in glaucous gull eggs, where a decreasing trend is apparent. In both species, BDE28 is present in the lowest concentrations of all other lower brominated BDEs, followed by BDE183. Based on average concentrations throughout the study, glaucous gull eggs have a pattern dominated by BDE47, followed by 100, 153 and 99, while in sparrowhawk eggs BDE 99 is the most dominant congener on average, followed by 47, 153 and 100.

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