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Decabromodiphenylether trends in the European environment: Bird eggs, sewage sludge and surficial sediments

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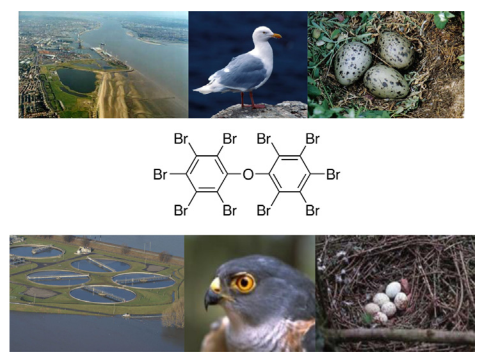
HIGHLIGHTS

- Unique 8-year monitoring program of decaBDE in Europe
- High decaBDE concentrations in sediments and sludge from UK
- Relation between decaBDE levels in sediment and textile industry
- Voluntary emission control by industry only had local effect.
- DecaBDE clearly detected in sparrowhawk and glaucous gull eggs.
- DecaBDE unlikely to disappear from the European environment within decades

GRAPHICAL ABSTRACT



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ABSTRACT

Concern on relatively high levels and the potential bioaccumulation of decabromodiphenylether (BDE209) has led to a European 8-year monitoring program on trends in BDE209 concentrations in birds, sewage sludge and sediments from seven countries. BDE209 was analysed in four environmental matrices: sparrowhawk eggs (UK), glaucous gull eggs (Bear Island, Norway), sewage sludge (UK, Ireland and the Netherlands) and sediment (France, Germany, the Netherlands, UK and Ireland). BDE209 was detected in most of the glaucous gull and sparrow hawk eggs but neither increasing nor decreasing trends in these BDE209 levels were observed. An indication for debromination of BDE209 in sparrowhawk eggs was found. BDE209 concentrations in sediments ranged from very low ng/g (88 ng/g on an organic carbon (OC) basis) concentrations, in the rivers Elbe, Ems, Seine and the Outer Humber, to high μg/g (120 μg/g OC), in the Western Scheldt, Liverpool Bay and River Mersey. Apart from decreasing values in the Western Scheldt sediment no further decreases in BDE209 concentrations were observed over time, neither in sediment nor in sewage sludge showing that the voluntary emissions control program of the bromine industry only had a local effect. In contrast to the sewage sludge samples from the Netherlands (mean 355 ng/g dry weight (dw) or 1026 ng/g OC), the BDE209 concentrations in the UK increased at all sites from 2006 to 2011 (8092 ng/g dw or 22,367 ng/g OC). The BDE209 levels in several UK sediments and sewage sludge were still very high at the end of the program in 2012, most likely caused by frequent use of BDE209 in the textile industry. This may be indicative of the persistence of BDE209 and the limited degradation into lower brominated congeners in sediment, although it cannot be excluded that ongoing BDE209 emissions have played a role as well.

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1. Introduction

Following reports from the 1990s on the occurrence and increasing concentrations of brominated flame retardants (BFRs) in the environment (De Boer et al., 1998; Norén and Meyronité, 2000), many research groups, worldwide, started studies on BFRs and initially found substantial concentrations of tetra- and pentabrominated diphenylethers (BDEs), both related to the use of the so-called PentaMix as a flame retardant (FR) in upholstery textile and electric instruments and electronics. Soon, it appeared that decabromodiphenylether (BDE209) was applied in even higher volumes in textile and housing of electronics, and was also present in sediments at high concentrations (Law et al., 2008). Zegers et al. (2003) reported the presence of BDE209 concentrations in sediment cores from Europe. Moon et al. (2007) reported very high BDE209 concentrations (>2000 μg/g dry weight (dw)) in South-Korean sediments. Several studies showed the presence of BDE209 in bird eggs (Lindberg et al., 2004; Holden et al., 2009). Ross et al. (2009) claimed that the BDE209 concentrations in various environmental compartments had already surpassed the legacy polychlorinated biphenyls (PCBs) and DDT as the top contaminant by concentration. They also found BDE209 in biota samples but those were lower than the BDE209 levels in sediments would predict. These observations initiated a debate about the bioaccumulative properties of BDE209 and its possible degradation to lower brominated BDE congeners. In Europe a very early indication on elevated BDE209 concentrations in sediments was found in the DIFFCHEM study from 1995 (Anon, 1997). In 2002 the LOES study (Vethaak et al., 2002) reported the first monitoring data on BDE209 in Dutch sediments, characterizing those data the highest BDE209 concentrations measured to date. The alarming signals from scientists led to concern with European authorities, while the bromine industry was also concerned about the effects of their product. Finally this led to a unique initiative on monitoring BDE209 in the European environment. This monitoring program was developed through a collaboration of the European Union, the bromine industry, represented by the Bromine Science and Environmental Forum (BSEF), and four European research groups. The development of this monitoring program benefited from the comments and input from an expert panel, which initially met in London on 11 August 2004, and the UK Environment Agency. Through its stewardship programs, the bromine industry had proposed measures to reduce the emission of BDE209 from point sources (voluntary emissions control program), and recognized the need to perform time trend monitoring of BDE209 in the environment. The European Union was concerned about possible effects of BDE209 on the environment and human health. The aim of this study was to follow the long-term trend of BDE209 in various environmental matrices (bird eggs, sewage sludge and sediment) to visualise possible effects of the reductive measures taken at point sources. The types of samples were selected because it was known from previous studies that low BDE209 concentrations could be present in some bird eggs (Lindberg et al., 2004; Holden et al., 2009), and BDE209 has a high affinity for sediment and sludge (Ross et al., 2009). A time trend study in guillemot (*Uria* spp.) eggs suggested that while chemicals brought on the market may quickly appear in environmental samples, reductive measures taken by industry can in some cases lead to relatively rapid decreases in concentrations measured in biota over time (Sellström et al., 2003). Although the results obtained with Peregrine falcons (*Falco peregrinus*) were convincing, we finally selected sparrowhawks (*Accipiter nisus*) for the present study. The sparrowhawk's biology (e.g. migration patterns, varied diet) is relatively well understood. Being good accumulators of organohalogen contaminants, sparrowhawks are suitable for time trend monitoring of BDE209. Sparrowhawks were not endangered, could be sampled without disturbing the populations, breed in very small colonies in northern Europe (not in the UK), have egg sizes sufficiently large for analysis, have a wide geographic distribution, and egg samples (failed eggs) can be easily collected by licensed volunteers. Sparrowhawks lay 3–6 eggs per clutch, and so the laying period can last between 5 and 11 days. Incubation of the eggs can last between 31 and 37 days. Glaucous gulls are coastal birds, which scavenge for carrion, shellfish, birds' eggs and scraps. Clutches consist of three eggs, laid a couple of days apart. The feeding ecology of these gulls is very important to the concentrations of environmental contaminants measured, making it crucial to return to the exact same site for each sampling (Bustnes et al., 2000).

The objectives of this study were the following: i) to monitor BDE209 concentrations in eggs of the sparrowhawk (*Accipiter nisus*) in the UK and eggs of the glaucous gull (*Larus hyperboreus*) in an Arctic region of Norway; ii) to monitor BDE209 concentrations in sewage sludge from sewage treatment plants (STPs) in the UK, Ireland and the Netherlands, representing both domestic wastewater and sewage from industries where FRs are in use; iii) to monitor BDE209 concentrations in sediments at sites in the UK, Netherlands, Ireland, France, and Germany, including sites near point sources and those with diffuse sources; and iv) to establish time trends of BDE209 concentrations in these matrices over the period 2005–2012.

2. Materials and methods

2.1. Sampling

The following relevant monitoring compartments were selected: eggs of birds of prey, sewage sludge and sediment (Table 1). Eurasian sparrowhawk (*Accipiter nisus*) eggs (UK) were used to monitor diffuse sources at remote locations in the UK, while glaucous gull (*Larus hyperboreus*) eggs from the Arctic region (Bear Island/Bjørnøya, Norway) were sampled to provide information on exposure in areas that may be affected by long-range transport of BDE209. Sampling birds' eggs as opposed to tissues from adult birds has the advantage of less variation in concentrations within the egg. Pooling individual egg samples is not recommended since the variation between individuals can be quite high, and experience has shown that pooling eggs makes time trend analysis difficult (Henriksen et al., 1997; Sellström et al., 2003). Avian sampling was done on a yearly basis, with 12 eggs

Table 1
Sampling characteristics including sample type and size, location and frequency.

	Sparrowhawk egg	Glaucous gull egg	Sewage sludge	Sediment
Number of sites	Various	1	12	10
Samples per site	12 (total all sites)	12	3 composite samples (of 1 week)	4 (composite)
Locations	Entire UK[a]	Bear Island, Norway	Netherlands (6), UK (5), Ireland (1)	Netherlands (1), Germany (2), France (1), UK (4), Ireland (1)[b]
Number of samples per sampling year	12	12	36	40
Sampling frequency	Annual	Annual	Biennial	Biennial
Actual number of samples taken	59	89	144	146

[a] Sparrowhawk eggs were collected by volunteers over the entire UK.
[b] Netherlands: Western Scheldt, Germany: Elbe and Ems, France: Seine, UK: Outer Humber, Thames, Tees Bay, Liverpool Bay, River Mersey, Ireland: Dublin Harbour.

measured per species. This is an appropriate number of eggs from the point of view of bird colony and population sizes to be sampled, and is in accordance with recommendations for the number of samples for the determination of persistent organic pollutants (POPs) in biota in the HELCOM monitoring program (HELCOM, 1988). It was shown to be sufficient in other time trend studies in birds (Sellström et al., 2003). The collection of sparrowhawk eggs by volunteers took place annually between 19th June and 24th July. Sampling locations were indicated by UK Ordnance Survey codes.

The colony of glaucous gulls that was sampled on Bear island, inhabits the "top cliff" area of the island. It consists of 50–60 nests and has been present there at least since the 1960's. Bird eggs, such as guillemot (Uria *spp.*), are eaten mainly by the top cliff colony, as opposed to a second colony near sea level, which mainly feeds on fish. Because fish-eating birds are unlikely to accumulate BDE209, the higher colony was the preferred choice for BDE209 monitoring. Sampling was carried out each year in May and June. For both sparrowhawks and glaucous gulls the first egg was the priority for sampling, and not one laid at a later date (if first eggs in the nest are lost, the mother may sometimes lay more eggs). This can prevent an important source of within-year variation. For sparrowhawks, this variation is more difficult to avoid, but there is a better chance of this with glaucous gulls.

Sewage sludge was sampled every other year (Table 1). Sewage sludge sampling consisted of three composite samples of secondary sludge taken over a period of one week at each of the 12 sites. Secondary sludge is sludge to which microorganisms have been added to consume the organic matter in the wastewater. A sample volume of ca. 2 L provided sufficient dry mass for the analysis of BDE209. Although no two facilities operate exactly the same treatment processes, the sampling points were selected per site to include secondary sludge in every case. In some facilities this was sampled in combination with primary sludge, which are the suspended solids and organics in the primary treatment process through gravitational sedimentation. On request of most of the sewage treatment plants the locations of the sewage samples taken for this study are coded in this paper.

The sediment samples were taken by a mini Van Veen grab or a Day-grab (for offshore samples), ensuring that only the top layer (ca. 2 cm) is sampled, which represents newly deposited sediments. Four samples, each based on a pool of nine sub-samples from an area of ca. 100 m^2, were taken per location (Table 1).

The sediment sampling locations were selected based on sufficient sedimentation rate, sediment surface undisturbed by fishing trawlers and representation of several different European countries (Table 1). The sites sampled in this study were already identified in a previous study (Anon, 1997). Five years later, the authors of the present study sampled sediments again at a selection of these locations (De Boer et al., 2002). A number of the sampling locations included in the program show significant BDE209 concentrations so that a decrease in BDE209 concentrations could easily be recognized, for example, the locations in the textile industry area around Manchester (Mersey River) and in the Western Scheldt, another area influenced by various BDE209 users (textile industry). An overview of all sampling locations is shown in Fig. 1.

Care was taken to provide enough raw monitoring data in relevant matrices to draw conclusions on time trends within a 10-year study period, although in the end it turned out to be an 8-year study. With this approach the expected decreasing trend of BDE209 as a consequence of the reductive measures taken by the bromine industry and users should be effectively visualized. The actual samples for all matrices studied taken are shown in Table 1.

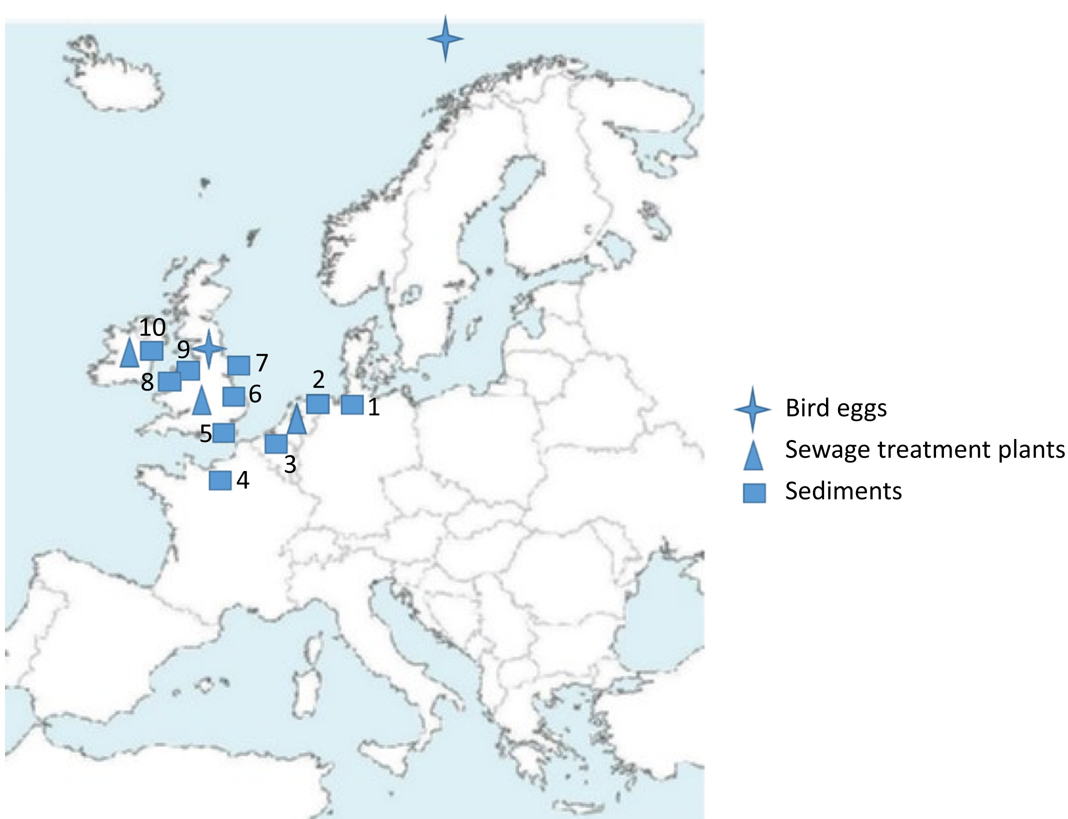

Fig. 1. Sampling locations of glaucous gull eggs (Bear Island, Norway), sparrowhawk eggs (UK), sewage sludge (the Netherlands, UK and Ireland) and sediments (Germany, France, the Netherlands, UK and Ireland).

2.2. Chemical analysis

Analyses were carried out based on De Boer et al. (2001). Briefly, samples of sediments and sewage sludge were freeze-dried or air-dried and Soxhlet-extracted with hexane:acetone 1:1 (*v*/v). They were cleaned with alumina and silica columns. Whole eggs were homogenized in a blender, dried with sodium sulphate, and Soxhlet-extracted with hexane:acetone 1:1 (v/v). Lipids in birds' eggs were removed by acidic silica gel column chromatography. A sample of max. 8 g was taken for the glaucous gull eggs. Because of smaller sample masses of the sparrowhawk egg homogenates, less than 8 g was weighed in for BDE analyses. The sample intake for the freeze-dried sediment and sewage sludge samples was between 1 and 2 g. ^{13}C-labelled BDE209 was added as internal standard to all samples prior to the extraction step. The final extracts were concentrated to 600 μL, and analysed by GC/ECNI-MS. A 15 m DB-5 (internal diameter 0.2 mm, film thickness 0.1 mm) or DB-1 column (internal diameter 0.25 mm, film thickness 0.25 μm) was used to avoid on-column degradation. Two blank samples and one in-house reference material were analysed in each series of samples. Quantification of BDE209 was based on the fragments m/z 484.4 and 486.4. Screening for BDEs 28, 47, 99, 100, 126, 153, 183 was performed in selected egg, sediment and sewage sludge samples. These BDE congeners were analysed by GC/ECNI-MS using 50 m DB5 columns to enhance the separation. For quality assurance (QA) purposes we analysed an internal reference material in each series, both for sediments and eggs (for which we used a fish material). Quality control charts were made for BDE209 in sediment, BDE209 in fish and also for the blanks. Throughout the years the relative standard deviation (RSD) for BDE209 in sediment was around 5–6% and for biota around 55%. The latter value was obviously due to the low BDE209 level in the biota reference material. The certified reference material used and led to satisfactory results (RSD 8%, $n = 3$) was a sediment from NIST, SRM 1944 (New York/New Jersey Waterway sediment). We participated in the QUASIMEME annual proficiency test for BDE209 (and other BDEs) with satisfactorily z-scores between −2 and 2 except in two instances, the exceptions again being test materials of biota with very low BDE209 levels. For a correct interpretation of the data produced it is important to look at the entire data set. For example, if the mean of a series of ten concentrations needs to be calculated and all data are between 10 and 20, except one, which is below the limit of detection (LOD), one could use half of the LOD value as the concentration for that sample (Glass and Gray, 2001). This is considered a more realistic approach than taking zero as value for that specific sample. However, in case most data are <LOD, this is less realistic, as the compound may not be present at all in most samples. In that case one could use zero or, preferably, consider the entire data set (and not calculate a mean value) (Antweiler and Taylor, 2008; Perkins et al., 2010). The latter situation was observed on several occasions in this study. Data that were between LOD and LOQ are reported with an asterisk. Closer to the LOQ, the data will be more realistic, closer to the LOD, the data contain a higher uncertainty but still indicate that the compound is present (Huber, 1998).

For normalization purposes the total lipid contents in eggs and the organic carbon contents in sediment samples were determined. The lipid contents of eggs were determined according to Bligh and Dyer (1959) or Smedes and Thomassen (1996). Total organic carbon was determined by AL-West B.V. (Deventer, the Netherlands) using an elementary analysis method (ISO 10694). The organic carbon content is calculated from the total carbon content after correcting for carbonates present in the sample. The egg results were expressed on a wet weight (ww) basis because total lipid contents in both egg species were very stable, in glaucous gull eggs around 10% and in sparrowhawk eggs around 8%, whereas the OC contents in sewage sludge samples and sediments in particular varied more, so requiring normalization on OC basis.

2.3. Statistics

For the glaucous gull and sparrowhawk egg data, we investigated a linear trend by fitting a random effects model (Pinheiro and Bates, 2000). For the *i*th observation in the *j*th year, this is of the form

$$\ln\left(BDE_{ij}\right) = \alpha + \beta YEAR_j + b_j + \epsilon_{ij} \tag{1}$$

where α and β are linear regression intercept and intercept parameters respectively, b_j is a random effect for the *j*th year such that $b_j \sim N(0,\sigma_b^2)$ and ϵ_{ij} is an independent error term such that $\epsilon_{ij} \sim N(0,\sigma^2)$. The R (R Core Team, 2020) library *lme4* was used to fit these models by Maximum Likelihood. The statistical significance of the slope value β was obtained by using a likelihood ratio test to compare model (1) with a reduced model that did not contain the "$\beta YEAR_j$" term.

This random effects model fits well with the data shown in Figs. 1 and 2 where there seem to be random differences between years – perhaps caused by natural variation and analytical error.

For the sediments and sewage data there is only four year of data. For these data, the expected change in trends could not be statistically assessed with the expected level of significance over the period monitored, and therefore, we present the temporal plots supporting our main discussion and conclusions.

3. Results and discussion

The three sample sets, bird eggs, sediments and sewage sludge were selected for the following reasons: i) to carry out a time trend monitoring of the load of BDE209 on the environment in Europe, ii) to see if bioaccumulation occurred at all and iii) to check for possible environmental hot spots of BDE209. The time trend was important because the bromine industry had started a stewardship program and was interested in the effects thereof, while the EU was concerned about possible rising trends of BDE209. All three sample types could be used for a trend study, although the sparrowhawks were maybe the least strong as they were collected over a large area, in fact the entire UK. For bioaccumulation the bird eggs were used, not to disturb any other animal populations and because excellent data were obtained earlier by peregrine falcon eggs (Lindberg et al., 2004) and sparrowhawk studies. The sediments in particular were useful for detecting hot spots as they were mainly taken in rivers and estuaries and several of the samples could be compared with a useful study from the past (Anon, 1997).

3.1. BDE209 levels in glaucous gull eggs

The BDE209 concentrations in the glaucous gull eggs from 2005 until 2012 are shown in Fig. 2a. BDE209 concentrations detected in the glaucous gull eggs in 2012 were slightly higher (up to 2.6 ng/g ww) compared to previous years (up to 0.9 ng/g ww) (Table 2). However, they were generally lower than the values detected in sparrowhawk eggs of this study, as well as being below historical values reported in peregrine falcon eggs in Sweden (Lindberg et al., 2004). Notably, these authors reported BDE209 in wild peregrine falcon eggs for the first time, ranging from <7 to as high as 430 ng/g lipid weight (lw). Fig. 2b shows a plot of the natural log data. The means of the log values are also shown in the plot. There is no obvious trend. This was backed up by the lack of statistical significance of the trend parameter β (Eq. (1)), which had a p-value of 0.26. Other studies indicated that BDE209 was the most concentrated in liver samples, e.g. in Eastern Canadian Arctic glaucous gulls from Cape Dorset, Nunavut, up to 8 ng/g ww in males (Verreault et al., 2018). The authors suggested that dietary exposure came from the local marine food web and possibly from nearby community landfills. Interesting was the presence of several known or suggested debromination products of BDE209 in the livers of glaucous gulls, although at lower concentrations relative to

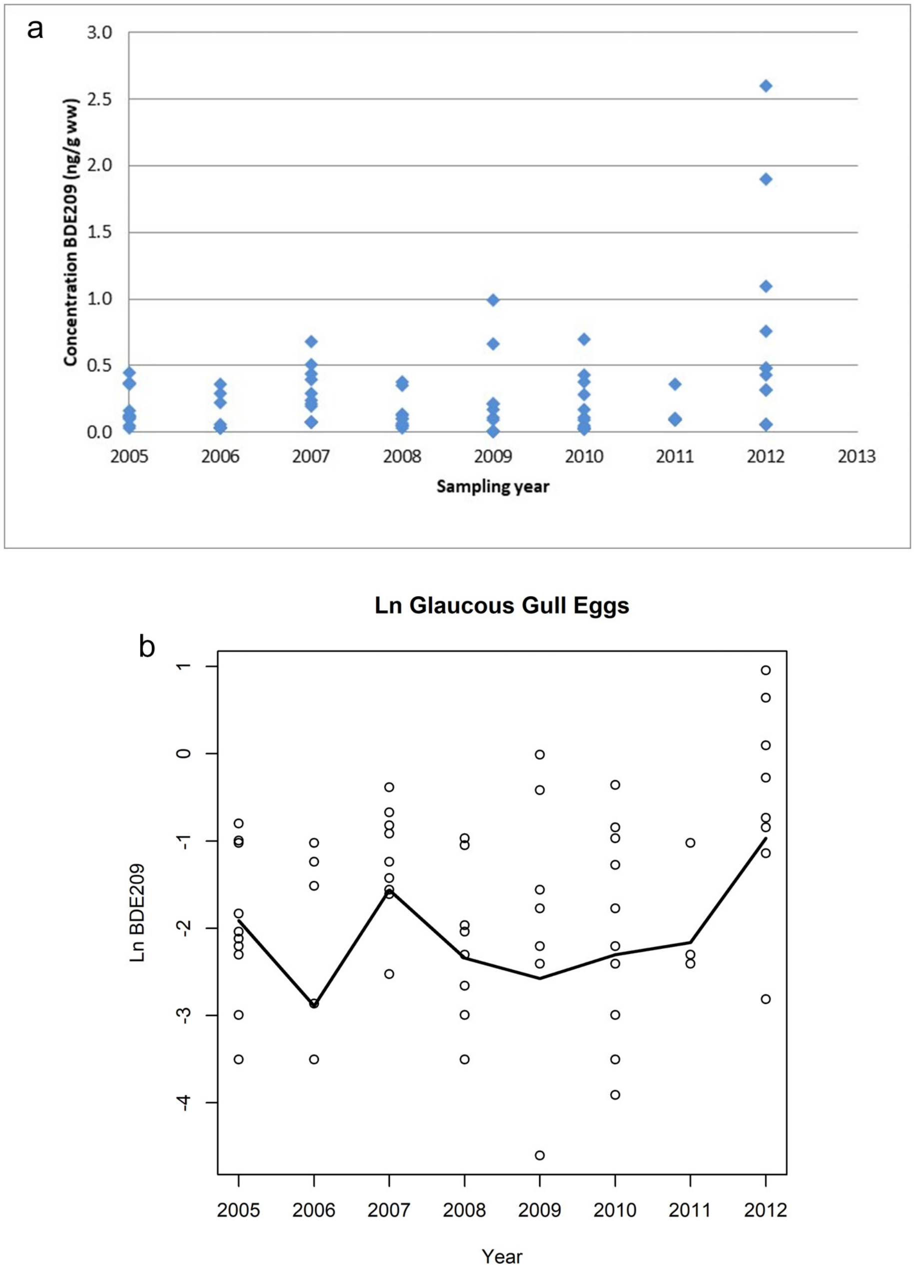

Fig. 2. a) Overview of BDE209 concentrations (ng/g wet weight) in individual glaucous gull eggs collected between 2005 and 2012 (note: the 32 non-detects measured to date are plotted on this graph as zero). b) Plot of Ln(BDE) against year for Glaucous Gulls eggs. The solid line shows the yearly means. The random effects model (1) showed a non-statistically significant term for the trend ($p = 0.26$).

BDE209 itself (BDE209 ≫ 207 > 197 > 208 > 201–183 > 196–206 > 203), suggesting a possible degradation of BDE209 in gull livers.

3.2. BDE209 levels in sparrowhawk eggs

Fig. 3a shows the complete BDE209 data set for sparrow hawk eggs from the start of the program in 2005 till the last sampling year, 2012. The BDE209 concentrations vary between <LOD and 12 ng/g ww. In seven samples BDE209 was below the LOD. When disregarding the one sample from 2007 showing 12 ng/g BDE209, all samples were between LOD and 6 ng/g ww. Clearly, no temporal trend is visible. The log plots are shown in Fig. 3b. As with the glaucous gull eggs, there is no obvious trend and this was confirmed by a p-value of 0.61 for the trend parameter β.

A study on BDE209 in bird tissues sampled in China reported a higher frequency of BDE209 detects (79.4% of samples) with mean BDE209 levels (in ng/g lw) well above LODs: e.g. sparrow hawk muscle (192), liver (254), kidney (83 ng/g lw); and in common kestrel muscle (2150), liver (2870) and kidney (483 ng/g lw) (Chen et al., 2007). Our results also showed the presence of nonabrominated diphenylethers in some sparrowhawk eggs. We analysed a few sparrowhawk eggs for nonaBDE's and indeed found them, in higher ratios compared to nonaBDE's originating from the ^{13}C labelled BDE209 during analysis, which indicates that debromination of BDE209 is taking place.

3.3. BDE209 levels in sewage sludge

BDE209 was detected in all sewage sludge samples from all sites in all years. The organic carbon contents varied for all samples between 15 and 49% of the dry weight (dw). The BDE209 concentrations in sewage sludge samples from the Netherlands ranged from 223 to 540 ng/g dw (420 to 1520 ng/g OC) (Fig. 4a). No clear visible trend of decreasing

Table 2
BDE209 concentrations in sparrowhawk eggs, glaucous gull eggs, sewage sludge and sediments from Europe during the entire project, 2005–2012. Range and number of samples (n) are given.

Location	Sparrowhawk eggs (ng/g ww)	Glaucous gull eggs (ng/g ww)	Sewage sludge (ng/g dw)	Sediment (ng/g dw)
UK	<0.07–12 (59)*			
Bear Island, Norway		<0.1–2.6 (89)**		
The Netherlands			150–750 (72)	
UK			184–16,100 (60)	
Ireland			4030–14,300 (12)	
Western-Scheldt, Netherl.				270–1620 (16)
Ems, Germany				3.4–12 (16)
Elbe, Germany				0.61–3.5 (16)
Seine, France				1.3–9.4 (16)
Outer Humber, UK				<0.1–2.1 (16)
Tees Bay, UK				5.2–12 (12)
Thames, UK				1.0–11 (11)
Liverpool Bay, UK				24–785 (16)
Mersey, UK				97–3290 (16)
Dublin Harbour, Ireland				14–93 (11)

ww: wet weight; dw: dry weight.
* Seven values were below the LOD.
** 32 values were below the LOD.

or increasing BDE209 concentrations was observed in the sludge samples from the Netherlands collected between 2006 and 2011. At some locations (AM, BT) some decrease was observed but at others a varying pattern (BR, KV) or even a slight increase (UT, EH) was found.

In the sewage sludge samples from the UK and Ireland, mean BDE209 concentrations ranged from 5380 to 12,000 ng/g dw (11,200 to 55,000 ng/g OC) (Table 2 shows the range of *individual* sewage sludge and sediment samples). In contrast to the sewage sludge samples from the Netherlands the BDE209 concentrations in the UK increased at all sites from 2006 to 2011 (Fig. 4b). The highest increase in BDE209 concentration between 2005 and 2011 was seen at site MB, 8.6-fold from 2388 ng/g OC in 2006 to 20,600 ng/g OC in 2011. The sewage sludge from site LP showed an extremely high BDE209 level in 2009 (55,700 ng/g OC). Less clearly visible trends were observed at the Irish site (DB). Further investigations into the incoming wastewater of these sewage treatment facilities are recommended.

The mean concentration over all the UK and Ireland sites (8092 ng/g dw or 22,367 ng/g OC) was again remarkably higher than in the Netherlands (355 ng/g dw or 1026 ng/g OC), close to a factor of 23 difference between the two regions. We hypothesize that this may have to do with the stricter fire safety regulations in the UK, which causes the use of higher volumes of flame retardants, including BFRs. Different from other European countries, the UK and Ireland require domestic upholstered furniture to be flame retarded (House of Commons, 2019). The BDE209 concentration at the sites in the Netherlands appear to be independent of urban or rural input. Also, industrial input at the EH, BT, KV sites did not substantially increase concentrations relative to other sites.

3.4. BDE209 levels in sediment

All surficial sediment samples from the Netherlands, France, Germany, UK and Ireland contained BDE209. The organic carbon contents for the samples from the UK and Ireland varied between 0.1 and 4.1% dw, whereas for the samples from the Netherlands, France and Germany it varied between 0.95 and 8.5% dw. The lowest BDE209 levels were detected at the sites in the rivers Elbe, Ems, Seine and the Outer Humber, where mean concentrations ranged from 0.92 to 9.8 ng/g dw (88 to 379 ng/g OC). Surficial sediment from Dublin Harbour showed higher BDE209 concentrations, up to 11,500 ng/g OC in 2009 and 8300 n/g OC in 2011, both more than the double of the 2005 levels (Fig. 5b). Very high BDE209 concentrations were measured in surficial sediment of the Western Scheldt, Liverpool Bay and the river Mersey (Fig. 5b, Table 2), with mean levels varying between 21,500 and 119,000 ng/g OC. These levels are 10 to more than 100-fold higher than those in the river sediments from the European continent. Again, it may reflect the high volumes of BDE209 used in the UK in relation with strict fire safety regulations. It is most likely also related to the dense textile industry in the Manchester/Liverpool area. For the same reason, a dense textile industry in Flanders, Belgium, the Western Scheldt may show such high BDE209 concentrations in its sediment. However, The Western Scheldt seems to be the only site with a clear decrease in BDE209 concentrations in sediment (from 1290 ng/g dw or 53,300 ng/g OC in 2005 to 310 ng/g dw or 23,500 ng/g OC in 2011), which may reflect the success of the voluntary emissions control program in that region. No clear visible trend of decreasing or increasing BDE209 concentrations were observed for the other sediment samples. The OC normalized BDE209 concentrations in the Seine, Elbe, and Ems were in the same range as the concentrations reported in sediments from the same locations in the Diffchem study (sampled in 1995) (Anon, 1997). On the other hand, in the Diffchem report, the mean BDE209 concentration (of three samples measured) in Western Scheldt sediment is 200 ng/g dw, which is considerably lower than the concentrations found in this study. This shows the enormous increase in BDE209 concentrations in the late 1990s and 2000s. Wang et al. (2015) reported median BDE209 levels in sediment from Shanghai of 46 ng/g dw, which is much lower than the BDE209 concentrations we find in the Western Scheldt and some UK rivers. They claimed that risk quotients (RQ) showed that this level posed a high potential ecological risk (RQ > 1) to the sediment dwelling organisms, and decaBDE was one of the major ecological risk drivers. The same ecological risk warning was given by Cheng and Ko (2018) but based on much higher levels of PBDE's in the Danshui River basin, Taiwan: Σ19PBDEs in sediments ranging from 2.3 to 10,490 ng/g dw with BDE209 making up 77.5 to 99.9% of the total.

Abassi et al. (2015) estimated that considering only the first use (no reuse and/or storage) of PBDE-containing products, approximately 60% of the US/Canadian stock of PBDEs in 2014 or ca. 70,000 tons, 95% of which consist of BDE209, will still be in use in 2020. Although the numbers in Europe may be different, a similar trend is expected. Although BDE209 can degrade when exposed to light (Keum and Li, 2005), the actual degradation of BDE209 may be very slow because light penetration in water and sediment is normally very limited. Given this persistence of BDE209 in sediments and the availability in products and likely future release into the environment, substantial decreases of BDE209 concentrations in sediments are not expected in the near future. Ross et al. (2009) previously predicted the creation of large environmental reservoirs of BDE209. Based on an analysis of octabrominated diphenylethers, Zennegg et al. (2013) did not find indications of debromination of BDE209 in digested sewage sludge. Tokarz et al.

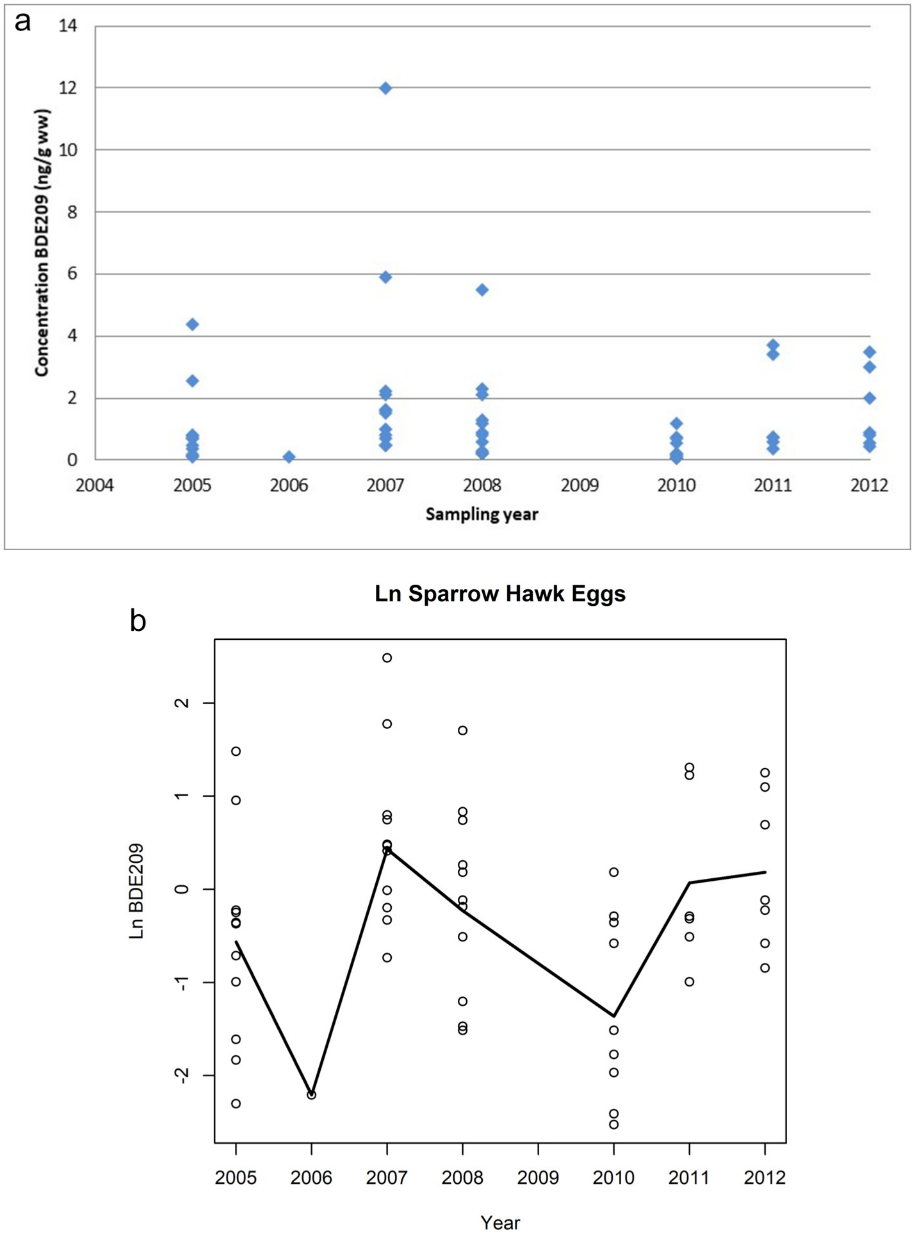

Fig. 3. a) Overview of BDE209 concentrations (ng/g wet weight) in individual sparrowhawk eggs collected between 2005 and 2012 (note: the seven non-detects found were plotted as zero on this graph). b) Plot of Ln(BDE) against year for Sparrow Hawk eggs. The solid line shows the yearly means. The random effects model (1) showed a non-statistically significant term for the trend ($p = 0.61$).

(2008) reported half-lives of between 6 and 50 years for reductive debromination of BDE209 in sediment. This means that at the locations studied lower brominated congeners may become available at relatively low levels over a very long period. Abbasi et al. (2019) estimate a period of 50 years for PBDEs to disappear from the environment. Based on atmospheric PBDE concentrations, Hites et al. (2021) estimate at least a similar period for BDE209. From earlier problems with other halogenated compounds such as PCBs, organochlorine pesticides and chlorinated dibenzo-*p*-dioxins, we know that this may be a serious concern for future generations.

3.5. Lower brominated BDEs

In a number of selected samples the lower brominated congeners 28, 47, 99, 100, 153 and 183 were also analysed: in glaucous gull eggs ($n = 2$), sparrowhawk eggs (n = 2), annually; in sewage sludge samples from two sites ($n = 6$ samples in total) and sediment samples from four sites ($n = 8$ samples in total). All the lower PBDE congeners (BDEs 28, 47, 99, 100, 153, 183 and 126) were detected in both the glaucous gull and sparrowhawk eggs sampled in 2012. The dominant congeners in birds' eggs were the BDEs 47, 99, 100 and 153, which are also dominant congeners found in the sewage sludge. The PBDE levels in glaucous gull eggs collected in 2012 ranged from 0.19 ng/g ww for BDE183 to 17 ng/g ww for BDE47. The PBDE levels in the sparrowhawk eggs ranged from 0.22 ng/g ww for BDE28 to 110 ng/g ww for BDE99. These levels are in line with a study on PBDEs (without BDE209) in sparrowhawks from the UK between 1985 and 2007, in which BDE99 was reported as the dominant BDE with mean levels between 27 and 179 ng/g wet weight (Crosse et al., 2012). Here, generally, low concentrations of the BDEs 47, 99, 100, 153 and 183 were detected in sediment. The dominant congeners in the sewage sludge and sediment samples were BDE47 and BDE99.

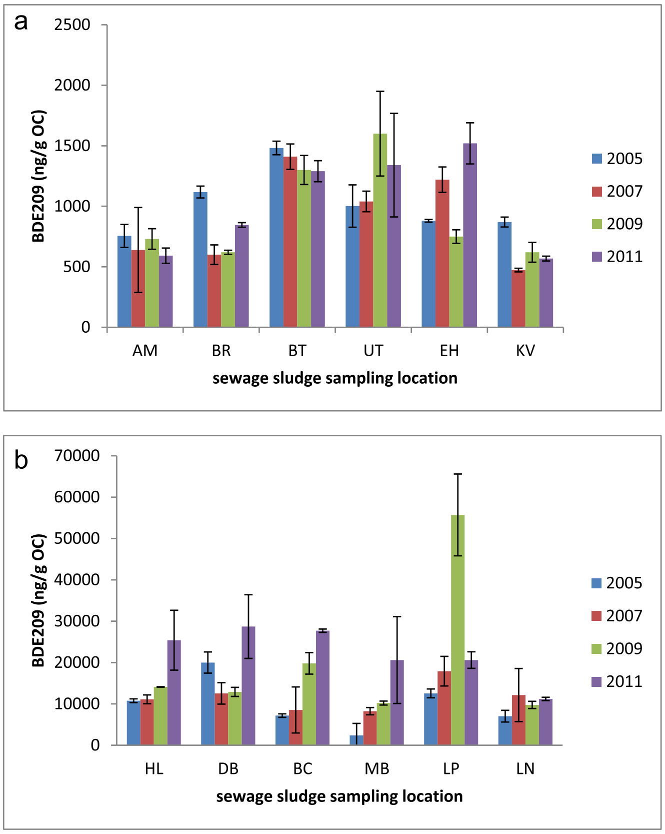

Fig. 4. Overview of BDE209 concentrations (ng/g OC) in sewage sludge collected in between 2006 and 2011 from sampling sites Concentrations are an average of three week-composite samples per site in the sample year. a) The Netherlands, sample location codes: AM, UT, BR: mainly domestic wastewater, BT: domestic and industrial wastewater, KV: Large capacity STP including domestic and industrial wastewater, EH: domestic wastewater, industrial wastewater (25%) and rainwater run-off from roads. b) UK and Ireland, sample location codes: BC: and HL: domestic wastewater, LP: mainly textile industry input, MB: mixed domestic and industrial wastewater, LN: domestic wastewater (urban), Ireland: DB: domestic wastewater.

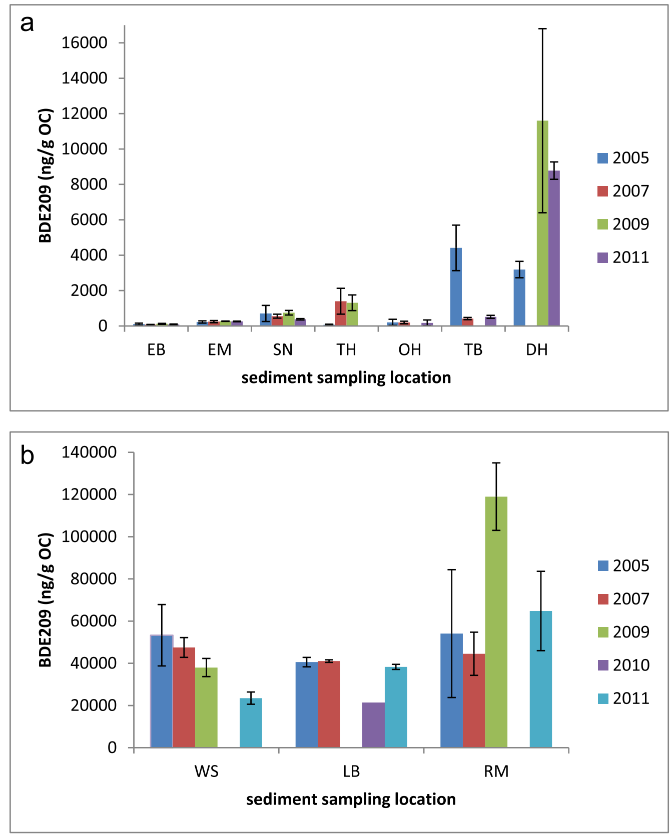

Fig. 5. Overview of BDE209 concentrations (ng/g OC) in surficial sediments collected between 2005 and 2011. Concentrations are an average of four surficial sediment samples in the sampling year. a) sampling sites: Elbe (EB), Ems (EM), Seine (SN), Thames (TH), Outer Humber (OH), Tees Bay (TB) and Dublin Harbour (DH). Note that the BDE209 concentrations in the Outer Humber sediments were < LOQ (based on samples taken and analysed in 2010). Tees Bay 2009 data is not plotted because no samples were available from the UK national monitoring program due to changes in the annual sampling program. In 2011 no samples were taken from location TH. b) sampling sites: Western Scheldt (WS), Liverpool Bay (LB) and River Mersey (RM).

3.6. Synthesis

All three time series show a constant decaBDE level during the eight years of sampling, within the given uncertainties. Only at the Western Scheldt location in the Netherlands is a decreasing trend observed. That can be related to stewardship program carried out with the textile industries sites upstream the river in Belgium. The high BDE209 levels in several UK sediments and sewage sludge remained unchanged during the program, most likely caused by frequent use of BDE209 in the textile industry. This may reflect a limited degradation into lower brominated congeners in sediment, but ongoing BDE209 emissions cannot be excluded. The three sampling series are complementary and support each other, again, within the given uncertainties. BDE209 obviously deviates in properties from other POPs such as lower brominated BDEs and for example PCBs. The present study suggests a risk of a very slow degradation of BDE209 into lower brominated BDEs which will remain for very long periods in the environment and may bioaccumulate, causing a risk for future generations. It also shows several rivers and estuaries have been very seriously contaminated by this high production volume chemical and that BDE209 can even migrate to remote areas such as northern Norway.

4. Conclusions

This 8-year study on BDE209 levels in the European environment has shown that seriously elevated levels are present in sediments in some rivers in the Netherlands (Western Scheldt) and the UK (Mersey, Liverpool Bay). Sewage sludge BDE209 concentrations in UK and Ireland samples were 10 to 20-fold higher than those in samples from the Netherlands. The stable levels over the 8-year monitoring period underpin the hypothesis that BDE209 will not quickly disappear from these locations studied. BDE209 was found in glaucous gull eggs from a remote location and in sparrow hawk eggs from the UK. This shows that BDE209 is able to bioaccumulate in birds, although to a relatively low level. Indications for debromination of BDE209 in eggs were found.

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CRediT authorship contribution statement

H. Leslie: Conceptualization, writing
S. Brandsma: writing, review and editing
J. Barber: sampling, methodology, writing, review and editing
G. Gabrielsen: glaucous gull egg sampling, writing
Ph. Bersuder: methodology, writing, sampling UK and Ireland, review and editing
J. Barry: data curation, statistics, review and editing
R. Shore: methodology, sparrowhawk egg sampling, review and editing

L. Walker: sparrowhawk egg sampling, review and editing

J. de Boer: Conceptualization, writing, funding acquisition, supervision

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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In Memoriam - Just before finalizing this manuscript we received the sad news that our colleague and co-author Richard Shore passed away. Professor Richard Shore was a dedicated researcher who greatly contributed to wildlife science, and an esteemed colleague who will be deeply missed.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.145174.

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