Article (refereed) - postprint

Crosse, John D.; Shore, Richard F.; Wadsworth, Richard A.; Jones, Kevin C.; Pereira, M. Glória. 2012 Long-term trends in PBDEs in sparrowhawk (Accipiter nisus) eggs indicate sustained contamination of UK terrestrial ecosystems. *Environmental Science & Technology*, 46 (24). 13504-13511. 10.1021/es303550f

Long term trends in PBDEs in sparrowhawk (*Accipiter nisus*) eggs indicate sustained contamination of UK terrestrial ecosystems

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Abstract

PBDE contamination in terrestrial biota is relatively poorly characterised and robust data on temporal trends are scarce. We determined long term (1985 – 2007) trends in the UK terrestrial environment by measuring PBDE concentrations in the eggs of a sentinel species, the sparrowhawk (*Accipiter nisus*). Five BDEs were the most abundant (BDE 99> 47>153> 100> 154) and their concentrations, and that of the sum PBDEs (ΣPBDE), increased from the mid-1980s, peaking in the mid-late 1990s at levels that were sustained until the end of the study. This, and the predominance of BDE99, contrast with patterns in piscivorous species and suggest sparrowhawks, and perhaps terrestrial species more widely, may be relatively poor metabolisers of penta-BDEs. BDE 196, 197, 201 and 203 concentrations increased linearly through the study, indicating ongoing, increasing contamination, possibly from the presence of these congeners in, and/or debromination of, deca-BDE formulations. Overall, ΣPBDE concentrations in eggs (34 - 2281 ng/g wet weight) were some of the highest ever reported in birds from Europe. We found no relationship between ΣPBDE concentrations and eggshell thickness but 18% of the sparrowhawk eggs collected between 1994 and 2007 had concentrations >1000 ng/g, a threshold concentration associated with adverse reproductive effects in other raptors.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are flame retardants added to plastics, textiles, foams and other materials to enhance their fire resistive properties (*1*). They have been used globally since the 1970s (*2*) in three technical formulations, Penta- (PeBDE), Octa- (OBDE) and Deca- (DeBDE). Although legislation has led to the phasing out or banning of PeBDE and OBDE mixtures in the EU and North America, in-use products act as contemporary sources with dust and vapour releases a significant pathway (*3*). Levels in environmental matrices and biota are enhanced in and around urban areas and industrial conurbations (*4*, *5*). DeBDE it is currently unrestricted for non-electronic/electrical uses, which made up the bulk of its applications (*6*), and may be a source of lower brominated congeners. Several studies have demonstrated degradation of BDE209, the primary component of DeBDE, in biotic and abiotic systems (*7*, *8*).

In some countries, such as the UK, the cessation of use of PeBDE and OBDE technical mixtures has resulted in a subsequent decline in soil and air concentrations of some of the BDEs associated with these technical mixtures (*9*, *10*, *11*). Analysis of sediment cores from the UK coast also indicate that concentrations of some lighter congeners have decreased (*12*, *13*). Similar temporal trends have been observed in Swiss lake sediments (*3*). Studies of temporal changes in PBDEs concentrations in biota from the European Union have largely focussed on aquatic species (*12*, *14-16*) although only four have reported temporal trends in any detail (*14*, *17-19*). Generally, levels of PBDEs in aquatic organisms mirror the legislatively-mediated reductions in environmental inputs and concentrations.

PBDE contamination has been less widely studied in terrestrial wildlife (*20*) and studies have often focussed primarily on spatial rather than temporal variation in contamination (*4*, *21*). Trends in DeBDE concentrations in terrestrial raptors from the UK and Sweden have been reported (*22*) and there have been two detailed time-trend studies of wider PBDE contamination from mainland Europe, one in tawny owl (*Strix aluco*) eggs (*23*) and the other in peregrine falcon (*Falco peregrinus*) eggs (*24*). Detected PBDEs declined in concentration over time in tawny owl eggs, but only significantly for BDEs 47 and 153. PBDEs concentrations in peregrine eggs rose and then subsequently declined, a pattern similar to that in aquatic fauna, and it is unclear to what extent the peregrines may have fed on seabirds rather than, or as well as, terrestrial prey. The differences in temporal PBDE trends between these studies, and the scant availability of data overall, suggest there is no clear general temporal pattern for PBDE contamination in the eggs of terrestrial birds. There are no long-term data on PBDE concentrations in terrestrial species in Britain.

The sparrowhawk, an apex terrestrial predator that preys on small passerine birds, nests largely in rural woodland but also in urban areas where the opportunity arises (*25*). They have been used as a sentinel species for monitoring trends in environmental contamination with organochlorine pesticides (*26*), polychlorinated biphenyls and mercury (*27*). Our overall aim in the present study was to determine temporal and spatial trends in PBDE contamination in the UK terrestrial ecosystem using sparrowhawk eggs as an environmental monitoring tool. We had several specific objectives. The first was to determine how individual congener PBDE concentrations, sum PBDE (ΣPBDE) concentrations and congener profile varied in eggs over time. The second objective was to examine if PBDE concentrations in sparrowhawk eggs varied spatially such that they were positively associated with proximity to human populations. This was because the density of people has previously been found to be positively correlated with ΣPBDE concentrations in birds eggs in North America and Europe (*4*, *5*), and with more highly brominated congeners in peregrine falcon eggs in the US (*28*), consistent with the concept that environmental PBDE concentrations are highest in proximity to anthropogenic sources (*5*). As part of this spatial analysis, we also explored whether PBDE concentration varied in relation to land-use type as sewage applied to agricultural land may also be a potential source of PBDEs to the terrestrial food chain (*29*). Our final objective was to determine if there was any relationship between egg PBDE concentrations and eggshell thickness, as PBDEs have recently been associated with eggshell thinning in at least one raptor, the American kestrel (*Falco sparverius*) (Fernie *30*).

EXPERIMENTAL SECTION

Egg sampling and analysis. Failed or abandoned sparrowhawk eggs were taken from nests by licensed egg collectors and archived as part of the monitoring activities of the Predatory Bird Monitoring Scheme (PBMS) in the UK (*27*; *31*). Egg weight, length and breadth were measured and the eggs were then blown or cracked open. The shells were washed, air-dried and reweighed, while the egg contents were homogenised and stored in glass jars at -20°C until analysed. Samples were selected from the PBMS archive for PBDE analysis based on the criteria of covering the longest temporal period in eggs from the smallest possible geographical area, which was found to be the region of England directly east and within 250 km of the Welsh border (Figure SI-1). Sampling years were determined by the availability of eggs in the archive, the criterion being that three-five eggs, each from a different nest, were available for analysis for each sampling year. There were sufficient eggs for 10 sampling years that spanned the period 1985-2007. When more than one egg was available from any given nest, the egg for analysis was selected at random as laying order was not known.

Egg homogenates were extracted, cleaned and analysed as described elsewhere (Crosse *19*). The mean (± SD) wet weight (wet wt.) and % lipid content of egg homogenates (n = 43) were 1.98 ± 0.34 g and 8.35 ± 6.30%, respectively. The cleaned-up extract was analysed by

Gas Chromatography Mass Spectrometry (GC-MS, Thermo-Finnigan Trace MS) fitted with a ThermoQuest AS2000 autosampler and using a 30m CPSIL-8 CB pesticide column (0.25 mm diameter, 0.12 µm internal diameter) and calibrated using seven PBDE standards in a linear range 2.5-250 pg/ul. Eggs were analysed for a suite of 27 PBDE tri-Octa BDE congeners (17, 28, 32, 35, 37, 47, 49, 51, 66, 71, 75, 77, 85, 99, 100, 118, 119, 126, 128, 138, 153, 154, 166, 183, 190, 196, 197).

Instrument Limit of Detection (LoD), defined as the lowest observable calibration standard, ranged from 2.5 pg/ul for tri-hexa BDEs to 5 pg/ul for BDE183 and 12.5 pg/ul for Octa BDEs; these were equivalent to average egg LODs of 0.0631, 0.126 and 0.316 ng/g wet wt. respectively. A total of five procedural blanks were run alongside samples and samples were blank-corrected. Mean recoveries for $^{13}C_{12}$ labelled BDE congeners 28, 47, 99, 100, 153, 154 and 183 (Wellington Laboratories, Guelph, Ontario, Canada) ranged between 73.4 and 95.6% across homologue groups and concentrations were recovery corrected (*19*). A quality control (QC) standard was used to ensure precision and was analysed together with unknowns. The QC contained five PBDEs that encompassed tri-hepta homologue groups at concentrations of 2.5-250 pg/ul. Batches of samples were only deemed to pass quality control if concentrations were +/- 10% of expected values.

In addition to the PBDEs in the calibration standard, we identified during the course of the study three additional potential octa-brominated BDEs. These were detected, along with known octa homologues (BDEs 196 and 197), with mass fragments of 640 and 643 and further confirmed using additional masses of 320 and 802, as done elsewhere (*32*, 33). These five octa homologues comprise a distinctive pattern of peaks in the chromatogram (Figure SI-2) that has been reported in several other studies (*3*, *7*, *8*); the three additional peaks are BDEs 201, 202 and 203. The distinctive chromatographic pattern and the confirmation of the potential octa-BDEs using three qualifier ions are strongly indicative of BDEs 201, 202 and 203 and they are reported as such in this study. Because of the absence of these congeners in our calibration standard, we 'semi quantified' the concentrations of these congeners using the calibration curves generated for BDEs 196 and 197.

Statistical analyses. Individual PBDE congener and ΣPBDE concentrations are presented on a wet wt. basis and were corrected for desiccation by multiplying concentrations by the total egg weight/volume ratio. Egg volume was estimated using the equation $V = 0.51 \times LB^2$, where L is egg length and B is egg breadth (*34*). Some eggs were damaged on receipt and mean volume/weight ratios could not be calculated. In those cases, the mean volume/weight ratio for other eggs received that year was used to adjust for desiccation. Egg shell index, a measure of shell thickness, was calculated as shell weight (mg)/shell length x breadth (mm) (*35*).

Concentrations below the LoD were recorded for congeners in at least some of the eggs. Ascribing a single value to all observations below a LoD can introduce misleading biases into analysis of statistical properties and when estimating correlations and regressions (*36, 37*). We therefore interpolated values for "below LoD" observations (*36*) for those congeners when the overall percentage of such observations across all eggs was less than 20%, This was not done for those congeners that had more "below LoD" concentrations in more than 20% of eggs and no statistical analyses were conducted on those datasets. Congener sum PBDE concentrations (ΣPBDE) were calculated as the sum concentrations of all congener concentrations that were determined but, for this calculation, concentrations below the LoD were assigned a value of zero. The data sets for individual congeners and ΣPBDE concentrations were skewed and Box-Cox transformations were employed to ensure normality and that the underlying assumptions of statistical tests were met.

Associations between ΣPBDEs, PBDE congeners and shell index were evaluated using Pearson's rank correlation coefficient. Temporal trends were analysed using linear, second order polynomials or split-line regressions and relationships between concentrations and time, land-use, human population density and eggshell thickness were modelled using linear and polynomial regression. Suitability of models was assessed using Akaike Information Criterion (AIC). Analyses that included shell index were performed only on samples for which shell index could be reliably calculated (i.e. undamaged eggs).

Human population density in proximity to nest sites was estimated by the "sphere of influence" approach (*10*) at a 200m resolution using population data from the 2001 UK census (*38*) . This approach considered inputs from the whole of England and Wales with populations closer to the sampling point having the most influence. In this calculation,

$$\mathbf{A=\Sigma(\mathit{pop_i/r_i^2})}$$

where pop_i = population density, $r_i^2 = (E_i-E_0)^2+(N_i-N_0)^2$, E_i is any/all Easting coordinates in England, E_0 is the Easting of the nest site, N_i is any/all Northing coordinates in England and N_0 is the Northing of the nest site.

Land use was classified within a $10km^2$ area around the nest site from which an egg was taken; this represented the approximate foraging range for individual nesting sparrowhawks (*39*, *40*). Land use was determined by GIS using data from the 2000 UK Land Cover Map (*41*) at 1km resolution. For simplicity, land use classifications were condensed into five groups: urban, arable, grassland, woodland and semi-natural. Land use within the 10km radius was considered both as percentages of the whole that these five classes made up and as an overall class based on the majority land use within the 10km. These land-use types were then used to model ΣPBDE and BDE congener concentrations in the sparrowhawk eggs.

RESULTS AND DISCUSSION

Congener profile. A total of 27 congeners were detected in one or more eggs (Tables SI-1, 2). BDEs 47, 99, 100, 153 and 154 were detected in all eggs, BDEs 35, 66, 138, 183, 196 197, 201, 203 were detected in >80% eggs and BDEs 28, 49, 77, 85, and 202 were detected in >50% of eggs. Only BDEs 32, 75 and 166 were not detected in any eggs. BDE99 was the dominant congener in eggs (Figure 1), and five PeBDE-associated congeners dominated the overall PBDE profile (BDE 99>BDE 47>BDE 153>BDE 100>BDE 154; Figure 1), occurring in concentrations an order of magnitude higher than all other congeners in most years. These five congeners comprised, on average, almost 90% of the ΣPBDE concentration and each was significantly correlated with concentrations of ΣPBDEs and each other (Table SI-3). This suggests that the PeBDE mixture is likely to be the most important source of PBDE contamination in sparrowhawk eggs in Britain.

The dominance of BDE 99 in the present study was consistent with that found in sparrowhawk tissues elsewhere (*42*, *43*) and in the eggs of other terrestrial birds of prey such as tawny owl and little owl (*Athene noctua*) (*44*, *45*). This contrasts markedly to the congener profile for marine systems (*12*, *15*, *46-48*) and in the eggs of piscivorous birds (*14*, *16*, *19*, *20*, *49*) where BDE47 has been found to predominate. BDE47 is both a major component of the PeBDE mixture and a breakdown product of BDE99 (*50*). The dominance of BDE99 (rather than BDE 47) in sparrowhawks and owls suggests this congener may not be readily degraded by terrestrial predatory birds and it has been reported that PBDE half lives are in the order of months to years in some raptor species (*21*). However, poor metabolism of BDE99 in terrestrial species may extend beyond birds of prey as BDE99-dominated congener profiles have reported in lower trophic terrestrial species such as the great tit (*Parus major*) (*4*), blue tit (*Cyanistes caeruleus*), (*51*) and common magpie (*Pica pica*) (*52*). A relative lack of breakdown of BDE99 in terrestrial systems may well be due to a lack of metabolic capability that, in aquatic systems, is provided by certain fish species that have been shown to be good metabolisers of PeBDE and more brominated homologues (*53*).

Temporal patterns in PBDE concentrations. ΣPBDE concentrations increased linearly up until the 1990s (R^2=39.7, $F_{1, 42}$=17.5, P<0.001) and then remained at the same concentration up until the 2007, the last sampling year; temporal trends for BDEs 47, 99, 100, 153 and 154 were similar (Figure 2). The statistically determined "breakpoints" after which concentrations ceased to increase ranged between 1992 and 1998 for the different congeners and for ΣPBDEs but all were co-correlated (Table SI-3) and the geometric standard deviations for concentrations in those years were relatively high. Thus, there is no underlying rationale to suggest that difference in the timing of the breakpoints between congeners was significant.

The persistence of the predominant PeBDE associated congeners in sparrowhawk eggs in the present study, with concentrations remaining high throughout the late 1990s and 2000s despite the phasing out of the PeBDE and OBDE technical products, is atypical of other European studies. A rise and subsequent decline in PBDEs has been observed in the eggs of aquatic and terrestrial birds from Europe (*14*, *19*, *24*, *45*, *49*), in other aquatic organisms (*12*, *15*, *17*), and in air and soils in the UK and Norway (*10*, *54*). One possible reason for the maintained concentrations in eggs may be relatively poor metabolism of PeBDE-associated congeners by sparrowhawks and perhaps terrestrial species generally, as suggested by the general predominance of BDE99 in the congener profiles of terrestrial birds. Other factors may include exposure to re-circulating sources such as dust, and/or the existence of fresh PBDE sources, such as disposal of waste electronic and electrical equipment and application of sewage sludge to land. Finally, usage in non-electrical products has shifted from PeBDE and OBDE to DeBDE and levels of BDE209 have increased in marine sediments from the UK and Europe (*3*, *13*) and in sparrowhawk eggs (*22*). Debromination of deca-BDE may result in some new contamination of wildlife by lower brominated congeners.

In contrast to the PeBDE associated congeners, concentrations of the hexa-BDE 138 and the octa-BDEs 196, 197, 201and 203 increased linearly over time ($0.105 \leq R^2 \leq 0.404$, $F_{1,42} > 5.30$, $P<0.05$ in all cases; Figure 3). Concentrations of the octa-BDE congener, BDE 202, also increased linearly over time from 1990, the year it was first detected in samples (data not shown). One or more of the five octa-BDEs have previously been reported in other bird eggs (*5*, *18*, *55*). All but BDE 202 are components of the OBDE formulations and BDEs 196 and 197 are also present in small quantities in the DeBDE formulation Bromkal 82-ODE (*32*). However, all four congeners are frequently suggested as breakdown products of BDE209, as is BDE202 which is not native to any technical product (*3*, *32*, *56*). Debromination of BDE209 has been demonstrated experimentally in several studies (*7*, *57*, *58*) and proposed pathways include one or more of these five octa-BDEs as breakdown products (*50*). The continuing rise in the concentration of these BDEs in sparrowhawk eggs in the current study suggest ongoing and increasing contamination associated with OBDE and/or DeBDE formulations.

Unlike all the other congeners for which we examined time trends , BDE35, detected in 93% of sparrowhawk eggs, declined linearly in concentration over time, although this was did not quite achieve statistical significance ($R^2=0.085$, $F_{1, 41}=3.69$, $P=0.06$; Figure 3). This congener has been found in other biota from the UK and elsewhere (*9*, *18*) and similar long-term (1976-2006) linear declines in concentrations have been detected in gannet eggs from two colonies in Scottish waters (*19*). The underlying mechanism both for the formation and decline of this congener appears to be independent of inputs of more highly brominated PBDEs into the environment. This congener is only reported in EU studies and in one study from the vicinity of an E-waste recycling centre in China, suggesting that this congener is somehow “unique” to EU systems or is generally unreported.

Spatial trends. Interpretation of relationships between PBDE concentrations and either land use or population density are likely to be confounded by temporal changes in inputs of PBDEs into the environment. We therefore restricted our analysis of the relationship between egg PBDE concentrations and human population density for the time period when concentrations of the main congeners were relatively stable which was after the break-points identified in the long term time trends (Figure 2).

Concentrations of ΣPBDE or any individual BDE congeners were not correlated with either the % of urban land cover or the % of arable land (to which sewage sludge may be applied) in the proximity of the nest site ($R^2 \leq 0.075$, $F_{1, 21} \leq 1.64$, $P>0.05$). When the area around the sparrowhawk nest site was simply characterised by majority land use type, there was no difference in PBDE concentrations in eggs from different land use types. Unsurprisingly, human population density was correlated with % urban land cover ($R^2=0.855$, $F_{1, 41}=236.1$, $P<0.001$) and, consistent with the lack of any relationship between % urban land use and PBDE concentrations, there were no significant relationships between concentrations of ΣPBDE, BDEs 47, 99, 100, 153 or 154 and weighted population density ($R^2 \leq 0.202$, $F_{1, 24} \leq 4.12$, $P>0.05$ in all cases). These results contrast to other studies where proximity to urban areas has significantly explained some of the variation in PBDE concentrations in air, sediments and birds eggs (*4-6*, *47*). One possible reason why there was no detectable relationship between proximity of the nest site to urban locations/human populations and egg PBDE concentrations may be that sparrowhawks spatially integrate PBDE contamination over a wide area because their hunting areas are relatively large and their prey are also highly mobile.

ΣPBDE concentrations and potential toxicity. ΣPBDE concentrations in sparrowhawk eggs ranged from 34 – 2281 ng/g wet wt, equivalent to 382 -54,972 ng/g lipid weight. There was no significant association between ΣPBDEs and shell index (Figure 4) nor between any of the major individual congeners and shell index (data not shown). This contrasts to studies on in American kestrels where negative associations have been found (*30*) for PBDE concentrations that were of similar wet wt. magnitude to those reported in the current study. In fact, shell index in sparrowhawks increased positively over time (R^2= 0.114, $F_{1, 41}$= 5.00, $P<0.05$; Figure 4) and this is most likely due to falling DDE concentrations and subsequent recovery from the shell-thinning effects of DDE (*25*).

Although the PBDE congener profiles in sparrowhawk eggs (Figure 1**)** are similar to the profiles found in the eggs of other terrestrial birds in Europe (*4*,*44*), yearly arithmetic mean concentrations of ΣPBDE in sparrowhawk eggs exceeded the concentrations reported in those studies by one-two orders of magnitude. ΣPBDE concentrations in sparrowhawk eggs in the present study were comparable to those reported in the eggs of coastal peregrine falcons from Sweden (*24*) and Spain (*59*), although concentrations in the sparrowhawk eggs exceed those in terrestrial Spanish peregrine eggs by more than double in later years. Generally, ΣPBDE concentrations in eggs from the present study are more akin to those in bird eggs from North America (*20*, *59*) than in eggs from elsewhere in Europe. This may reflect greater consumption of PBDEs in Britain compared with elsewhere in Europe (*1*) and later phasing out of use and production of PeBDE.

A ΣPBDE concentration of 1000 ng/g wet wt. has been suggested as a “threshold” concentration in ospreys (*Pandion haliaetus*) above which there may be impacts on productivity (*60*). No such thresholds have yet been proposed for sparrowhawks but four of eggs in the present study had concentrations >1000 ng/g wet wt. It is therefore possible that PBDEs may have been a contributory factor in the failure of those eggs. They were collected between 1994 and 2007, the period when ΣPBDEs were at a maximum, and represented 18% of all the eggs from that period that we examined. The UK sparrowhawk population increased rapidly through the 1980s, a recovery from the impacts of organochlorine insecticides (*26*); this was also before ΣPBDE concentrations peaked in sparrowhawk eggs (Figure 2). However, the sparrowhawk population in England, from where all the eggs in the present study were sourced, was estimated to have declined by 26% between 1994 and 2007, despite an increase in potential prey species (*61*). This decline in population size at the time of maximal egg ΣPBDE concentrations may be simply coincidental, but the high and maintained (until at least 2007) PBDE contamination in sparrowhawks raises significant concerns about the fate and toxicological potential of PBDEs in the terrestrial ecosystem in Britain. Monitoring of current levels of contamination and impacts are needed.

Acknowledgements

John Crosse was supported by a Natural Environment Research Council (NERC) studentship ((DTG) NE/G523571/1). Egg material was provided by the Predatory Bird Monitoring Scheme (PBMS) which is currently co-funded by the NERC Centre for Ecology & Hydrology, Natural England, the Environment Agency, the Campaign for Responsible Rodenticide Use (CRRU) and the Royal Society for the Protection of Birds (RSPB). We thank the licensed volunteers who collected the eggs, and Lee Walker, Sabino Del Vento and Dave Hughes for logistical support.

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Figure 1 BDE congener profile in sparrowhawk eggs collected between 1985 and 2007 and in the DE-71 and 70-5DE PeBDE technical formulations (La Guardia et al 2006). Relative abundance data for each congener in eggs was the % contribution to the ΣPBDE concentration and the average for all eggs within the year was taken.

Figure 2 Trends over time (split line regression models of Box-Cox transformed wet wt. concentrations) in PBDE congeners (47, 99, 100, 153, 154) and ΣPBDE concentrations in sparrowhawk eggs. Data with different symbols distinguish the years before and after the break-points in the regression models.

Figure 3 Trends over time (linear regression models of Box-Cox transformed wet wt. concentration data) in PBDE congeners (35, 138, 196, 197,201, 203) in sparrowhawk eggs.

Figure 4 Scatterplot of eggshell index against (Box-Cox transformed) wet wt. ΣPBDE concentration (upper graph) and relationship between shell index and date of collection (bottom graph) for sparrowhawk eggs.

Figure SI-1 Location in Britain of sparrowhawk nests from which eggs were sampled

Figure SI-2 Chromatogram of 5 Octa-BDE congeners. From left to right: BDE 201, 203, 197, 203, 196. Masses from (*32*, *33*).

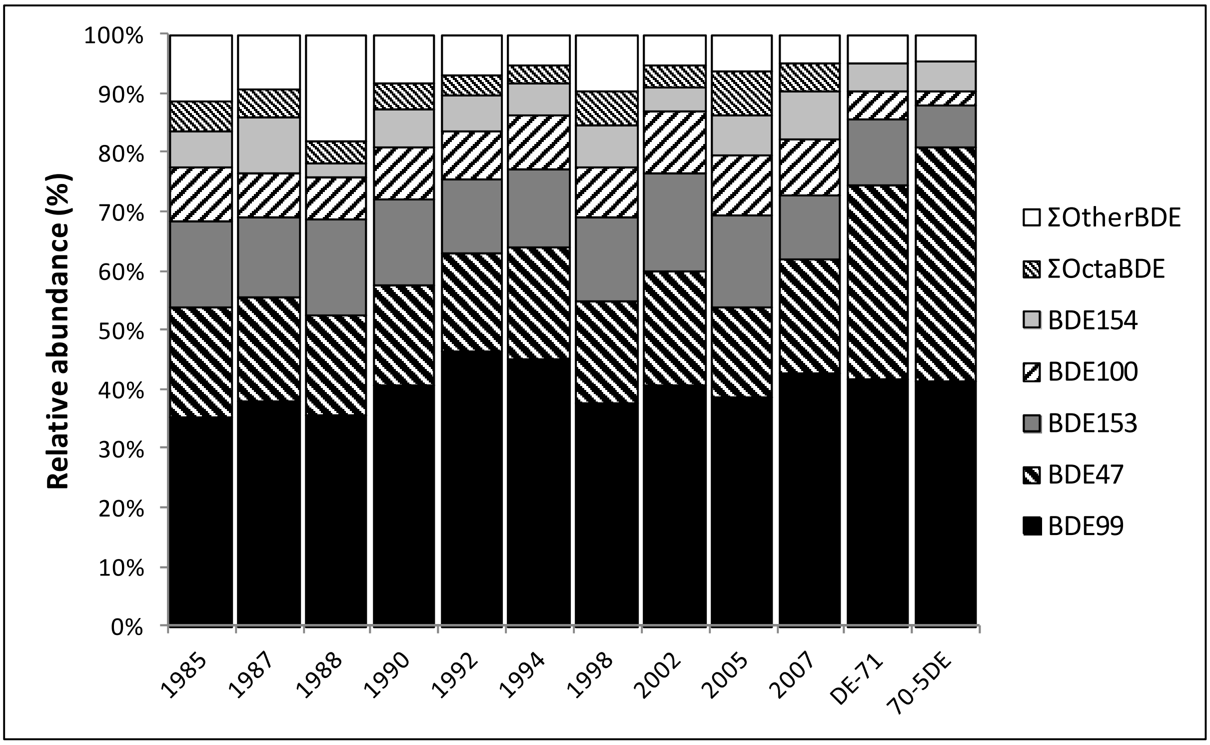
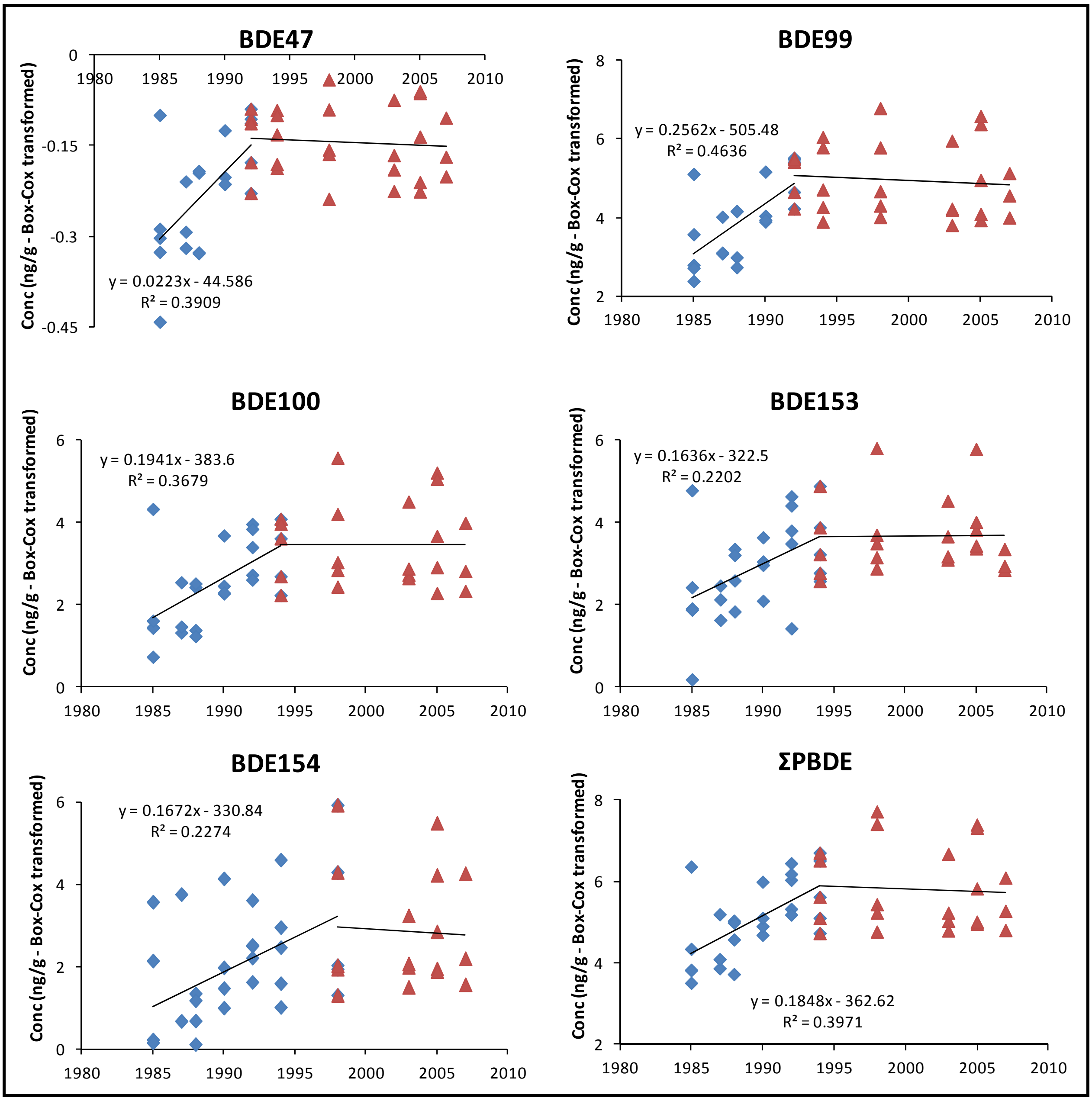

Relative abundance (%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1985
1987
1988
1990
1992
1994
1998
2002
2005
2007
DE-71
70-5DE
ΣOtherBDE
ΣOctaBDE
BDE154
BDE100
BDE153
BDE47
BDE99

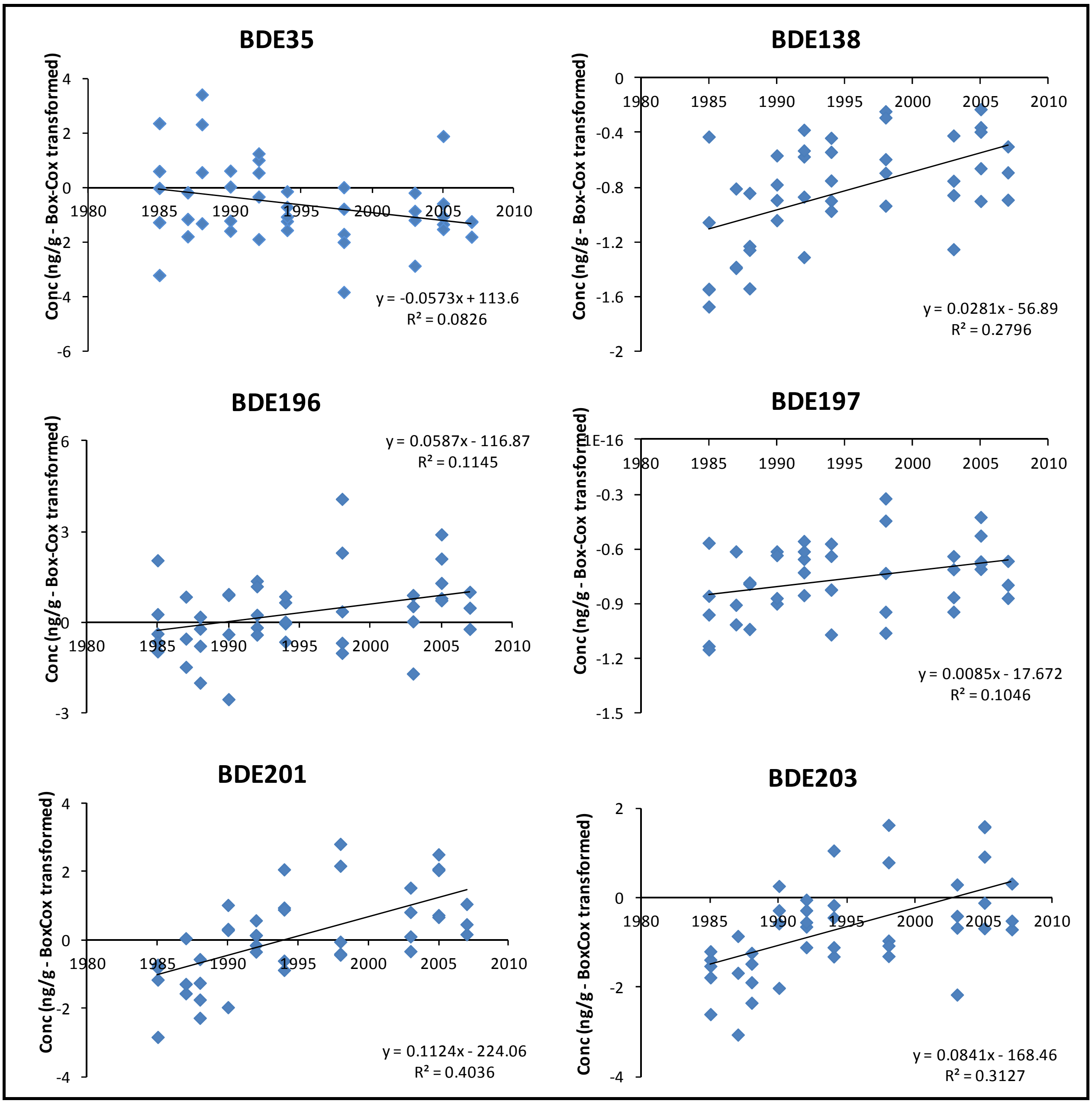
Figure 1

632



633 Figure 2

634



635 Figure 3

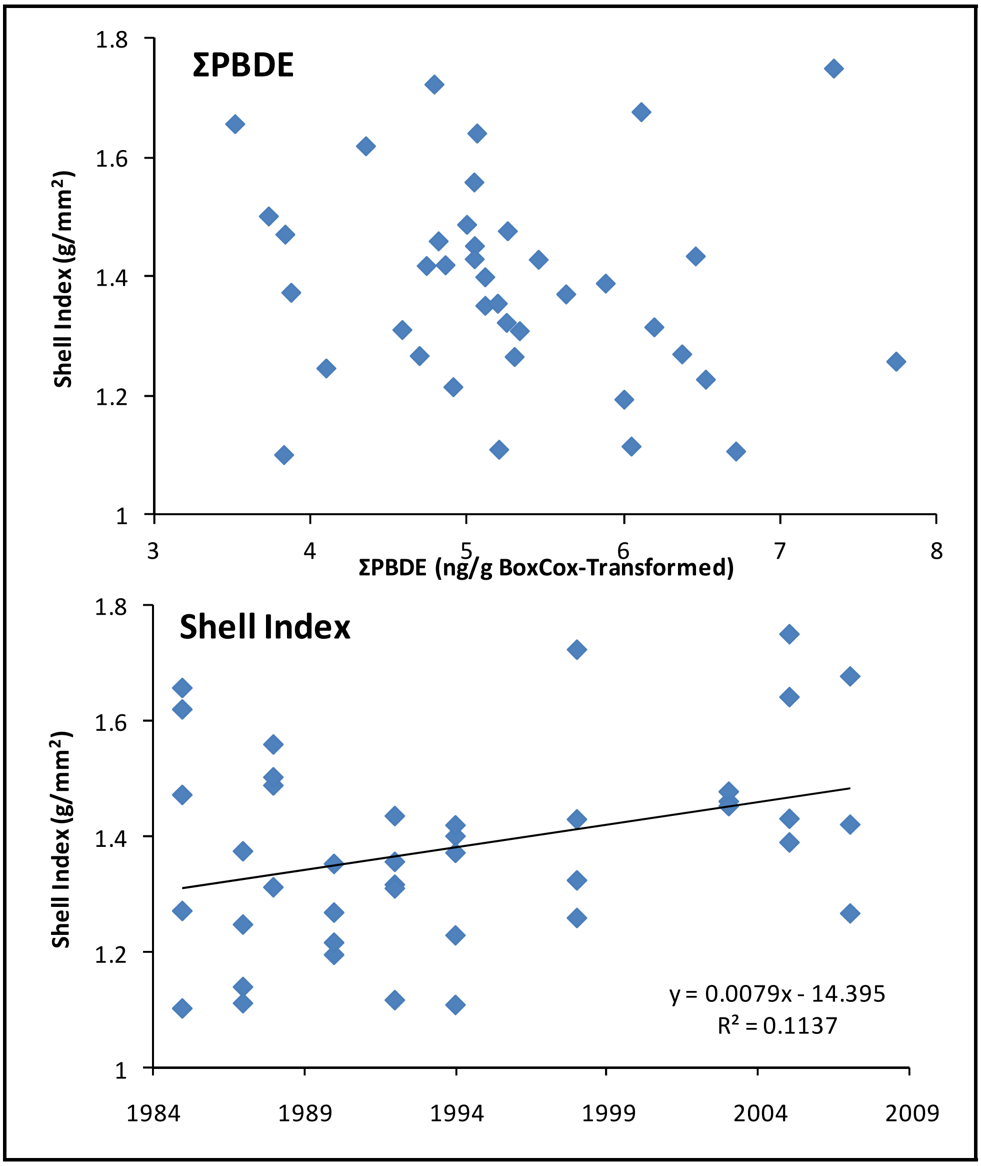

ΣPBDE
Shell Index (g/mm²)
1.8
1.6
1.4
1.2
1
3
4
5
6
7
8
ΣPBDE (ng/g BoxCox-Transformed)
Shell Index
Shell Index (g/mm²)
y = 0.0079x - 14.395
R² = 0.1137
1984
1989
1994
1999
2004
2009

Figure 4

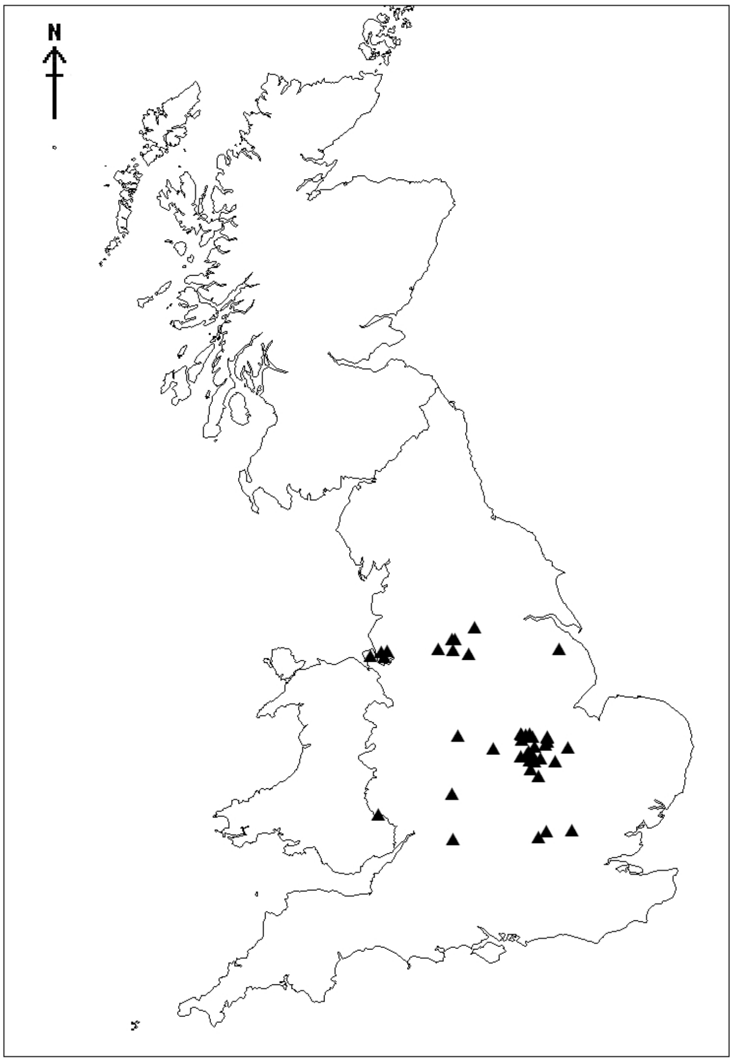


Figure SI-1

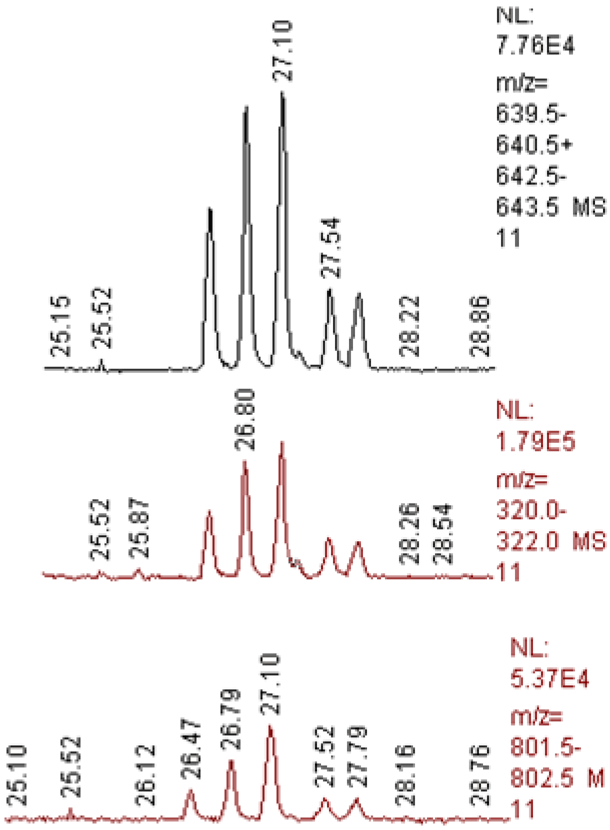
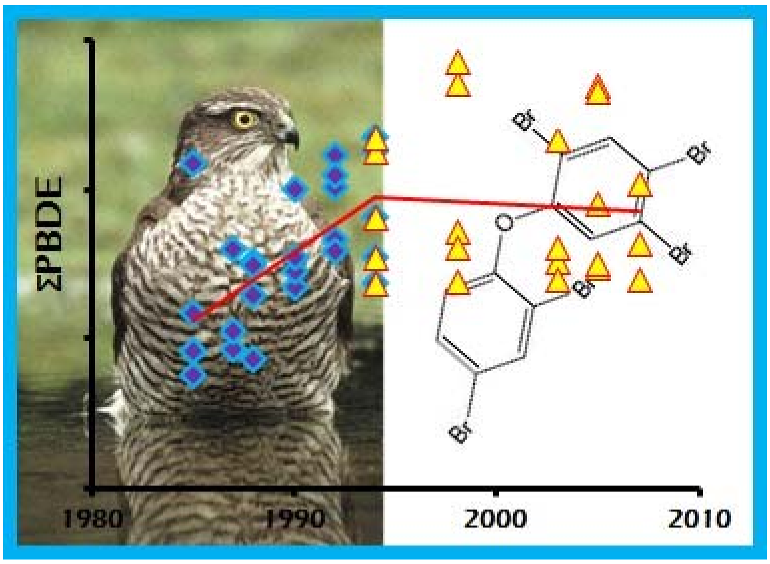


Figure SI-2



Abstract graphic

Table SI-1 Yearly geometric mean concentrations (ng/g), standard deviation and range of all BDE congeners, and ΣPBDE, detected in sparrowhawk eggs at frequencies of 80% or higher.

Table SI-2 Yearly median concentrations (ng/g), range and frequency of detects of BDE congeners detected in sparrowhawk eggs at frequencies of less than 80%.

Table SI-2 Correlation matrix of BDE congeners detected in sparrowhawk eggs at frequencies of 80% or higher and ΣPBDE.

Table SI-1. Annual geometric mean concentrations (ng/g) wet wt.), geometric standard deviation and total range of those BDE congeners detected in ≥ 80% of eggs and ΣPBDE concentrations.

		1985	1987	1988	1990	1992	1994	1998	2003	2005	2007
BDE35	**Mean**	**0.73**	**0.35**	**3.45**	**0.58**	**1.12**	**0.39**	**0.19**	**0.28**	**0.59**	**0.24**
	STDEV	0.09-0.59	0.16-0.79	0.44-27.4	0.21-1.64	0.31-4.00	0.23-0.67	0.04-0.81	0.09-0.087	0.15-2.37	0.17-0.33
	Range	0.04-10.5	0.17-0.83	0.27-30.1	0.20-1.85	0.15-3.47	0.21-0.87	0.02-1.01	0.06-0.82	0.22-6.56	0.16-0.29
BDE47	**Mean**	**14.5**	**13.8**	**15.8**	**29.5**	**55.7**	**57.2**	**72.4**	**43.6**	**69.9**	**43.2**
	STDEV	4.67-45.2	8.83-21.5	8.61-29.0	17.6-49.7	25.4-122	29.6-111	18.3-286	16.3-116	19.6-249	21.8-85.6
	Range	5.14-101	9.82-22.8	9.30-26.3	21.9-64.2	19.2-126	28.6-120	17.7-605	19.7-181	19.6-276	24.8-92.6
BDE99	**Mean**	**27.7**	**30.2**	**33.6**	**71.1**	**158**	**140**	**166**	**94.3**	**179**	**96.0**
	STDEV	9.29-82.4	17.7-51.4	15.8-71.7	38.9-130	87.8-284	54.7-359	52.4-523	36.2-245	51.7-620	54.6-169
	Range	10.9-166	22.0-55.8	15.5-64.6	49.4-175	68.7-250	49.2-423	55.3-881	45.2-385	51.2-721	54.7-169
BDE100	**Mean**	**6.88**	**6.02**	**6.73**	**14.7**	**27.7**	**27.9**	**37.7**	**24.5**	**46.4**	**21.3**
	STDEV	1.72-27.5	3.09-11.7	3.43-13.2	7.51-28.9	14.9-51.4	12.4-63.1	10.6-135	10.2-59.2	12.8-168	9.12-49.9
	Range	2.12-76.4	3.82-12.9	3.50-12.5	9.84-40.2	13.8-53.2	9.46-60.2	11.6-265	14.2-91.2	9.94-184	10.5-54.6
BDE138	**Mean**	**0.79**	**0.74**	**0.71**	**1.56**	**2.25**	**2.10**	**4.23**	**1.71**	**4.85**	**2.19**
	STDEV	0.25-2.45	0.40-1.39	0.43-1.17	0.92-2.61	0.86-5.86	1.07-4.15	1.33-13.5	0.69-4.2	1.66-14.2	1.23-3.90
	Range	0.36-0.42	0.52-1.53	0.42-1.41	0.92-3.11	0.58-6.94	1.06-5.20	1.14-16.9	0.64-5.64	1.23-19.2	1.26-3.98
BDE153	**Mean**	**9.50**	**8.08**	**15.8**	**19.1**	**35.2**	**32.4**	**45.4**	**37.5**	**60.0**	**21.3**
	STDEV	1.82-49.5	5.32-12.3	7.92-31.6	10.1-36.0	9.89-126	12.7-82.7	14.3-145	19.5-72.3	22.4-161	16.3-27.9
	Range	1.29-120	5.19-11.9	6.37-29.1	8.24-38.4	4.23-104	13.3-133	18.0-334	22.3-93.2	29.4-327	17.5-28.9
BDE154	**Mean**	**3.25**	**4.06**	**2.30**	**8.57**	**12.1**	**12.5**	**22.2**	**9.03**	**26.5**	**14.5**
	STDEV	0.64-16.4	0.50-32.7	1.32-4.00	2.15-34.2	5.89-24.9	3.15-49.5	3.19-154	4.33-18.8	5.62-125	3.55-29.5
	Range	0.81-35.4	0.80-42.7	1.19-3.85	2.72-62.5	5.08-37.0	2.77-98.5	3.70-372	4.50-25.5	6.60-241	4.80-70.9

Table SI-1 continued

		1985	1987	1988	1990	1992	1994	1998	2003	2005	2007
BDE183	**Mean**	**6.22**	**4.82**	**3.69**	**6.92**	**7.58**	**6.42**	**6.52**	**2.55**	**11.36**	**4.66**
	STDEV	2.06-18.7	1.04-22.4	1.29-10.6	1.51-31.8	1.26-45.4	1.10-37.3	0.51-83.5	0.71-9.13	2.05-62.9	1.97-11.0
	Range	2.15-35.8	1.16-24.6	1.02-11.0	0.87-27.7	0.44-54.2	0.70-57.1	0.59-464	0.79-12.9	0.95-111	2.61-12.5
BDE196	**Mean**	**1.06**	**0.67**	**0.49**	**0.76**	**1.55**	**1.18**	**2.74**	**0.94**	**4.78**	**1.52**
	STDEV	0.32-3.53	0.21-2.17	0.19-1.27	0.15-3.88	0.70-3.46	0.65-2.16	0.32-23.5	0.30-2.96	1.88-12.1	0.82-2.81
	Range	0.38-7.76	0.23-2.33	0.13-1.19	0.08-2.53	0.66-3.92	0.52-2.36	0.50-59.1	0.18-2.45	2.06-18.3	0.80-2.73
BDE197	**Mean**	**1.59**	**2.45**	**2.21**	**4.05**	**6.40**	**3.49**	**8.32**	**3.20**	**11.86**	**3.36**
	STDEV	0.41-6.22	0.71-8.50	1.15-4.24	1.56-10.6	2.95-13.9	1.10-11.1	0.76-90.7	1.38-7.42	4.23-33.3	1.77-6.4
	Range	0.51-14.5	0.93-9.97	0.83-3.14	1.64-9.99	2.10-15.8	0.73-14.0	0.76-206	1.30-8.22	5.00-56.5	1.93-6.8
BDE201	**Mean**	**0.29**	**0.40**	**0.24**	**0.94**	**1.10**	**1.66**	**2.31**	**1.73**	**5.08**	**1.79**
	STDEV	0.12-0.70	0.17-0.95	0.11-0.49	0.26-3.45	0.68-4.30	0.49-5.58	0.49-10.9	0.77-3.92	2.18-11.9	1.14-2.80
	Range	0.06-0.49	0.21-1.07	0.10-0.58	0.14-2.84	0.72-1.81	0.42-8.03	0.66-16.9	0.73-4.70	1.99-12.5	1.21-2.92
BDE203	**Mean**	**0.19**	**0.16**	**0.18**	**0.53**	**0.60**	**0.68**	**0.84**	**0.49**	**1.96**	**0.75**
	STDEV	0.11-0.32	0.05-0.48	0.11-0.29	0.12-0.40	0.40-0.90	0.27-1.74	0.23-3.14	0.17-0.37	0.71-5.46	0.4-1.3
	Range	0.08-0.31	0.05-0.43	0.10-0.30	0.13-1.32	0.34-0.97	0.27-2.91	0.27-5.17	0.12-1.37	0.51-5.00	0.5-1.39
ΣPBDE	**Mean**	**79.7**	**80.5**	**98.1**	**177**	**344**	**311**	**459**	**233**	**465**	**226**
	STDEV	25.2-252	39.6-164	53.4-180	99.8-314	198-598	131-736	119-1770	99.7-545	145-1500	120-426
	Range	33.6-582	48.0-181	41.6-155	109-402	179-634	114-821	120-2280	123-809	154-1640	129-449

Number of eggs analysed per year were 3 in 1987 and 2007, 4 in 1988, 1990 and 2003, and 5 in all other years

Table SI-2. Annual median concentrations (ng/g wet wt.) and range s of those BDE congeners detected in less than 80% of eggs

		1985	1987	1988	1990	1992	1994	1998	2003	2005	2007	%
BDE17	no. of detects	0	0	0	0	1	0	1	2	1	0	9.30
	Median	**-**	**-**	**-**	**-**	**ND**	**-**	**ND**	**0.11**	**ND**	**-**	
	Range	-	-	-	-	ND-0.28	-	ND-0.17	ND-0.28	ND-0.31	-	
BDE28	no. of detects	2	2	2	1	4	2	3	3	3	1	53.5
	Median	**0**	**0.13**	**0.08**	**ND**	**0.27**	**ND**	**0.26**	**0.30**	**0.13**	**ND**	
	Range	ND-0.64	ND-0.18	ND-0.18	ND-0.11	ND-0.72	ND-0.22	ND-7.39	ND-0.42	ND-0.40	ND-0.36	
BDE37	no. of detects	0	0	1	1	1	3	3	1	3	1	32.6
	Median	-	**-**	0	0	ND	0.12	0.16	ND	0.14	0.32	
	Range	-	-	ND-6.39	ND-0.11	ND-0.14	ND-0.21	ND-0.21	ND-0.21	ND-0.42	ND-0.32	
BDE49	no. of detects	1	0	0	1	2	4	4	5	4	3	55.8
	Median	**ND**	**-**	**-**	**ND**	**0**	**0.26**	**0.23**	**0.35**	**0.47**	**0.20**	
	Range	ND-1.33	-	-	ND-0.08	ND-0.63	ND-0.35	ND-0.47	0.29-1.32	ND-1.76	0.17-0.62	
BDE51	no. of detects	0	0	0	0	0	0	0	1	2	2	11.6
	Median	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**ND**	**ND**	**0.11**	
	Range	-	-	-	-	-	-	-	ND-0.17	ND-0.31	ND-0.32	
BDE66	no. of detects	2	3	3	3	3	4	5	3	5	3	79.1
	Median	**ND**	**0.26**	**0.32**	**0.67**	**0.62**	**1.20**	**1.39**	**0.95**	**1.14**	**0.41**	
	Range	0-0.52	0.22-0.29	ND-0.39	ND-0.91	ND-0.84	ND-1.25	0.3-15.87	ND-1.54	0.32-2.96	0.34-1.23	
BDE71	no. of detects	0	0	0	0	1	0	1	2	0	0	9.30
	Median	**-**	**-**	**-**	**-**	**ND**	**-**	**ND**	**0.11**	**-**	**-**	
	Range	-	-	-	-	ND-0.24	-	ND-0.22	ND-0.56	-	-	
BDE77	no. of detects	0	0	1	2	3	4	4	2	4	3	53.5
	Median	**-**	**-**	**0**	**0.09**	**0.13**	**0.27**	**0.27**	**0.14**	**0.41**	**0.22**	
	Range	-	-	ND-0.15	ND-0.19	ND-0.22	ND-0.36	ND-0.34	ND-0.44	ND-1.69	0.16-0.66	

Table SI-2 continued

		1985	1987	1988	1990	1992	1994	1998	2003	2005	2007	%
BDE85	no. of detects	0	1	2	3	4	5	5	4	4	2	69.8
	Median	**-**	**0**	**0.24**	**1.36**	**0.95**	**2.01**	**1.69**	**1.37**	**0.80**	**1.78**	
	Range	-	ND-0.93	ND-0.63	ND-2.09	ND-3.30	0.56-2.18	0.56-5.42	0.75-2.07	0.46-6.43	ND-3.01	
BDE118	no. of detects	2	1	1	2	2	4	3	0	3	3	48.8
	Median	**ND**	**ND**	**0**	**0.46**	**ND**	**1.04**	**0.91**	**-**	**1.52**	**1.19**	
	Range	ND-0.31	ND-0.073	ND-0.46	ND-2.31	ND-1.55	ND-3.12	ND-3.42	-	ND-4.53	0.67-3.02	
BDE119	no. of detects	0	0	0	1	2	2	3	4	3	2	39.5
	Median	**-**	**-**	**-**	**ND**	**ND**	**ND**	**0.34**	**0.57**	**0.30**	**1.16**	
	Range	-	-	-	ND-0.29	ND-1.07	ND-0.48	ND-2.61	0.28-1.85	ND-1.17	ND-1.63	
BDE126	no. of detects	0	0	0	0	0	2	0	0	2	1	11.6
	Median	**-**	**-**	**-**	**-**	**-**	**ND**	**-**	**-**	**ND**	**ND**	
	Range	-		-	-	-	ND-0.24	-	-	ND-0.71	ND-0.43	
BDE128	no. of detects	0	0	0	0	0	0	1	1	0	0	4.65
	Median	**-**	**-**	**-**	**-**	**-**	**-**	**ND**	**ND**	**-**	**-**	
	Range	-	-	-	-	-	-	ND-0.93	ND-0.68	-	-	
BDE190	no. of detects	0	0	1	1	2	0	2	2	0	0	18.6
	Median	**-**	**-**	**0**	**ND**	**ND**	**-**	**ND**	**0.13**	**-**	**-**	
	Range	-	-	ND-0.21	ND-0.15	ND-0.30	-	ND-0.22	ND-0.31	-	-	
BDE202	no. of detects	0	1	0	3	4	3	5	2	5	3	60.5
	Median	**-**	**0**	**-**	**0.42**	**0.44**	**0.84**	**0.46**	**0.21**	**1.32**	**1.43**	
	Range	-	ND-0.35	-	ND-0.65	ND-0.82	ND-3.96	0.36-7.58	ND-4.64	0.79-3.80	0.77-2.63	

BDEs 32, 75 and 166 were not detected in any eggs. Number of eggs analysed per year were 3 in 1987 and 2007, 4 in 1988, 1990 and 2003, and 5 in all other years

Table SI-3. Correlation matrix for concentrations of those BDE congeners detected in ≥ 80% of eggs and for ΣPBDE concentration

		BDE35	BDE47	BDE99	BDE100	BDE138	BDE153	BDE154	BDE183	BDE196	BDE197	BDE201	BDE203
BDE47	r	0.107											
	p	*0.495*											
BDE99	r	0.108	0.971										
	p	*0.493*	*0*										
BDE100	r	0.109	0.98	0.974									
	p	*0.485*	*0*	*0*									
BDE138	r	0.119	0.884	0.877	0.887								
	p	*0.448*	*0*	*0*	*0*								
BDE153	r	0.364	0.727	0.741	0.746	0.723							
	p	*0.016*	*0*	*0*	*0*	*0*							
BDE154	r	-0.071	0.823	0.821	0.851	0.788	0.35						
	p	*0.649*	*0*	*0*	*0*	*0*	*0.021*						
BDE183	r	0.104	0.202	0.26	0.231	0.398	0.022	0.468					
	p	*0.507*	*0.193*	*0.092*	*0.136*	*0.008*	*0.89*	*0.002*					
BDE196	r	0.191	0.657	0.655	0.695	0.799	0.467	0.769	0.568				
	p	*0.219*	*0*	*0*	*0*	*0*	*0.002*	*0*	*0*				
BDE197	r	0.23	0.722	0.737	0.759	0.747	0.524	0.812	0.501	0.831			
	p	*0.191*	*0*	*0*	*0*	*0*	*0*	*0*	*0.001*	*0*			
BDE201	r	0.256	0.640	0.657	0.657	0.718	0.414	0.635	0.346	0.702	0.685		
	p	*0.097*	*0*	*0*	*0*	*0*	*0.006*	*0*	*0.023*	*0*	*0*		
BDE203	r	0.247	0.596	0.605	0.602	0.667	0.368	0.720	0.239	0.628	0.595	0.926	
	p	*0.110*	*0*	*0*	*0*	*0*	*0.015*	*0*	*0.122*	*0*	*0*	*0*	
ΣPBDE	r	0.498	0.968	0.989	0.975	0.940	0.873	0.873	0.418	0.757	0.836	0.687	0.621
	p	*0.001*	*0*	*0*	*0*	*0*	*0*	*0*	*0*	*0*	*0*	*0*	*0*