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Key factors affecting liver PBDE concentrations in sparrowhawks (*Accipiter nisus*)

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ABSTRACT

High PBDE concentrations have been detected in the eggs of the sexually dimorphic Eurasian sparrowhawk (*Accipiter nisus*) but little is known about contamination levels in adult birds and how this may vary with age and sex. We characterised liver PBDE concentrations in 59 sparrowhawks that had died in central Britain between 1998 and 2009 and determined how concentrations varied with sex, age, body condition and breeding status. Five BDE congeners (99>153>47>100>154) predominated and ΣPBDE concentrations were 10-15 fold and 2-3 fold higher in starved than non-starved adult and juvenile sparrowhawks, respectively. This was likely due to a combination of remobilisation of residues from other tissues and liver wastage. Liver ΣPBDE concentrations did not vary with sex but were greater in adults than juveniles, suggestive of accumulation with age. Overall, liver ΣPBDE concentrations ranged from 43.4 to 68,040 ng/g lipid weight, amongst the highest concentrations reported in birds anywhere.

Keywords: polybrominated diphenyl ethers, sparrowhawk, body condition, penta-BDE, starvation, bioaccumulation, age class

Capsule: Liver PBDE concentrations in UK sparrowhawks are amongst the highest reported anywhere but vary markedly with body condition and age class.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants that have been used globally in a variety of products since the 1970s (Prevedouros et al., 2004; Rahman et al., 2001). There were principally three types of technical formulations, Penta- (PeBDE), Octa- (OBDE) and Deca- (DeBDE). The PeBDE and OBDE mixtures are no longer used in the European Union and North America but environmental releases from in-use products still occur, particularly through dust and vapour release (Batterman et al., 2009). PBDEs are readily assimilated into food webs and there have been numerous studies of contamination in people and wildlife; these have been reviewed by Chen and Hale, (2010); Hites (2004); Law et al., (2006).

Birds have been widely used as monitors or sentinels of environmental contaminants, including PBDEs. Measurement of PBDE concentrations in tissues and eggs has been carried out to characterise the extent of contamination (and associated potential toxicity) and both temporal and spatial trends in contamination (Chen and Hale, 2010; Marteinson et al., 2010; Newsome et al., 2010). These studies have demonstrated that, in European aquatic systems, PBDE contamination in piscivorous birds rose during the 1980s, peaked in the 1990s, and then fell sharply (Crosse et al., 2012a; Sellstrom et al., 2003), largely reflecting modelled usage of PeBDE formulations (Prevedouros et al., 2004). However, the nature of long-term time trends in PBDE concentrations in terrestrial-feeding birds in Europe is equivocal, with decreases in recent years reported in some studies, but not others (Bustnes et al., 2011; Leslie et al., 2011; Johansson et al., 2011). Variation between studies in observed trends over time may be due to a number of factors, such as differences in the range of PBDEs that were monitored, geographical variation in the extent of usage of PBDEs, inter-specific differences in accumulation and metabolism, and differences in the pharmacokinetic partitioning of PBDEs between different tissues that are then sampled for analysis.

Long term trends in contaminant concentration in terrestrial UK habitats have been tracked previously by measuring concentrations in the eggs and body tissues of the Eurasian sparrowhawk (*Accipter nisus*), a terrestrial species found throughout most of Britain and which mostly preys on small birds (Newton, 1986). Previous studies have focussed on determining temporal and spatial variation in organochlorine insecticides, polychlorinated biphenyls, mercury and arsenic (Newton 1986; Newton et al., 1993; Erry et al., 1999; Broughton et al. 2003) but a recent study has also reported UK long-term trends in PBDE concentrations in sparrowhawks eggs (Crosse et al., 2012b). Sum PBDE (ΣPBDE) concentrations were some of the highest concentrations ever reported in bird eggs or tissues from Europe and were of a magnitude associated with adverse reproductive effects. Unlike trends reported in the majority of studies from the rest of Europe, concentrations did not decline after reaching peak levels in the late1990s, despite the phasing out of PeBDE and OBDE in the European Union.

Contaminant concentrations in the eggs of investment breeders (Drent and Daan, 1980) are thought largely to provide a snapshot of exposure in females in the days before egg production, although female sparrowhawks can also eliminate bioaccumulated persistent organic contaminants into eggs (Newton et al., 1981), presumably from retained fat deposits laid down earlier. Eggs are therefore a readily available and homogeneous biomonitor of exposure in females that can be directly related to reprotoxic effects, but the time period of exposure may be uncertain. Egg concentrations do not provide direct information on body residues in females or necessarily on exposure in males. The latter may be particularly true for sexually dimorphic species such as the sparrowhawk where males and females specialise on different sized prey, although male sparrowhawks feed females during the period when eggs are developing (Newton.1986). Overall, egg residues may provide little or no information on either the extent of bioaccumulation or the magnitude of residues [and associated toxicity] in body tissues. The overall objective of the present paper was to more fully characterise the large-scale PBDE contamination in sparrowhawks in Britain that was revealed by the earlier analysis of eggs (Crosse et al., 2012b). The specific aims were to characterise and quantify current PBDE concentrations in the sparrowhawk livers and determine how concentrations varied with age class and sex. As part of this analysis, we also examined whether liver PBDE concentrations were affected by body condition at the time of death, as this has been shown to markedly influence the magnitude of liver concentrations of other persistent organic pollutants (Wienburg and Shore, 2004).

2. Materials and methods

2.1. *Sample collection*

Dead sparrowhawks from throughout Britain were collected by volunteers and submitted to the Predatory Bird Monitoring Scheme (http://pbms.ceh.ac.uk/; Walker et al., 2008). Provenance, collection date, age, sex, body weight and body condition (assessed visually using a six point scoring system) were recorded and a necropsy was performed during which a putative cause of death was determined. Various body tissues were collected from each carcass, weighed and archived at -20°C. However, whole liver and body weights were not obtained for all birds, including some used in the present study, usually because carcasses had been partly damaged through trauma or scavenging, or organs were provided by taxidermists who had not recorded the body weight of the bird.

Archived livers from birds that had died between 1998 and 2009 from central England, directly east and within 250 km of the Welsh border (**S.I. Figure 1**), were selected for the present study. Sample selection was restricted in this way to minimise potential confounding temporal and spatial variation; previous analysis of sparrowhawk eggs suggested that exposure in females was largely constant across this time period and geographical region (Crosse et al., 2012b). Selection of birds was further stratified such that individuals were representative of one of eight groups characterised by sex (male/female), age class (adult/ juvenile) and body condition (starved/ non-starved birds). Juveniles were defined as birds that hatched in the current or previous calendar year while starved birds were those which, at post-mortem inspection, had a complete lack of fat deposits or at most trace amounts of fat typically around the heart but nowhere else. The numbers of birds in each of the eight groups varied between five and 11 and the total number of birds analysed was 59.

2.2. *Determination of PBDE concentrations in livers*

For each bird, approximately 1g wet weight of liver (mean ± SD: 0.97 ± 0.22 g) was excised from various parts of the whole liver to obtain a representative sample, and was then homogenised. Homogenates were weighed accurately, extracted and cleaned up, and lipid content determined gravimetrically as described by Crosse et al. (2012a); the mean (± SD) % lipid in livers was 6.88 ± 4.86 %. The cleaned-up extract was analysed by Gas Chromatography Mass Spectrometry (GC-MS, Thermo-Finnigan Trace) 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. Livers were analysed for a suite of 30 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, 201, 202, 203) as described by Crosse et al. (2012b). BDE209 was not quantified as the above method was not amenable to its determination, returning poor recovery figures.

The instrument Limit of Detection (LoD) was defined as the lowest observable calibration standard (2.5 pg/ul for tri-hexa BDEs and BDE183 to 5 pg/ul for Octa BDEs) which was equivalent to 0.25 ng and 0.5 ng, respectively, in the liver samples that were analysed. Eight procedural blanks were run alongside the samples and these demonstrated that there was no background contamination. Mean recoveries for $^{13}C_{12}$ labelled BDE congeners 28, 47, 99, 100, 153, 154 and 183 (Wellington Laboratories, Guelph, Ontario, Canada) ranged between 74.4 and 88.2% across homologue groups and concentrations were recovery corrected using these data as described by Crosse et al. (2012a). To ensure precision, a quality control (QC) standard, consisting of five PBDEs that encompassed tri-hepta homologue groups at concentrations of 2.5-250 pg/ul, was analysed alongside unknowns. Batches of samples were only fit if QC concentrations were +/- 10% of expected values.

2.3. *Statistical analyses*

All statistical analysis was performed using Minitab 16.0. General linear models (GLM) were used to determine whether age, sex, body condition and breeding status significantly explained variation in the concentrations of individual PBDE congeners, ΣPBDEs or physiological characteristics of the liver, such as liver mass and liver % lipid. Because of the biologically plausible complex triple interactive effects of body condition, age and sex on liver residues, we conducted analysis of the effects of age and body condition on liver BDE concentrations in males and females separately. PBDE concentrations and % lipid data were log and arcsine square-root transformed, respectively, so that the underlying assumptions of equal variance and normality of residuals in the GLM were met. The majority of congener data sets had some values recorded as below the LoD and, for congeners where the percentage of values below the LoD was less than 80%, the below LoD values were assigned an interpolated value following the method described by Hesel, (1990, 2006).

3. Results

The data associated with this study are available from the CEH Information Gateway (https://gateway.ceh.ac.uk/) and can be identified from their digital object identifier: http://dx.doi.org/10.5285/1c4f835c-d243-4593-a9b4-71410b9b4bf0

3.1. *Congener profiles and concentrations.*

A total of 26 congeners were detected in one or more livers. BDEs 47, 99, 100, 153 and 154 were detected in the livers of all the birds, BDEs 138 and 183 in >80%, and BDEs 66, 118, 119, 196, 197, 201, 202 in >50% of birds. Only BDEs 32, 128, 166, and 190 were not detected in any of the livers. The PeBDE-associated congeners BDEs 99, 153, 47, 100 and 154 dominated the congener profile, comprising almost 90% of the ΣPBDE concentration (Figure 1). The geometric mean concentrations of these congeners varied between 103 and 945 ng/g lipid weight (lwt) and were generally an order of magnitude higher than those of all other detected congeners (Table 1 and S.I. Table 1). The two other most frequently occurring congeners, the hepta-BDE 183 and the hexa-BDE 138, made lesser contributions to the overall congener profile (Table 1, Figure 1). The concentrations of all seven congeners were highly correlated with each other and with that of the ΣPBDEs ($r \geq 0.887$, $P<0.001$ in all cases). The octa-brominated BDEs 197, 201, 202 and 203 occurred in fewer livers but, when present, were detected in similar amounts to BDE183; the geometric mean concentrations of the other congeners, when detected, ranged from 4.42-31.5 ng/g lwt (S.I. Table 1). Overall, the geometric mean ΣPBDE concentration was two-three fold higher than that that of BDE 99, the most abundant congener, and approximately at least an order of magnitude greater than the concentrations of all other congeners (Table 1 and SI Table 1).

3.2 Factors associated with variation in liver PBDE concentrations

In male sparrowhawks, body condition and age class between them explained 51.3% of the variation in liver ΣPBDE concentrations. Residues were higher in starved than in non-starved birds and in adults compared with juveniles ($F_{(1,21)} \geq 5.28$, $P<0.05$ in both cases; Figure 2). The interaction term between age and body condition was also significant ($F_{(1,21)} = 4.77$, $P<0.05$) as the difference in liver concentrations between starved and non-starved birds was 15-fold in adults but only two-fold in juveniles (Figure 2). In female sparrowhawks, body condition explained 23.3% of variation in liver ΣPBDE concentration, residues again being greater in starved than non-starved birds ($F_{(1,30)} = 8.87$, $P<0.01$, Figure 2). . However, unlike in males, age class was not a significant factor in females nor was the interaction term between age class and body condition ($F_{(1,30)} \leq 1.03$, $P>0.05$ in both cases), even though starvation was associated with an average elevation of liver ΣPBDE of 10 fold in adult females but only three fold in juveniles (Figure 2). Unsurprisingly, given the high degree of correlation between the concentrations of the individual main congeners and the ΣPBDE, the effects of body condition and of age class (males only) on each of the individual main congeners were similar to those on ΣPBDE concentrations (data not shown).

Starvation can affect liver concentrations of persistent organic pollutants potentially by altering the lipid content of the liver, through liver wastage associated with starvation, and through remobilisation of contaminants from fat depots and other tissues that subsequently leads to increased accumulation of residues in the liver. We analysed whether starvation, as measured by body condition, was associated with either altered liver lipid content or a decrease in liver mass in all birds, and included age class and sex as additional factors in the analysis. There was no effect of body condition, nor of sex or age class, on % liver lipid content ($F_{(1, 44)} \leq 1.93$, $P>0.05$ for all factors/interaction terms; Figure 3), whereas both body condition and sex were significantly associated with variation in liver mass ($F_{(1,44)} > 7.97$, $P<0.01$ in both cases; Figure 3). Liver mass, on average, was approximately 20% less in starved than non-starved birds of the same sex and age class, and was also approximately 25% lower in males than females, reflecting sexual dimorphism in body weight (Figure 3).

One possible explanation why age class was a statistically significant predictor of liver ΣPBDE concentrations in male but not female sparrowhawks may be because adult breeding females transfer a proportion of their maternal PBDE burden into eggs. To test this hypothesis, we examined whether liver PBDE concentrations in adult sparrowhawks that died within the breeding season (April-September) were lower than in those collected outside the breeding season (October-March). We included males in the analysis, as they effectively acted as controls against which to test the hypothesis; body condition, sex, and season were factors in the model. There was no effect of season, sex, nor any interaction between sex and season, on liver ΣPBDE concentrations ($F_{(1,19)} < 0.39$, $P>0.05$ in all cases; S,I, Figure 2). The only significant factor affecting liver BDE concentration was body condition and concentrations were greater in starved than non-starved birds ($F_{(1,19)} = 21.0$, $P<0.001$; S.I. Figure 2). There were likewise no significant effects of season on liver concentrations of any of the major congeners (data not shown).

The above model indicated that sex did not significantly explain variation in liver ΣPBDE concentrations in adult sparrowhawks. Analysis of data for juvenile birds showed that there was likewise no effect of sex on liver ΣPBDEs in this age class ($F_{(1,28)} = 0.25$, $P>0.05$).

4. Discussion

4.1. *Congener profile*

The seven congeners that dominated the BDE congener profile in sparrowhawk livers (99>153>47>100>154>183>138) occurred in similar relative proportions in most birds. Concentrations were also in broadly similar proportions to those in the PeBDE technical mixtures DE-71 and Bromkal 70-5DE (Figure 1). This suggests the PeBDE mixture is the most important source of PBDE contamination in sparrowhawks, although the detection of octa-brominated congeners also indicates some contribution of the OBDE and/or DeBDE mixture, of which these congeners are either components or potential degradation products. This congener profile in livers was consistent with that detected in sparrowhawk eggs from the same area (Crosse et al., 2012b) and demonstrates that the congeners associated with the PeBDE technical mixture remain a major source of contamination, despite the banning or phasing out the technical products in the European Union.

4.2. *The effect of condition and age on liver PBDE concentrations*

The concentrations of BDEs that were detected varied with a number of factors. Starvation was clearly the most important, with concentrations of the major individual BDE congeners and ΣPBDEs elevated in birds in poor body condition. This was, in part, due to a reduction in liver size, presumably a result of liver glycogen being depleted during starvation. However, the elevation in ΣPBDE concentrations in starved birds (10-15 fold in adults and 2-3 fold in juveniles) was disproportionate to the degree of liver wastage (25% reduction in mass). This strongly indicates that liver BDE residues are elevated during periods of starvation because of remobilisation of residues from fat stores and possibly other biological compartments. Starvation has been found similarly to elevate liver PCB residues in raptors (Wienburg & Shore, 2004) and to affect the concentrations of persistent organic pollutants, including PBDEs, in the eggs of tawny owls (*Strix aluco*) (Bustnes et al., 2011).

The presence of greater liver ΣPBDE concentrations in adult than juvenile males, and the difference between adults and juveniles in the impact that starvation had on liver residues, are both consistent with bioaccumulation of BDEs with age, although differences in dietary exposure between adults and juveniles cannot be ruled out. Adult birds, because they are older, have longer than juveniles to bioaccumulate residues in fat and other tissues and so larger residues are subsequently remobilised during starvation. Such bioaccumulation is likely to vary to some extent between congeners and, in the present study, was most readily detectable for the hexa-brominated BDEs 138, 153 and 154 in males; age class alone was a significant factor ($P \leq 0.01$; data not shown) in the statistical models for these congeners. All three have been reported to have long biological half-lives and/or high biomagnification factors (BMFs) in birds (Drouillard et al., 2007; Lindberg et al., 2004; Voorspoels et al., 2007), likely due to their high Log_{kow} values (Voorspoels et al., 2007). BDE183 has been reported to have an even higher BMF (Voorspoels et al., 2007). Although age class alone was not statistically significant in our model that examined which factors explained variation in liver BDE183 residues in males, the interaction between age class and body condition was significant ($P < 0.05$; data not shown). This indicated that residues were more elevated in starved adults than juveniles. This is again consistent with accumulation with age.

Liver PBDE concentrations in female sparrowhawks did not differ from those in males, suggesting that exposure of males and females to BDEs is similar, despite females taking different, typically larger, prey species than males (Newton, 1986). The effect of starvation in elevating liver residues was also the same in females as males. Although there was no statistically significant evidence that liver BDE residues in females increased with age class, liver ΣPBDE concentrations did not differ between adult males and females. Such a difference might be expected if males bioaccumulated residues but females did not. Furthermore, starvation had a much bigger impact on liver residues in adult females than in juveniles, just as in males. This is also consistent with the concept that both males and females bioaccumulate PBDEs with age.

Analysis of the factors associated with variation in liver PBDE residues in females may be confounded by maternal transfer of PBDE burdens into eggs. Such transfer clearly occurs as PBDEs have been detected in sparrowhawk eggs (Jaspers et al., 2006; Chen et al., 2007; Crosse et al., 2012b), but it is unknown to what extent egg PBDE concentrations are derived from maternal diet or from the female's body burden. Altricial or semi-altricial birds, such as raptors, are thought to use less maternal lipids and proteins in the formation of eggs compared to precocial species (Drouillard & Norstrom, 2001; Verreault et al., 2006). It has been estimated that, in chickens, some 1- 20% of maternal body burdens of some organohalogen compounds are transferred to eggs (Bargar et al., 2001) although this can further vary with physiological and chemical factors (Van den Steen et al., 2009). Thus, transfer of maternal PBDE burden into eggs in sparrowhawks may be relatively small. In the present study, liver PBDE concentrations of adult females that died between April and September (a period covering the breeding season) were not lower than those outside of this period, nor did they differ from concentrations in males. This suggests that maternal transfer of PBDEs into eggs does not result in significant depletion of female liver BDE residues in sparrowhawks. However, it was not known whether birds that had died between April and September had laid eggs and so the reported liver concentrations may be representative of a mixture of pre and post laying females. Thus, our ability to detect significant transfer of PBDEs from females to eggs from analysis of liver concentrations in this way may be limited.

4.3 Comparisons with PBDE contamination in birds elsewhere

Overall, liver ΣPBDE concentrations ranged from 43.4 – 68,040 ng/g lwt (equivalent to 7.93 to 7,447 ng/g wet wt). To the best of our knowledge, 68,000 ng/g lw is currently the highest (tri – octa) ΣPBDE concentration recorded in birds anywhere (Guerra et al., 2012) and is only exceeded by the (tetra – deca) ΣPBDE reported in the egg of a peregrine falcon (*Falco peregrinus*) from the north-eastern USA (Chen et al., 2008). Geometric mean liver concentrations in sparrowhawks in the present study (2440 ng/g lwt) are within the range of terrestrial bird liver concentrations reported by Chen and Hale (2010) in a global review of PBDEs in birds. When compared with data for other sparrowhawk species elsewhere, ΣPBDE concentrations in this study were of a similar magnitude to those reported in birds from mainland Europe (Jaspers et al., 2006; Voorspoels et al., 2006), but exceeded mean liver ΣPBDE concentrations in Japanese sparrowhawks (*Accipiter gularis*) from China by roughly five-fold (Chen et al, 2007). The similarities in ΣPBDE liver concentrations between those reported in this study and other sparrowhawks from mainland Europe contrasts with the observations by Crosse et al. (2012) that ΣPBDE concentrations in the eggs of UK sparrowhawks were considerably higher than those of other European birds. This apparent anomaly may be related to differences between studies in the body condition of birds which has a major impact on the magnitude of liver residues.

The toxicological significance of the liver PBDE residues in the present study is unknown. This is because, in contrast to studies on PBDEs and other organohalogen compounds in eggs (Chen et al., 2010; Fernie et al., 2009; Harrris and Elliott, 2011; Henny et al., 2009; Marteinson et al., 2010), there is a lack of data that relates the potential toxicity of PBDEs in avian livers to adverse effects. This is an area that merits further investigation.

5. Conclusions

The present study has demonstrated that sparrowhawks in Britain accumulate some of the highest PBDE residues reported for terrestrial-feeding birds anywhere. Although this species is sexually dimorphic, there was no evidence that accumulation differed between males and females but it was higher in adults than juveniles. Starvation resulted in massive elevation of liver residues, caused primarily by remobilisation of residues (from body fat and potentially other organs) and partly from liver wastage. It seems likely therefore, that adult birds are likely to have the highest circulating liver PBDE concentrations, particularly during periods of starvation when they are unable to catch sufficient prey to maintain body reserves, and so may be most at risk from any toxic effects of PBDEs. The key role that body condition plays in mediating liver PBDE concentrations highlights the need to account for nutritional status when utilising raptor livers as a biomonitoring tool for PBDEs.

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References

Bargar, T.A., Scott, G.I., Cobb, G.P., 2001. Maternal transfer of contaminants: case-study of the excretion of three polychlorinated biphenyl congeners and technical-grade endosulfan into eggs by white leghorn chickens (*Gallus domesticus*). Environmental Toxicology and Chemistry 20, 61-67.

Batterman, S.A., Chernyak, S., Jia, C., Godwin, C., Charles, S., 2009. Concentrations and emissions of polybrominated diphenyl ethers from U.S. houses and garages. Environmental Science and Technology 43 2693-2700.

Broughton, R.K., Osborn, D., Shore, R.F., Wienburg, C.L., Wadsworth, R.A., 2003. Identifying pollution hot spots from polychlorinated biphenyl residues in birds of prey. Environmental Toxicology and Chemistry 22 2519-2524.

Bustnes, J.O., Yuccoz, N.G., Bangjord, G., Herzke, D,, Ahrens, L., Skaare, J.U., 2011. Impacts of climate and feeding conditions on the annual accumulation (1986-2009) of persistent organic pollutants in a terrestrial raptor. Environmental Science and Technology 45 7542-7547.

Chen, D., Hale, R.C., 2010. A global review of polybrominated diphenyl ether flame retardant contamination in birds. Environment International 36 800-811.

Chen, D., Hale, R.C., Watts, B.D., La Guardia ,M.J., Harvey, E., Mojica, E.K., 2010. Species-specific accumulation of polybrominated diphenyl ether flame retardants in birds of prey from the Chesapeake Bay region, USA. Environmental Pollution 158 1883-1889.

Chen, D., La Guardia, M.J., Harvey, E., Amaral, M., Wolfort,K., Hale, R.C., 2008. Polybrominated diphenyl ethers in peregrine falcon (*Falco peregrinus*) eggs from the northeastern U.S. Environmental Science and Technology 42 7594-7600.

Chen, D., Mai, B., Song, J., Sun, Q., Luo, Y., Luo, X., Zeng, E.Y., Hale, R.C., 2007. Polybrominated diphenyl ethers in birds of prey from Northern China. Environmental Science and Technology 41 1828-1833.

Crosse, J.D., Shore, R.F., Jones, K.C., Pereira, M.G., 2012a. Long term trends in PBDE concentrations in gannet (*Morus bassanus*) eggs from two UK colonies. Environmental Pollution 163 93-100.

Crosse, J.D., Shore, R.F., Wadsworth, R., Jones, K.C., Pereira, M.G., 2012b. Long term trends in PBDEs in sparrowhawk (*Accipiter nisus*) eggs indicate sustained contamination of UK terrestrial ecosystems. Environmental Science and Technology 46 13504−1351.

Drent, R.H., Daan, S., 1980. The prudent parent - energetic adjustments in avian breeding. Ardea 68 225-252.

Drouillard, K.G., Fernie, K.J., Letcher, R.J., Shutt, L.J., Whitehead, M., Gebink, W., Bird, D.M., 2007. Bioaccumulation and biotransformation of 61 polychlorinated biphenyl and four polybrominated diphenyl ether congeners in juvenile American kestrels (*Falco sparvarius*). Environmental Toxicology and Chemistry 26 313-324.

Drouillard, K.G., Norstrom, R.J., 2001. Quantifying maternal and dietary sources of 2,2',4,4',5,5' hexachlorobiphenyl deposited in eggs of the ringed dove (*Streptopelia risoria*). Environmental Toxicology and Chemistry 20 561-567.

Erry., B.V., Macnair, M.R., Meharg, A.A., Shore, R.F., Newton, I., 1999. Arsenic residues in predatory birds from an area of Britain with naturally and anthropogenically elevated arsenic levels. Environmental Pollution 106 91-5.

Fernie, K.J., Shutt, J.L., Letcher, R.J., Ritchie, I.J., Bird, D.M., 2009. Environmentally relevant concentrations of DE-71 and HBCD alter eggshell thickness and reproductive success of American kestrels. Environmental Science and Technology 43 2124-2130.

Guerra, P., Alaee, M., Jiminéz, B., Pacepavicius, G., Marvin, C., MacInnis, G., Eljarrat, E., Barceló, D., Champoux, L., Fernie, K., 2012. Emerging and historical brominated flame retardants in peregrine falcon (*Falco peregrinus*) eggs from Canada and Spain. Environment International 40 179-186.

Harris, M.L., Elliott, J.E., 2011. Effects of polychlorinated biphenyls, dibenzo-p-dioxins and dibenzofurans, and polybrominated diphenyl ethers in wild birds. In: Beyer, W.N., Meador, J.P. (Eds.), Environmental contaminants in biota, second edition. CRC Press, Boca Raton, pp. 477-528.

Henny, C.J., Kaiser, J.L., Grove, R.A., Johnson, B.L., Letcher, R.J., 2009. Polybrominated diphenyl ether flame retardants in eggs may reduce reproductive success of ospreys in Oregon and Washington, USA. Ecotoxicolgy18 802-813.

Helsel, D.R., 1990. Less than obvious: statistical treatment of data below the detection limit. Environmental Science and Technology 24 1766-1774.

Helsel, D.R., 2006. Fabricating data: how substituting values for nondetects can ruin results, and what can be done about it. Chemosphere 65 2434-2439.

Hites, R.A., 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environmental Science and Technology 38 945-956.

Jaspers, V.L.B., Covaci, A., Voorspoels, S., Dauwe, T., Eens, M., Schepens, P., 2006. Brominated flame retardants and organochlorine pollutants in aquatic and terrestrial predatory birds of Belgium: levels, patterns, tissue distribution and condition factors. Environmental Pollution 139 340-352.

Johansson, A-K., Sellstrom, U., Lindberg, B., Bignert, A., de Wit C.A., 2011. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in Swedish peregrine falcon (*Falco peregrinus*) eggs. Environment International 37 678-686.

La Guardia, M.J., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environmental Science and Technology 40 6247-6254.

Law, R.J., Alchin, C.R., de Boer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S., Tronczynski, J., de Wit, C.A., 2006. Levels and trends of brominated flame retardants in the European environment. Chemosphere 64 187-208.

Leslie, H.A., Leonards, P.E.G., Shore, R.F., Walker, L.A., Bersuder, P.R.C., Morris, S., Allchin, C.R., de Boer, J., 2011. Decabromodiphenylether and hexabromocyclododecane in wild birds from the United Kingdom, Sweden and The Netherlands: screening and time trends. Chemosphere 82 88-95.

Lindberg, P., Sellström, U., Häggberg, L., de Wit C.A., 2004. Higher brominated diphenyl ethers and hexabromocyclododecane found in eggs of peregrine falcons (*Falco peregrinus*) breeding in Sweden. Environmental Science and Technology 38 93-96.

Marteinson, S.C., Bird, D.M., Shutt, J.L., Letcher, R.J., Ritchie, I.J., Fernie, K.J., 2010. Multi-generational effects of polybrominated diphenylethers exposure: embryonic exposure of male American kestrels (*Falco sparverius*) to DE-71 alters reproductive success and behaviors. Environmental Toxicology and Chemistry 29 1740-1747.

Newsome, S.D., Park, J-S., Henry, B.W., Holden, A., Fogel, M.L., Linthicum, J., Chu, V., Hooper, K., 2010. Polybrominated diphenyl ether (PBDE) levels in peregrine falcon (*Falco peregrinus*) eggs from California correlate with diet and human population density. Environmental Science and Technology 44 5248-5255.

Newton, I., 1986. The Sparrowhawk. T & AD Poyser, London, UK.

Newton, I., Wyllie, I., Asher, A.A. 1993. Long-term trends in organochlorine and mercury residues in some predatory birds in Britain. Environmental Pollution 79 143-151.

Newton, I., Bogan, J., Marquiss, M., 1981. Organochlorine contamination and age in sparrowhawks. Environmental Pollution 25 155-160.

PBMS (Predatory Bird Monitoring Scheme). http://pbms.ceh.ac.uk/; (last accessed 7 February, 2013).

Prevedouros, K., Jones, K.C., Sweetman, A.J., 2004. European-scale modelling of concentrations and distribution of polybrominated diphenyl ethers in the pentabromodiphenyl ether product. Environmental Science and Technology 38 5993-6001.

Rahman, F., Langford, K.H., Scrimshaw, M.D., Lester, J.M., 2001. Polybrominated diphenyl ether (PBDE) flame retardants. The Science of the Total Environment 275 1-17.

Sellström, U., Bignert, A., Kierkegaard, A., Häggberg, L., de Wit, C.A., Olsson, M., Jansson, B., 2003. Temporal trend studies on tetra- and pentabrominated diphenyl ethers and hexabromocyclododecane in guillemot eggs from the Baltic Sea. Environmental Science and Technology 37 5496-5501.

Van den Steen, E., Jaspers, V.L.B., Covaci, A., Neels, H., Eens, M., Pinxten, R., 2009. Maternal transfer of organochlorines and brominated flame retardants in blue tits (*Cyanistes caeruleus*). Environment International 35 69-75.

Verreault, J., Villa, R.A., Gabrielsen, G.W., Skaare, J.U., Letche, R.J., 2006. Maternal transfer of organohalogen contaminants and metabolites to eggs of Arctic-breeding glaucous gulls. Environmental Pollution 144 1053-1060.

Voorspoels, S., Covaci, A., Jaspers, V.L.B., Neels, H., Schepens, P., 2007. Biomagnification of PBDEs in three small terrestrial food chains. Environmental Science and Technology 41 411-416.

Voorspoels, S., Covaci, A., Lepom, P., Jaspers, V.L.B., Schepens, P., 2006. Levels and distribution of polybrominated diphenyl ethers in various tissues of birds of prey. Environmental Pollution 144 218-227.

Walker, L.A., Shore, R.F., Turk, A., Pereira, M.G., Best, J., 2008. The Predatory Bird Monitoring Scheme: identifying chemical risks to top predators in Britain. Ambio 36 466-471.

Wienburg, C.L., Shore, R.F., 2004. Factors influencing liver PCB concentrations in sparrowhawks (*Accipiter nisus*), kestrels (*Falco tinnunculus*) and herons (*Ardea cinerea*) in Britain. Environmental Pollution 132 41-50.

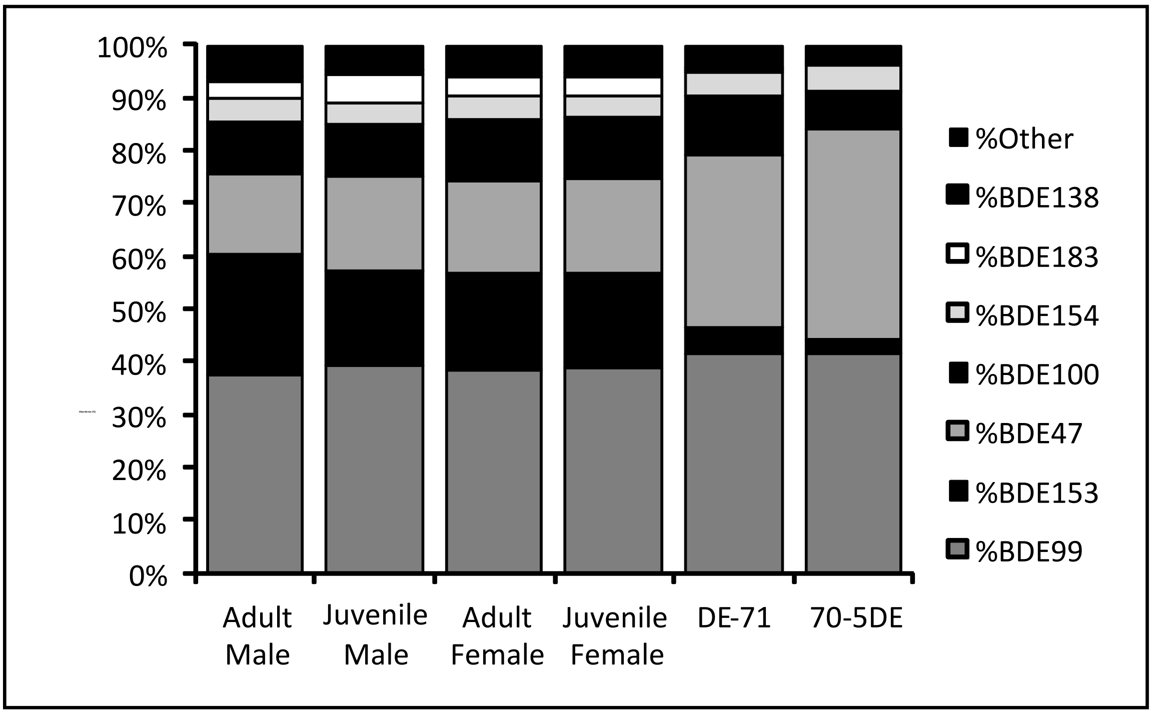


Figure 1. PBDE congener profile in sparrowhawk livers from birds that died between 1998 and 2009, and in the DE-71 and 70-5DE PeBDE technical formulations (La Guardia et al 2006). Relative abundance data for each congener in livers was the % contribution to the ΣPBDE concentration and the average for all livers within the age and sex category was taken.

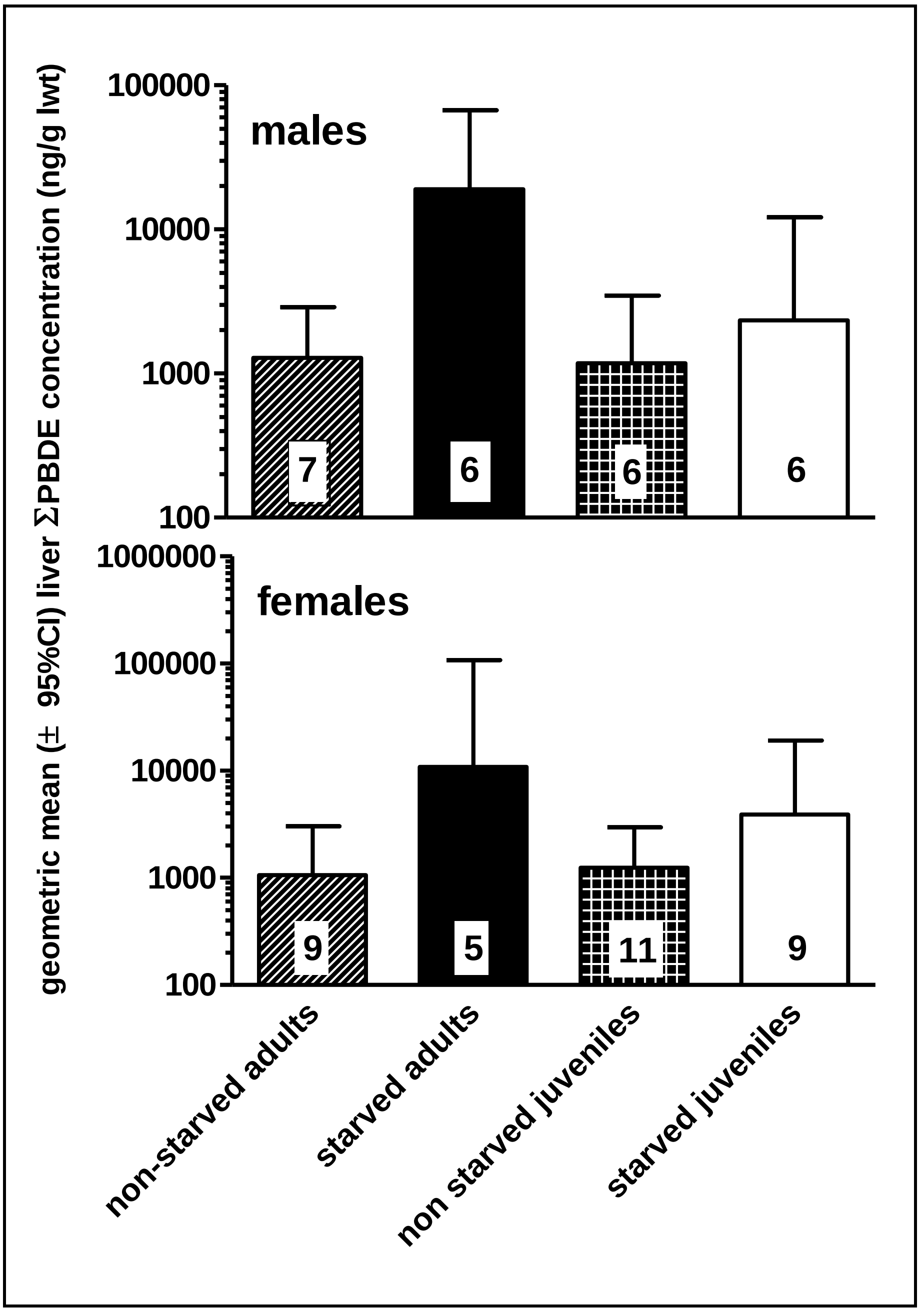


Figure 2. Geometric mean (95% Confidence Interval) liver ΣPBDE concentrations (ng/g lwt) in male (upper graph) and female (lower graph) sparrowhawks characterised by age and body condition. Numbers in columns indicate number of birds in each group.

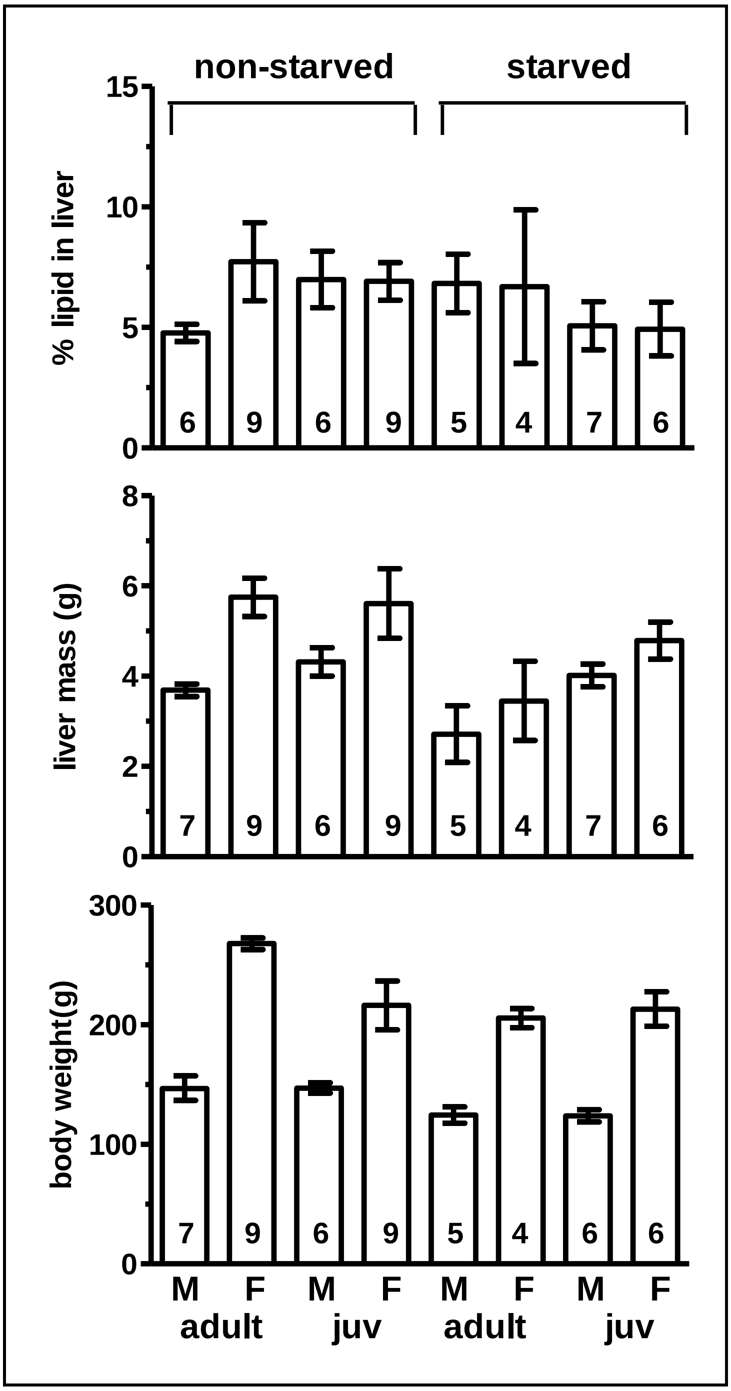


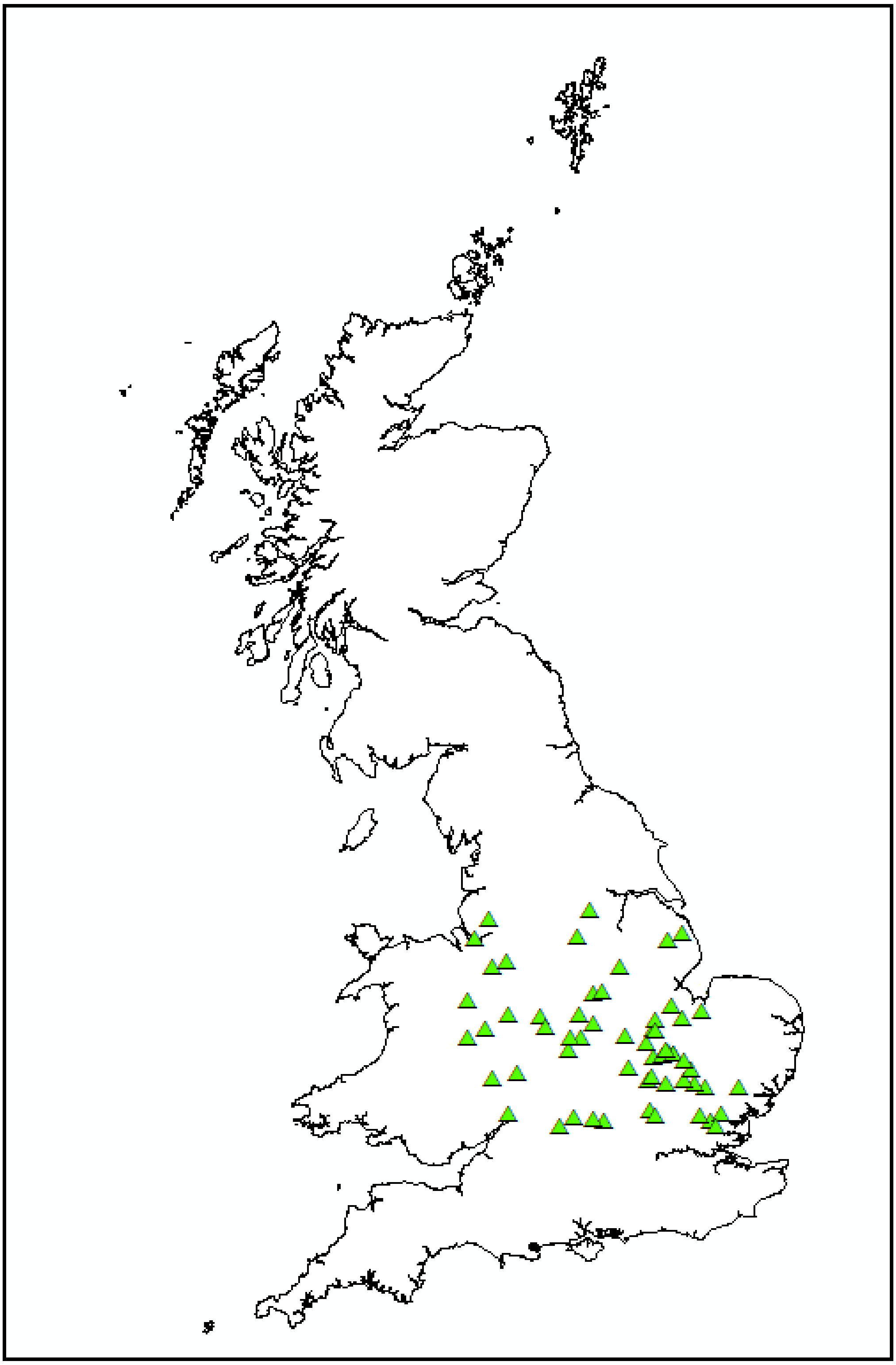
Figure 3. Mean (± SEM) % lipid liver, liver mass (g) and body weight (g) in sparrowhawks characterised by sex, age and body condition. Numbers in columns indicate number of birds in each group.

Table 1 Geometric mean and range (ng/g lwt) of concentrations for ΣPBDEs and the seven PBDE congeners detected in ≥ 80% of the 59 sparrowhawks analysed. Geometric mean values for concentrations calculated on a wet wt basis are also given for ease of comparison with other studies.

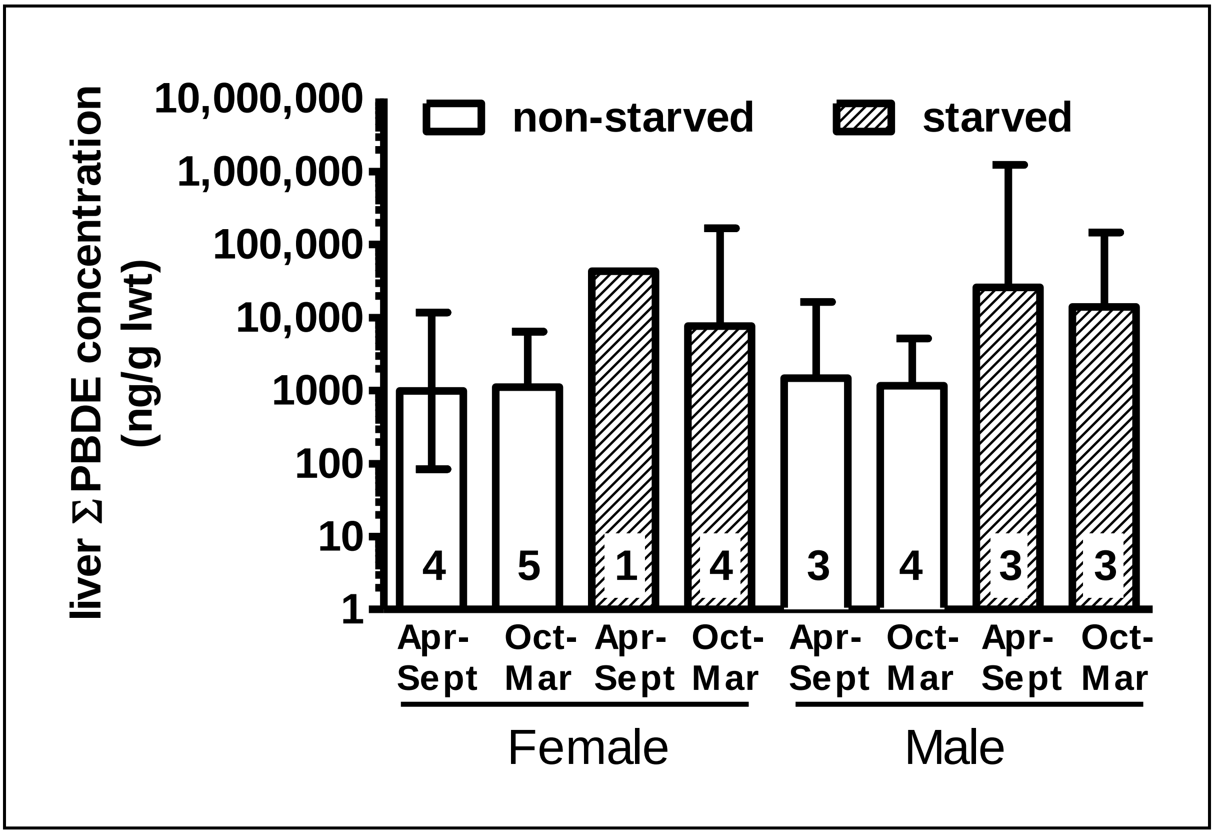
	Geometric mean (ng/g lipid)[1]	Range	Geometric mean (ng/g wet wt)
BDE 47	368	22.1-14400	23.7
BDE 99	945	44.4-28700	56.7
BDE 100	255	12.1-8600	15.3
BDE 138	24.0	1.79-473	1.38
BDE 153	452	12.6-16100	27.1
BDE 154	103	4.34-4150	6.20
BDE 183	63.8	1.36-2100	3.66
ΣPBDE	2440	117-68000	146

[1]Median (range) % lipid content in livers was 5.64 % (1.45-26.9%)

Supporting information



S.I. Figure 1: Map of locations where dead sparrowhawks were found.



S.I. Figure 2: Geometric mean (and 95% Confidence Interval) in liver ΣPBDE concentrations (ng/g lw) in adult sparrowhawks grouped by sex, body condition, and month of death. Numbers in columns indicate number of birds in each group.

S.I. Table.1 Geometric mean, and range (ng/g lipid) of the liver concentrations of PBDE congeners (17, 28, 35, 37, 49, 51, 66, 71, 75, 118, 119, 126, 196, 197, 201, 202, 203) that were present at detectable levels in less than 80% of sparrowhawks. Mean values are only for those livers that had detectable residues

	Number of samples < LoD	Geometric mean in livers with detected residues (ng/g lipid)	range
BDE 17	4	4.42	1.19-11.7
BDE 28	11	10.1	3.57-30.8
BDE 35	28	17.3	0.79-416
BDE 37	10	7.58	4.7-13.5
BDE 49	10	15.0	5.84-47.3
BDE 51	11	8.18	0.31-22.7
BDE 66	32	19.1	1.75-113
BDE 71	12	17.4	4.61-63.0
BDE 75	9	9.46	2.05-38.1
BDE77	17	11.9	1.02-41.9
BDE 85	23	17.6	1.66-182
BDE 118	38	31.5	2.16-330
BDE 119	29	25.0	3.93-217
BDE126	18	13.7	2.10-199
BDE 196	33	28.3	2.67-505
BDE 197	43	59.7	5.05-1530
BDE 201	30	54.6	2.83-537
BDE 202	36	52.3	6.17-1530
BDE 203	8	48.9	13.3-363