Brominated Flame Retardants in aquatic and terrestrial predatory birds of Belgium

Veerle Jaspers[1], Adrian Covaci[1], Stefan Voorspoels[1], Tom Dauwe[1], Marcel Eens[1], Paul Schepens[1]

[1]University of Antwerp - CDE

Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants (BFRs), which are commonly used in computer and TV housings, car interiors, furniture textiles and various plastics[1]. PBDEs are persistent compounds that readily accumulate within biological tissues and biomagnify along food chains[2], being therefore found in high concentrations in top predators. Predatory birds have been used as biomonitors in several studies, since they are sensitive to environmental changes and highly positioned on the food chain. Recently, Law et al.[2] have found a different profile of PBDEs between aquatic and terrestrial birds. The dominant PBDE congeners in peregrine falcon (*Falco peregrinus*) eggs were BDE 153 and BDE 99, while BDE 47 was the most prominent congener in guillemot (*Cepphus grille*) eggs[2]. Furthermore, it is assumed that the octa-PBDE mixture (containing mainly BDE 183) is not or only in relatively low levels present in aquatic ecosystems[2,3]. Consequently, it has been suggested that birds feeding in terrestrial environments may be more exposed to higher brominated congeners than aquatic birds[2,4].

The objective of this study was to compare the levels and profiles of PBDEs in 2 species of aquatic (grey heron - *Ardea cinerea*, great crested grebe - *Podiceps cristatus*) and 5 species of terrestrial (barn owl - *Tyto alba*, long-eared owl - *Asio otus*, common buzzard - *Buteo buteo*, kestrel - *Falco tinnunculus*, sparrowhawk - *Accipiter nisus*) predatory birds from Flanders, Belgium. Further, the distribution of these compounds between liver and muscle in the birds was examined to obtain information on allocation within the body.

Materials and Methods

Between October 2003 and June 2004, 49 carrions of different aquatic and terrestrial predatory birds (see above) were collected in collaboration with Wildlife Rescue Centres in Flanders (http://www.vogelbescherming.be). The birds collected for this study were found dead or had died shortly after collection. Frequent causes of death included traffic accidents, natural causes and starvation. Liver and pectoral muscle were excised and stored at -20°C.

Approximately 1.5 g muscle or liver was extracted according to previously described methods[5]. Analysis was done using a GC/MS operated in electron capture negative ionisation (ECNI) mode. In all samples, 7 PBDE congeners (28, 47, 99, 100, 153, 154, and 183) and brominated biphenyl (BB) 153 were analysed using a HT-8 capillary column (25 m x 0.22 mm x 0.25 µm). Additionally, BDE 209 was also investigated on an AT-5 capillary column (12 m x 0.18 mm x 10 µm) in 40 samples (muscle and liver) containing the highest concentrations of PBDEs.

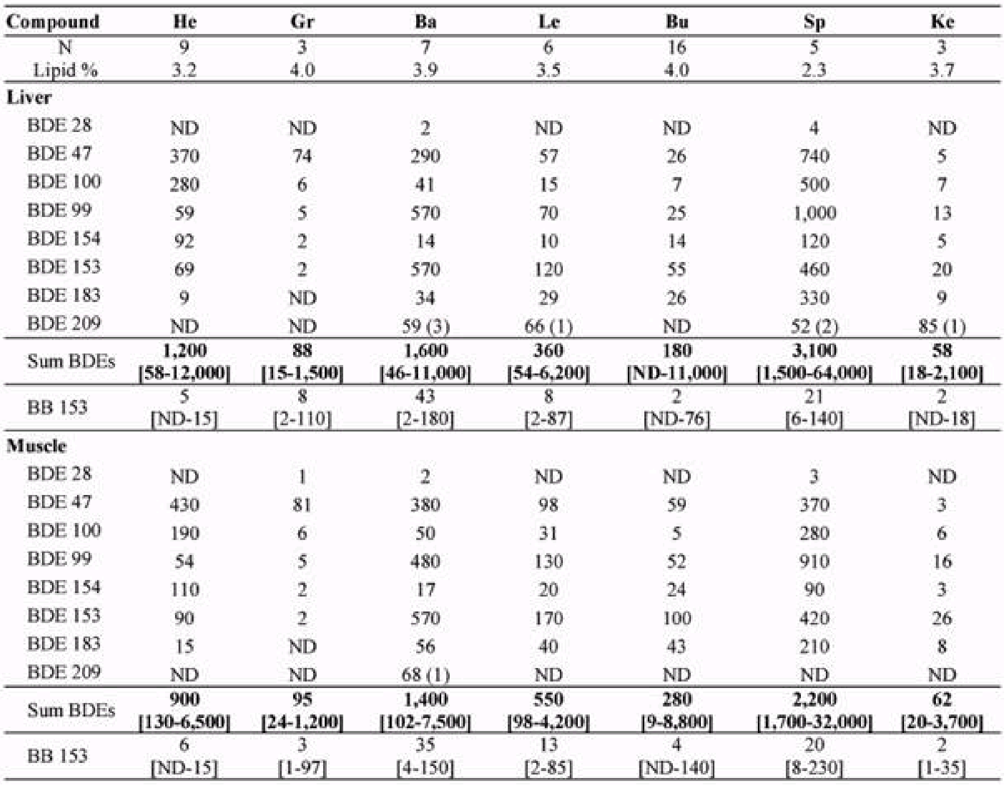
All statistical analyses were performed using Statistica for Windows (Statsoft 1997), GraphPadInstat® version 3.06 for Windows and XLStat©-Pro version 7.5 (Addinsoft 2004). Samples with levels below the limit of quantification (LOQ) were assigned a value of (1-p) x LOQ, with ‘p’ the proportion of measurements with levels below the LOQ[5]. BDE 28 and 209, which had over 50% of the measurements below LOQ, were excluded from statistical analysis. PBDE levels were not normally distributed (Shapiro-Wilks test, $p > 0.05$), thus non-parametric statistics were employed. The profile of PBDEs was compared between species by principal component analysis (PCA) on normalized concentrations. All performed correlations were carried out using Spearman Rank correlation. The level of significance was set at $\alpha = 0.05$.

Results and Discussion

Our results indicated moderately to high levels of PBDEs in different predatory birds from Flanders (Table 1). The high variability of concentrations within one species can probably be attributed to different feeding habits, seasonal variation of food composition, sampling area, age and condition of the birds. There was no indication that sex had an important influence on the variation in concentrations within one species.

PBDEs concentrations in our samples were markedly higher than concentrations reported for liver samples of black guillemots from Greenland[6] (median about 25 and 72 ng/g lipid weight). Law et al.[7]have measured concentrations in livers of common cormorants (*Phalacrocorax carbo*; sum PBDEs 1.8 - 140 ng/g ww) from the UK, that are in the range of levels assessed in livers of our birds, excluding the sparrowhawk. However, Lindberg et al.[4]have measured higher concentrations in eggs of peregrine falcons from Sweden (average sum of PBDEs 2,200 - 2,700 ng/g lipid, concentrations up to 39,000 ng/g lipid) than in our samples, with the exception of the sparrowhawk (concentration up to 64,000 ng/g lipid).

Table 1: Median concentrations (ng/g lipid weight) and [min-max] of different PBDE congeners in liver and muscle of aquatic and terrestrial predatory birds from Belgium. The number of samples in which BDE 209 was quantified is reported between brackets. Abbreviations: He: grey heron, Gr: great crested grebe, Ba: barn owl, Le: long-eared owl, Bu: common buzzard, Sp: sparrowhawk, Ke: kestrel



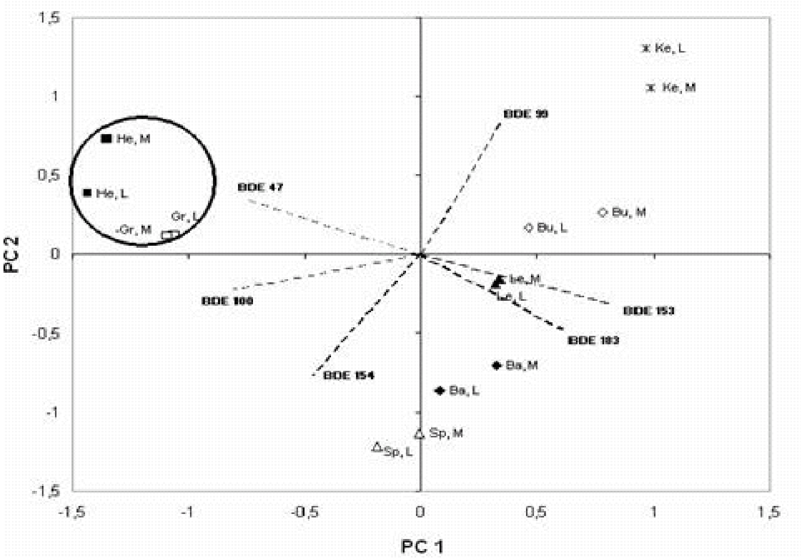
Compound	He	Gr	Ba	Le	Bu	Sp	Ke
N	9	3	7	6	16	5	3
Lipid %	3.2	4.0	3.9	3.5	4.0	2.3	3.7
Liver							
BDE 28	ND	ND	2	ND	ND	4	ND
BDE 47	370	74	290	57	26	740	5
BDE 100	280	6	41	15	7	500	7
BDE 99	59	5	570	70	25	1,000	13
BDE 154	92	2	14	10	14	120	5
BDE 153	69	2	570	120	55	460	20
BDE 183	9	ND	34	29	26	330	9
BDE 209	ND	ND	59 (3)	66 (1)	ND	52 (2)	85 (1)
Sum BDEs	**1,200** **[58-12,000]**	**88** **[15-1,500]**	**1,600** **[46-11,000]**	**360** **[54-6,200]**	**180** **[ND-11,000]**	**3,100** **[1,500-64,000]**	**58** **[18-2,100]**
BB 153	5 [ND-15]	8 [2-110]	43 [2-180]	8 [2-87]	2 [ND-76]	21 [6-140]	2 [ND-18]
Muscle							
BDE 28	ND	1	2	ND	ND	3	ND
BDE 47	430	81	380	98	59	370	3
BDE 100	190	6	50	31	5	280	6
BDE 99	54	5	480	130	52	910	16
BDE 154	110	2	17	20	24	90	3
BDE 153	90	2	570	170	100	420	26
BDE 183	15	ND	56	40	43	210	8
BDE 209	ND	ND	68 (1)	ND	ND	ND	ND
Sum BDEs	**900** **[130-6,500]**	**95** **[24-1,200]**	**1,400** **[102-7,500]**	**550** **[98-4,200]**	**280** **[9-8,800]**	**2,200** **[1,700-32,000]**	**62** **[20-3,700]**
BB 153	6 [ND-15]	3 [1-97]	35 [4-150]	13 [2-85]	4 [ND-140]	20 [8-230]	2 [1-35]

Significant differences in the sum of PBDEs were found between buzzard and sparrowhawk, similar to the results of Voorspoels et al.[8], which have indicated debromination processes and diet as principal causes for these differences. However, post hoc comparisons revealed no significant differences among other species, possibly due to small sample sizes.

Sparrowhawks had by far the highest levels (median 3,100 ng/g lipid), probably related also to the lowest lipid percentage for both liver and muscle (Table 1). In contrast, kestrels had low PBDE levels. Wienburg and Shore[9] also report lower levels for kestrels in comparison to sparrowhawks and herons. These species differences in contaminant load might be explained to a great extent by differences in dietary habits. The diet of the sparrowhawk consists almost entirely of small birds (up to 98%), while kestrels and buzzards feed mainly on small mammals, birds and earthworms[10]. In the aquatic birds, PBDE levels were higher in grey herons than in grebes (Table 1), although this could not be tested statistically due to the small sample size for grebe. Herons feed mainly on fish, but amphibians, small mammals, insects, birds and reptiles are also occasionally consumed[10]. Consequently, herons have a high position in the food chain. Herons feed on larger fish that may contain higher levels of POPs than young fish, which are preferred by grebes. Zimmermann et al.[11] have also measured higher PCB body burdens in herons than in grebes.

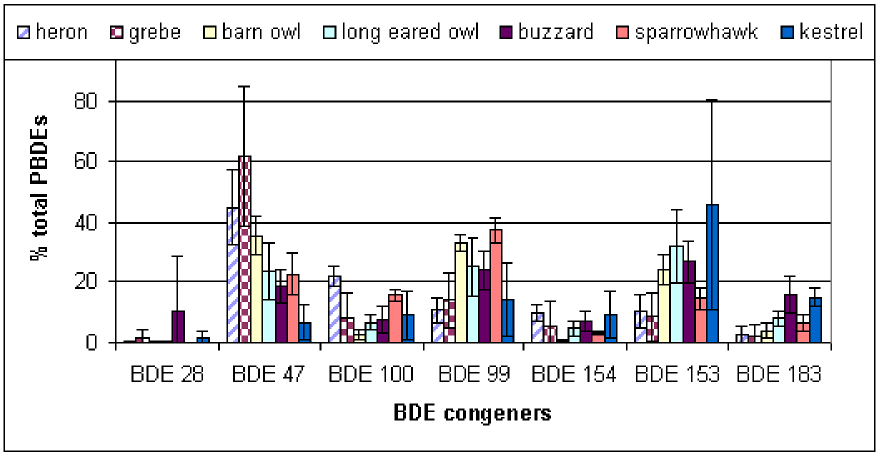
The results of the PCA for the profile of PBDEs in different bird species are presented in Figure 1. The PBDE profile in herons and grebes was clearly different compared to the terrestrial birds of prey. This discrepancy between terrestrial and aquatic species has previously been observed by Law et al.[2], which have suggested that birds feeding in terrestrial environments may be more exposed to higher brominated PBDE congeners than aquatic birds.

Figure 1:PBDEs in liver (L) and muscle (M) samples of different predatory birds from Belgium. Loading plot from the Principal Component Analysis:PC 1 (44% variance), PC 2 (30% variance).



Indeed, we measured higher levels of BDE 47 in herons and grebes (lower PC 1), while BDE 99 and 153 were the prominent congeners in the terrestrial species (Figure 2). In comparison, Jaspers et al.[12] have measured highest concentrations for BDE 99 in little owls (*Athene noctua*) from Belgium, while BDE 153 and BDE 47 had similar concentrations. Nevertheless, concentrations of BDE 47 were also high in sparrowhawks, which has been reported by Law et al.[2] as well. However, concentrations of most PBDE congeners were high in sparrowhawk and the PBDE profile was similar to other terrestrial predatory birds (Figure 2). The ratios of the PBDE congeners measured in our samples were different from the proportions of these congeners in the commercial mixtures, which suggests biotransformation of the commercial PBDE mixtures[13]. Covaci et al.[3]have measured the concentrations and profiles of PBDEs in different freshwater fish species of Flanders. BDE 47 was the dominant congener in muscle and liver samples of all fish species, followed by BDE 100, while BDE 99 was present at very low concentrations or was not detected. This is in concordance with our results for heron and grebe. BDE 183 was not detected in any of the fish samples[3,5] and was found at very low levels in herons and grebes from this study. Moreover, BDE 183 was measured at higher levels in the terrestrial birds of prey (Table 1). It has been suggested that the octa-PBDE mixture is not or only in relatively low levels present in aquatic ecosystems, compared to the penta-mix[2]. Consequently, our data confirm the assumption that the octa-mix may be more widespread in some terrestrial food webs than in the aquatic environment. Furthermore, BDE 209 was detected only in a few samples of terrestrial birds, but not in the aquatic species (Table 1). This provides further evidence that higher brominated PBDEs may accumulate in terrestrial food webs, as has already been shown by Lindberg et al.[4].

Figure 2: Contribution of selected PBDE congeners to the total PBDE load (mean % total PBDEs ± 2SE) in liver tissue of different aquatic and terrestrial predatory birds from Belgium.



According to our data (Table 1) there was no significant difference in concentrations or patterns of PBDEs between liver and muscle of individual birds (Wilcoxon test, $p > 0.05$), which suggests that these compounds are homogeneously distributed within the lipids of these organs, as already proposed by Zimmermann et al.[11]. This was also confirmed by the close concurrence of values for liver and muscle from the same species in Figure 1. All correlations between liver and muscle were found to be highly significant ($r > 0.90$; $p < 0.001$).

Acknowledgements - This study was supported by the Fund for Scientific Research Flanders (FWO-project G.0397.00 and FWO project G.0137.04), by a GOA-project (BOF 2001 UA), by the University of Antwerp and by a FWO Research Assistantship Grant to Veerle Jaspers.

References

1. WHO (1994) Environmental Health Criteria 162: Brominated Diphenyl Ethers, Geneva, Switzerland.

2. Law R. J., Alaee M., Allchin C.R., Boon J.P., Lebeuf M., Lepom P., Stern G.A. (2003) *Environ Intern* 29: 757-770.

3. Covaci A., Bervoets L., Hoff P., Voorspoels S., Voets J., Van Campenhout K., Blust R., Schepens P. (2005) *J Environ Monit* 7: 132-136.

4. Lindberg P., Sellström U., Häggberg L., de Wit C.A. (2004) *Environ Sci Technol* 38: 93-96.

5. Voorspoels S., Covaci A., Schepens P. (2003) *Environ Sci Technol* 37: 4348-4357.

6. Vorkamp K., Christensen J.H., Glasius M., Riget F.F. (2004) *Mar Pollut Bull* 48: 111-121.

7. Law R.J., Allchin C.R., Bennett M.E., Morris S., Rogan E. (2002) *Chemosphere* 46: 673-681.

8. Voorspoels S., Covaci A., Schepens P. (2004) Organohalogen Compounds 66: 3884 – 3892.

9. Wienburg C.L., Shore R.F. (2004) *Environ Pollut* 132: 41-50

10. Snow D.W., Perrins C.M. (1998) Oxford University Press, pp. 419-425, 741-745.

11. Zimmermann G., Dietrich D.R., Schmid P., Schlatter, C. (1997) *Chemosphere* 34: 1379-1388.

12. Jaspers V., Covaci A., Maervoet J., Dauwe T., Voorspoels S., Schepens P., Eens M. (2005) *Environ Pollut* 136: 81-88.

13. Hites R.A. (2004) *Environ Sci Technol* 38: 945-956.