Brominated flame retardants in Belgian little owl (Athene noctua) eggs

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Introduction

Since the 1960s, polybrominated diphenylethers (PBDEs), a class of brominated flame retardants (BFRs), are widely used in textiles, plastics, electronic equipment and other materials[1]. Their massive use has led to the ubiquitous presence of PBDEs in the environment and in biota in which the PBDE levels seem to increase rapidly[1]. High concentrations of some congeners may cause adverse effects in both wildlife and in human populations[1] and this has led to the growing concern of scientists over the last decade and to the need for more data on environmental levels of PBDEs[1].

The little owl (*Athene noctua*) is a small sedentary predator, which makes it a very suitable biomonitoring species[2,3]. This owl species feeds on a variety of preys, including small mammals and birds, reptiles, amphibians, earthworms and beetles, depending on the season and the local circumstances[4]. Because very limited information is available about contamination levels in the little owl, a study was conducted to determine the concentrations of PBDEs, polybrominated biphenyls (PBBs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in deserted or addled eggs of little owls in Belgium. Eggs have been used successfully as a monitoring tool for persistent organic pollutants (POPs) in several studies. Although the analysis of POPs in deserted or addled eggs has clear limitations, these can be partially avoided by analysing only highly persistent components, for which the original composition will not change due to 'post-hatching' microbiological degradation[5].

Methods and Materials

Between 1998 and 2000, 40 deserted or addled eggs from different nests of the little owl were collected in the surroundings of Charleroi (Belgium) during the breeding season. The eggs were stored at -20°C until sample preparation. Before analysis, the egg yolk and white were mixed and a homogenised sample of ~ 2g was weighed, mixed with anhydrous $NaSO_4$ and spiked with internal standards (ε-HCH, PCB 46 & 143, BB 103 & 155). Further sample treatment and analysis were performed according to previously described methods[6,7]. Briefly, extraction was carried out with 100 ml hexane/acetone (3:1, v/v) in a hot Soxhlet extractor for 2h. Afterwards the extract was cleaned up on an acid silica column and eluted with 15 ml hexane and 10 ml dichloromethane. The extract was concentrated to 100µl under a gentle nitrogen stream, and transferred to an injection vial.

For PBDEs and OCPs, analysis was done by GC/MS in electron capture negative ionisation (ECNi) mode, equipped with a HT-8 capillary column (25 m x 0.22 mm x 0.25 µm). For PCBs, a GC/MS in electron ionisation (EI) mode, equipped with a DB-1 capillary column (30 m x 0.25 mm x 0.25 µm) was used. In all samples 7 BDE congeners (28, 47, 100, 99, 154, 153, 183), BB 153, 27 PCB congeners, hexachlorobenzene (HCB), octachlorostyrene (OCS), chlordanes (*cis*-chlordane, *trans*-chlordane, *trans*-nonachlor and oxychlordane, expressed here as CHLs), hexachlorocyclohexanes (α-, β- and γ-HCHs) and DDTs (p,p'-DDE, p,p'-DDD and p,p'-DDT) were analysed. Additionally, BDE 209 and hexabromocyclododecane (HBCD) were investigated in a limited number of samples.

The distribution of the organohalogenated compounds was not normal, even after transformation. Except for PCBs, one sample was an outlier for each class of POPs and was further omitted from statistical analysis. Correlations were carried out using non-parametric Spearman rank correlation (Statistica for Windows). The level of significance was set at $p = 0.05$.

Results and Discussion

Our results revealed that PCBs constitute the major organohalogenated pollutants in the eggs of the Belgian little owl, with concentrations ranging from 780 - 23200 ng/g lipid and a median concentration of 2600 ng/g lipid (Table 1). This is in agreement with levels reported by Van den Brink et al.[8] in little owls from Dutch river floodplains. As indicated by these authors, current PCB levels in little owl eggs may pose a risk on the functioning and the condition of little owls in these floodplains[8].

Table 1: Median concentration (ng/g lipid) and range (minimum - maximum) in eggs of Belgian little owls. The contribution of different BDE congeners to sum PBDEs (% total PBDEs) and the contribution of each class of compounds to total organohalogen load (% total POPs) are also presented.

Compound	Number of samples	Median	Minimum	Maximum	% total BDEs	% total POPs
BDE 28	39	0.9	ND	1.7	0.8	0.02
BDE 47	39	24.4	3.4	171	22.6	0.5
BDE 100	39	3.3	0.5	30.8	3.0	0.1
BDE 99	39	33.7	9.2	270	31.2	0.7
BDE 154	39	3.9	0.7	20.5	3.6	0.1
BDE 153	39	24.9	9.5	94.4	23.0	0.5
BDE 183	39	10.2	4.1	31.0	9.4	0.2
Sum BDEs	39	108	29	572	100	2.3
BB 153	39	1.3	0.6	5.6	-	0.03
HCB	39	134	35.3	1073	-	2.8
OCS	39	3.4	0.5	7.3	-	0.1
Sum HCHs	39	27.3	5.5	356	-	0.6
Sum CHLs	39	1016	23.9	7113	-	21.1
Sum DDTs	39	826	200	7257	-	17.2
Sum PCBs	40	2600	786	23204	-	54.0
Lipids	40	7.95	5.24	13.74	-	-

DDTs levels in our egg samples were relatively low (Table 1), compared with p,p'-DDE concentrations reported by Van den Brink et al.[8] for the little owl. This variation in concentrations may originate from differences in pesticides use (i.e. land-use) and from differences in deposition patterns between Charleroi and Dutch river floodplains. However, concentrations were in the same range as reported for p,p'-DDE in burrowing owl (*Athene cunicularia*) eggs collected in California[9]. HCB was detected in all samples, but concentrations showed high variation (Table 1). Further, HCHs were detected at relatively low concentrations (Table 1). This is in accordance with low HCH concentrations found previously in great tit (*Parus major*) nestlings[6], which may suggest a relatively low contamination of the Belgian environment with HCHs. Finally, OCS was found in low concentrations in all the analysed eggs.

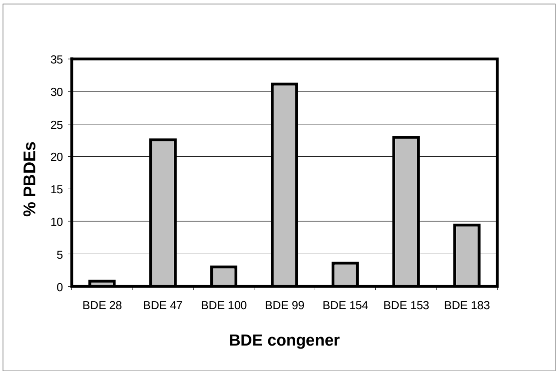
PBDEs were detected in all analysed samples (Table1), but the concentrations were much lower than for PCBs (levels of sum PBDEs were ~ 4% of levels of sum PCBs). However, concentrations were lower than levels detected in Swedish peregrine falcon (*Falco peregrinus*) eggs (geometric mean up to 2000 ng/g lipid)[10] and Great Lakes Herring gull (*Larus argentatus*) eggs (up to 7000 ng/g lipid)[11].

The most prevalent BDE congeners in little owl egg samples were BDE 99, BDE 47 and BDE 153. Furthermore, BDE 183 was detected in all little owl eggs (Table 1), which points to an additional source of the Octa-BDE mixture. Similarly, BDE 183 was measured (at higher levels) in all eggs of wild falcons from Sweden[10]. However, these results contrast with the lack of BDE 183 in the North Sea food web[7,12]. It has been suggested that the Octa-BDE mixture is not present in aquatic ecosystems or rather in relatively low levels, compared to the Penta-mix[13]. Consequently, our data confirm the assumption that the Octa-mix may be more widespread in some terrestrial food webs than in the aquatic environment.

In contrast, BDE 209 could be detected in only one egg sample at a level of 17 ng/g lipid (detection limit was 8 ng/g lipid). This sample contained also the highest levels of PBDEs (2180 ng/g lipid) and was the outlier eliminated during the statistical analysis. This is another piece of evidence that higher brominated BDEs, including BDE 209, may accumulate in terrestrial food webs, as already shown by Lindberg et al.[10]. The levels of BDE 209 in eggs of Swedish Peregrine falcon varied between < 7 and 430 ng/g lipid. This suggests that BDE 209 accumulates in the eggs of little owls to a much lesser extent compared to other birds of prey.

BB 153 was detected in all egg samples (Table 1), but concentrations were lower than levels in the eggs of wild peregrine falcons from Sweden[10]. HBCD could be identified and quantified only in 2 egg samples of the little owl, at levels of 20 and 50 ng/g lipid (detection limit was 5 ng/g lipid). HBCD could not be detected in eggs of captive Swedish peregrine falcons (< 8 ng/g lipid) as well, but it was present in all egg samples from wild peregrine falcons (up to 2400 ng/g lipid)[10].

Figure 1: Contribution of selected BDE congeners to the total PBDE load (% total PBDEs) in eggs of Belgian little owls.



Eggs of the little owl showed a very specific BDE profile dominated by BDE 99, followed by BDE 153 and BDE 47, and further by BDE 183, BDE 154 and BDE 100 (Figure 1). The ratios of these congeners in the egg samples were different from the proportions of these congeners in the commercial mixtures, which suggests transformation of the commercial BDE mixtures in biota[14]. Similar results were reported for eggs of peregrine falcons, merlins (*Falco columbarius*) and Gyrfalcons (*Falco rusticolus*) from Norway[13], which displayed highest concentrations for BDE 99 and BDE 153. However, the BDE profile was markedly different in Great Lakes Herring Gull eggs[11] and was dominated by BDE 47, followed by BDE 99, BDE 100 and BDE 153. This discrepancy between terrestrial and marine species has recently been documented by Law et al.[13], who suggested that birds feeding in terrestrial environments may be more exposed to the higher brominated BDE congeners than marine birds. However, metabolic capacity and degradation may differ between species as well.

Significant correlations were established among the analysed organohalogens (Table 2). Levels of sum BDEs were 70% correlated with levels of sum PCBs. All other correlations had lower correlation coefficients and may indicate separate sources of contamination, differences in exposure time or different persistency in the Belgian little owl.

Table 2: Results of the Spearman Rank correlation, r- and p-value (in brackets), among the different organohalogen contaminants in eggs of Belgian little owls are presented.

	Sum HCHs	Sum BDEs	Sum DDTs	Sum CHLs
Sum PCBs	0.62 (<0.001)	0.71 (<0.001)	0.42 (<0.01)	0.50 (<0.005)
Sum HCHs		0.46 (<0.005)	0.34 (<0.05)	0.36 (<0.05)
Sum BDEs			0.33 (<0.05)	0.40(<0.05)
Sum DDTs				0.55 (<0.001)

Acknowledgements - *We would like to thank Jacques Bultot for the collection of the eggs.*

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