Biomagnification potential of PBDEs in terrestrial food chains

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Introduction

Since their introduction on the market, environmental levels of polybrominated diphenyl ethers (PBDEs) are continuously increasing[1]. This is caused by spillage and emission during production and use, but also by improper disposal at the end-of-life of the products in which they are used. These chemicals are highly lipophilic and persistent, which results in bioaccumulation in fatty tissues of biota and biomagnification throughout the food chain[2]. Because PBDEs have a high toxicological potential[3], their biomagnification throughout the food chain can have health consequences for terrestrial top-predators, such as foxes and birds of prey.

Reports about PBDE concentrations in terrestrial species are scarce with most data being available for birds of prey[4-6], while very limited information is available for rabbits (*Oryctolaguscuniculus*), moose (*Alcesalces*) and reindeer (*Rangifertarandus*)[7]. Until now, there are no data on PBDE levels in terrestrial mammalian (wildlife) top-predators neither on their prey.

The aim of this study was to investigate the biomagnification potential of PBDEs in terrestrial food chains with birds of prey and foxes as representatives for top-predators and to expand the existing database regarding PBDE levels in prey species, such as mice and passerines.

Materials and Methods

Small rodents of three different species (wood mice (*Apodemussylvaticus*), bank vole (*Clethrionomysglareolus*), greater white-tooted shrew (*Crocidurarussula*)) were trapped at 8 different locations around Antwerp (Belgium) during February and March 2001 (n=70). The animals were killed and liver, muscle and brain were dissected. Fourteen pooled samples were created based on species and location and each pool consisted of 5 individuals. The pooled samples were stored at –20°C until further treatment. These small rodents constitute the main diet component of common buzzards (*Buteo buteo*) and make up to 40% of the red fox's diet (*Vulpesvulpes*).

Samples of passerines, such as great tits (*Parus major*) and blue tits (*ParusCaeruleus*), were obtained from different campaigns conducted between 2001 and 2003. Individual fat samples (n = 25) together with individual (n = 6) and pooled (n = 9) egg samples were available. Passerines, such as the great and blue tits, form the vast majority of the sparrow hawk's diet (*Accipiter nisus*).

The following PBDE congeners were targeted for analysis: 28, 47, 99, 100, 153, 154, 183, and 209. BDE 77 was used as internal standard (IS) for BDE 28, 47, 99, 100, 153, and 154, and BDE 128 was used as IS for BDE 183. ^{13}C-labelled BDE 209 was used as IS for BDE 209.

The analysis method has been previously described[8] and is briefly presented below. Between 0.3 and 5 g of homogenised sample, depending on tissue type, was dried with anhydrous Na_2SO_4, spiked with IS and hot Soxhlet extracted for 2 h using a hexane/acetone mixture (3:1, *v/v*). The extract was cleaned-up on 10 g of acidified silica (48% H_2SO_4, *w/w*) and elution of PBDEs was realized with n-hexane and dichloromethane. PBDEs were analysed using a GC/ECNI-MS operated in selected ion-monitoring mode. BDEs 28 to 183 were separated on 25 m ´ 0.22 mm ´ 0.25 µm HT-8 capillary column (SGE) and *m/z* = 79 and 81 were monitored. BDE 209 was analysed on 15 m ´ 0.18 mm ´ 0.10 µm AT-5 capillary column (Alltech) and ions *m/z* = 484.7 and 486.7 and *m/z* = 494.7 and 496.7 were monitored for BDE 209 and ^{13}C-labelled BDE 209, respectively.

The quality control was done by regular analyses of procedural blanks, blind duplicate samples, and random injection of solvent blanks and standards. The quality of the methods used, was verified by regular participation in interlaboratory exercises (Quasimeme). Procedural blanks were consistent and therefore the mean blank values were used for subtraction. Limit of quantification (LOQ) for PBDEs, based on the GC/MS performance and procedural blanks, was dependent of the sample intake and was set at 2 times the standard deviation (SD) of the procedural blanks for all congeners except BDE 209, for which 3 ´ SD was used. In order to facilitate statistical data treatment, measurements below LOQ were replaced by p ´ LOQ, where "p" is the fraction of measurements above LOQ.

Results and discussion

PBDE levels in rodents and passerines. PBDE levels found in small rodents can be considered low, with numerous measurements below LOQ (Table 1). Sum of PBDEs (BDE 28 to 183) ranged from 2.4 to 35 ng/g lw in liver, from 2.2 to 53 ng/g lw in muscle and from 0.23 to 4.9 ng/g lw in brain (Table 1). These low concentrations are explained by the herbivorous character of the rodent species, although voles may also eat insects. No significant difference was observed between PBDE levels measured in different rodent species, and therefore data were presented together (Table 1). The only available data on PBDEs in small terrestrial mammals are from rabbit muscle collected in 1993 in which levels of BDE 47, 99 and 100 were all < 1.8 ng/ lw[7].

Table 1. BFR levels (median, ng/g lw) and lipid% (SD) in the various tissues of small rodents (n=70) and passerines (n=40).

			BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	Sum PBDEs	BB 153	Lipid % (SD)
Rodents	Liver	Conc.	0.06	2.6	0.37	2.1	0.07	1.8	1.2	8.5	0.18	6.1 (0.48)
		% > LOQ	36	100	100	100	43	100	100	-	100	-
	Muscle	Conc.	0.08	2.8	0.40	2.1	0.07	1.4	1.4	7.6	0.15	2.4 (0.28)
		% > LOQ	36	79	86	71	29	100	93	-	57	-
Great tits	Eggs	Conc.	1.0	113	15	53	6.5	26	10	223	7.0	11 (1.7)
		% > LOQ	100	100	100	100	100	100	100	-	89	100
	Fat	Conc.	1.8	44	11	37	3.3	16	6.3	118	2.1	73 (7.7)
		% > LOQ	76	100	100	100	100	100	100	-	100	-

PBDE levels found in these passerines are higher compared to the rodents, probably due to their insectivorous diet (Table 1). Sum of PBDEs (BDE 28 to 183) ranged from 83 to 536 ng/g lw in eggs and from 50 to 500 ng/g lw in body fat (Table 1). All congeners, except BDE 28, could be measured in 100 % of the egg and fat samples.

BB 153. Although PBBs have never been extensively used in Europe[2], BB 153 could be found in nearly all rodent samples, with a tissue-dependent detection frequency (lower levels in muscle) (Table 1). The median concentration in rodent liver was 0.18 ng/g lw and can be considered as relatively low. In the passerines, the median concentration in fat was around 2 ng/g lw. Median BB 153 levels observed in liver of red fox from the same geographical region were around 0.57 ng/g lw.[10] BB 153 was also determined in sparrowhawks from the same area and median levels in liver were up to 200 ng/g lw[6].

Food chain transfer. Previously, PBDEs had been determined in tissues of red fox, buzzard and sparrowhawk (Table 2)[6,9,10]. PBDE levels in red fox can be considered as relatively low, which was quite unexpected for a

carnivorous terrestrial top-predator. However, similar to other mammals, foxes are more likely to possess strongly developed metabolization systems[11]. Contrarily, tissue levels of PBDEs in birds of prey are higher, with the sparrowhawk having a higher load than buzzard (Table 2).

Table 2. BFR-levels (median in ng/g lw) and lipid % (SD) in the various tissues of top-predators

		N	BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	Sum PBDEs	BB 153	Lipid % (SD)
Sparrowhawk	**Liver**	12	2.5	500	280	560	75	340	170	2100	14	3.0 (1.3)
	Muscle	12	4.6	400	270	710	80	340	200	2000	19	2.2 (2.0)
	Fat	2	1.6	475	250	630	85	320	175	1900	2.92	91 (3.8)
Buzzard	**Liver**	45	2.5	20	7.4	20	6.2	18	7.8	75	4.2	3.8 (1.3)
	Muscle	45	1.9	30	9.1	30	8.3	37	20	150	3.9	4.2 (2.3)
	Fat	16	0.17	15	4.2	15	3.1	15	5.4	60	0.83	106 (4.4)
Fox	**Liver**	30	< 0.04	0.33	0.05	0.11	0.02	1.2	0.61	2.4	0.57	5.8 (3.5)
	Muscle	33	< 0.05	1.4	0.02	0.74	0.02	0.83	0.14	3.4	0.19	3.4 (1.7)
	Fat	27	< 0.03	0.2	0.05	0.33	0.04	0.76	0.37	2.2	0.18	72 (22)

Because these 3 species occupy top positions in the food chain, it is likely that biomagnification from the preys of the present study to these top-predators is substantial.Small rodents, such as mice, voles and shrews are the main constituents of the fox's diet (> 40%). However, foxes do not have a strict dietary pattern and can adapt easily to available food sources in their territory. Nevertheless, these small rodents can provide valuable information on the PBDE exposure of foxes. Interestingly, the median levels of PBDEs measured in fox are lower than those in rodents (Tables 1 and 2). It has been previously shown that foxes and other canidae species possess a high metabolic ability to transform PCBs[11,12]. The structural similarity between PCBs and PBDEs suggests a similar metabolic capacity for the latter compounds as well, which may explain the low levels of PBDEs found in the tissues of fox.

The diet of sparrowhawks consists mainly of passerines (around 95 %), while the rest is composed of small rodents. Extensive biomagnification can be expected from passerines to sparrowhawks due to the fact that sparrowhawks need to feed approximately 25% of their own body weight each day.

Buzzards feed mainly on small mammals, such as mice, voles, rabbits and rats. Small birds, such as tits, only represent a small fraction of their diets. Transfer of PBDEs to buzzards can most likely be expected from small rodents rather than from passerines.

Biomagnification factors (BMFs) from prey to predator have been calculated for various tissues (Table 3), using the following formula: BMF = [predator]/[prey], all concentrations expressed in ng/g lw. The highest BMFs are found from rodents to buzzard (BMF up to 115 for BDE 154). Also BMFs from passerines to sparrowhawk are high with increasing BMFs as the degree of bromination increases (BMF=1 for BDE 28 to BMF=30 for BDE 183) (Table 3). Surprisingly, no biomagnification could be seen from rodents to foxes, although rodents constitute an important part of the fox's diet. The elevated metabolic capacity of the canidae species is most likely to be involved.

Table 3. Biomagnification factors of PBDEs from prey to predator

	BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	Sum PBDEs	BB 153
Rodents (L) => Buzzard (L)	40	10	20	10	85	10	5	10	25
Rodents (M) => Buzzard (M)	25	10	25	15	115	25	15	20	25
Rodents (L) => Fox (L)	n.a.	< 1	< 1	< 1	< 1	1	1	< 1	5
Rodents (M) => Fox (M)	n.a.	< 1	< 1	< 1	< 1	1	< 1	< 1	1
Passerines (F) => Sparrowhawk (M)	3	10	25	20	25	20	30	15	10
Passerines (F) => Buzzard (M)	1	1	1	1	2	2	3	1	2

n.a. = not available; L = Liver; M = Muscle; F = Fat

Table 4. Biomagnification factors of PCBs from prey to predator

	PCB 153	PCB 170	PCB 180	PCB 194
Rodents (L) => Buzzard (L)	25	20	15	50
Rodents (M) => Buzzard (M)	50	120	40	200
Rodents (L) => Fox (L)	2	4	4	5
Rodents (M) => Fox (M)	1	15	3	20
Passerines (F) => Sparrowhawk (M)	20	25	20	20
Passerines (F) => Buzzard (M)	2	3	3	3

n.a. = not available; L = Liver; M = Muscle; F = Fat

BMFs have also been calculated for the most persistent PCBs, such as PCB 153, 170 and 180 (Table 4). For these congeners, the highest BMFs were seen also from rodents to buzzard (BMF up to 200 for PCB 194). Consistent BMFs (around 25) were calculated from passerines to sparrowhawk. Although BMFs of PCBs from rodents to fox are higher than 1, no biomagnification could be seen for PBDEs. BMFs of PCBs are also higher for muscle than for liver, which is in accordance to the metabolic function of the latter tissue.

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