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# Higher Brominated Diphenyl Ethers and Hexabromocyclododecane Found in Eggs of Peregrine Falcons (*Falco peregrinus*) Breeding in Sweden

PETER LINDBERG

Swedish Society for Nature Conservation, Box 4625,  
SE-116 91 Stockholm, Sweden, and Department of Zoology,  
University of Göteborg, Box 463, SE-405 30 Göteborg, Sweden

ULLA SELLSTRÖM,  
LISBETH HÄGGBERG, AND  
CYNTHIA A. DE WIT\*

Laboratory for Analytical Environmental Chemistry,  
Institute of Applied Environmental Research (ITM),  
Stockholm University, SE-106 91 Stockholm, Sweden

Several brominated flame retardants (BFRs) were analyzed in peregrine falcon eggs collected in 1987–1999, including the constituents of the technical polybrominated diphenyl ether (PBDE) products Penta (BDE-47, -99, -100, -153, -154), Octa (BDE-183), and Deca (BDE-209), hexabrominated biphenyl (BB-153), and hexabromocyclododecane (HBCD). The eggs represented females from three different breeding populations, northern Sweden, southwestern Sweden, and a captive breeding population. All BFRs analyzed for were found, including BDE-183 and -209, and concentrations were much higher in wild falcons (geometric mean  $\Sigma$ PBDE, BB-153, and HBCD for northern/southern populations of 2200/2700, 82/77, and 150/250 ng/g lw, respectively) than in captive falcons (39, 8 ng/g lw, and not detected, respectively). This is the first time, to our knowledge, that BDE-183 and -209 have been quantified in high trophic level wildlife.

## Introduction

Polybrominated diphenyl ethers are widely used as flame retardants in textiles and plastics. The world market demand for the technical BDE products in 2001 was 7500 tons penta-, 3800 tons octa-, and 56100 tons decaBDE (1). Market demand for HBCD was 16100 tons (1). Based on recent risk assessments, penta- and octaBDE will be banned within the EU in 2004 (2). There are no restrictions on the use of decaBDE, which is the most used BDE technical product.

Products containing lower brominated BDEs as well as single congeners have been shown in experimental studies to produce effects in both fish and mammals (reviewed in refs 3 and 4). There are much less data on the effects of higher brominated BDEs and HBCD. However, BDE-153 and BDE-209 have been shown to cause the same types of neurobehavioral effects in neonatal mice as BDE-47 and -99 (5–7).

Most analyses of PBDEs in Swedish fauna have been on species belonging to marine/freshwater food webs or at lower

trophic positions in the terrestrial food web (8–13). For predatory birds, only muscle samples from the fish-eating osprey (*Pandion haliaetus*) and white-tailed sea eagle (*Haliaeetus albicilla*) have previously been analyzed (8, 11). Most data produced are for the components of the pentaBDE product with very few data so far for BDE-183 or -209 in the environment (reviewed in ref 4). Terrestrial organisms from lower trophic levels have lower BDE concentrations than are generally seen in aquatic food webs (4). BDE-47, -99, and -100 bioaccumulate and biomagnify in predatory fish, birds, and mammals from aquatic food webs (reviewed in ref 4). Piscivorous predatory birds and marine mammals also have a congener pattern dominated by BDE-47. Only preliminary analyses have so far been reported for terrestrial birds-of-prey (14, 15) and none for predatory mammals in the terrestrial food web.

Increasing environmental concentrations of the lower brominated BDEs have been seen on a global scale in both biota and in sediments (reviewed in ref 4). The only information available for BDE-209 is from a dated sediment core from Drammenfjord, Norway, which indicates that BDE-209 shows up approximately 10 years after other BDEs (16).

Peregrine falcons feed almost exclusively on other birds (17), and most populations of the species were previously endangered in the northern hemisphere because of the bioaccumulation of high concentrations of several organochlorine pesticides and mercury, which affected both reproduction and survival (18). Two breeding wild populations exist in Sweden, and a captive breeding population is also maintained. The northern wild population feeds on waders and ducks, while the southern wild population feeds on birds in the terrestrial food web (19). The captive population is raised on a controlled diet of domestic chickens. Concentrations of organochlorine compounds have declined significantly in peregrine falcons in Sweden, and the populations began to recover in the mid-1990s (P. Lindberg, unpublished data). However, the increasing temporal trends of PBDEs in the environment represent a potential new threat to this species if concentrations are high.

It was therefore of interest to determine if brominated organic compounds were present in wild and captive Swedish peregrine falcons, at what levels, and if any differences in the wild populations could be seen based on their diet, as has been shown previously for mercury (19, 20). We also hypothesized that BDE-209, if present in biota, would most likely be found in organisms from the terrestrial, not the aquatic environment, so some of the peregrine falcon eggs were screened for BDE-209.

## Methods

Peregrine falcon eggs were collected within the Swedish Society for Nature Conservation inventory program, with permission from the Swedish Environmental Protection Agency. Sampling sites for the wild falcons are shown in Figure 1. Egg contents were removed and stored frozen in tinted glass jars. Samples were from unfertilized eggs collected during the incubation period or unhatched eggs collected after normal incubation was completed. In some cases, eggs were collected during different years from the same female (maximum 4-year interval). Eggs from the southwestern population and the captive population were mainly fresh, infertile eggs. Most eggs collected in northern Sweden were collected after incubation. Only eggs lacking embryonic development were analyzed. Addled eggs may represent a bias as these eggs may be more contaminated than the eggs that have hatched. However, in a previous study, intraclutch

\* Corresponding author phone: +46 8 6747180; fax: +46 8 6747637; e-mail: cynthia.de.wit@itm.su.se.

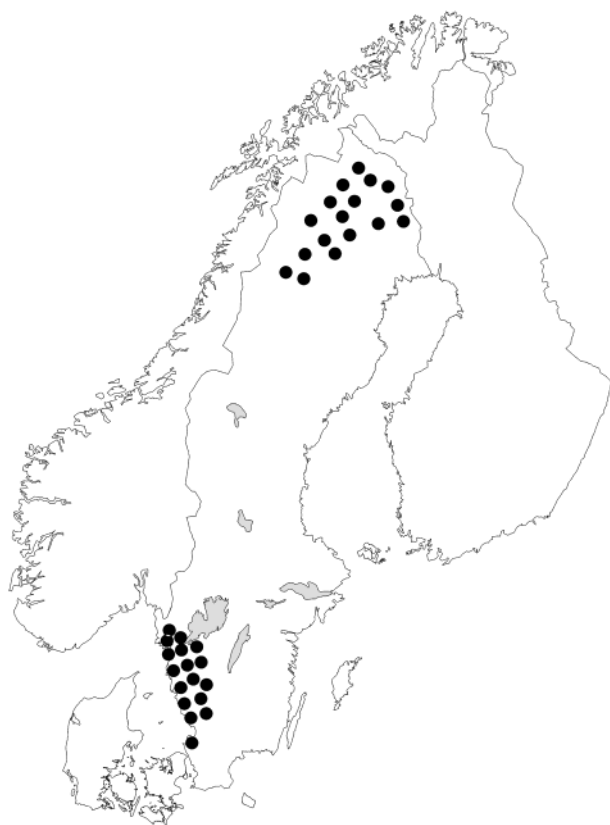


FIGURE 1. Sampling sites for peregrine falcon eggs in northern and southwestern Sweden.

variation in residue levels of organochlorines was low, while interclutch variation (different females) was high (21). Therefore, a single egg from a clutch was considered an unbiased sample representing the female for that breeding year. For southwestern Sweden, 24 eggs from 17 females collected between 1992 and 1999 were analyzed. For northern Sweden, 18 eggs from 18 females collected between 1991 and 1999 were analyzed. For the captive breeding population, 10 eggs from 8 females collected between 1987 and 1999 were analyzed. All but one of these females were hatched in captivity or collected as nestlings. Twenty-one eggs were analyzed for BDE-209 and HBCD (4 from the captive population, 9 from the southern population, 8 from the northern population). Samples were homogenized and extracted, the lipid weight was determined, and lipids were then removed (22, 23). Standards used were individual BDE congeners: BDE-47, -99, -100, -153, -154 from Cambridge Isotope Laboratories; commercial DeBDE (Dow FR-300BA, Dow Chemicals, Midland, MI); Firemaster BP-6 (recrystallized two times) for BB-153 (EPA); HBCD (Michigan Chemical, St. Louis, MI); and BDE-183 (90–95% purity, kind gift from E. Jakobsson, Stockholm University (24)). Due to lower purity of the BDE-183 standard, concentrations of this congener must be regarded as somewhat overestimated. Dechlorane (Hooker Chemical Corp.) was used as internal standard. Analysis was performed using GC/MS-ECNI (10) with the following modifications: the GC column was equipped with either a 40 m DB-5MS (methyl+5% phenyl) capillary column for analysis of BDEs-47 to -183 and BB-153 or a 12.5 m DB-5MS (methyl+5% phenyl) capillary column for analysis of BDE-209 and HBCD. The method for HBCD is semiquantitative.

QA/QC samples (aliquots of the laboratory reference material, a large herring homogenate) were extracted and analyzed in parallel with the eggs. The GC/MS analysis was performed mixing samples and calibration standards ran-

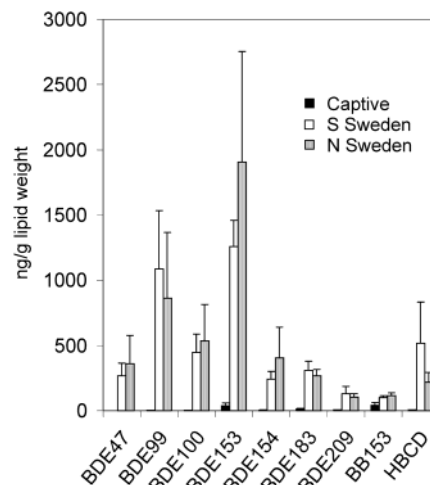


FIGURE 2. Concentrations (ng/g lipid weight, mean  $\pm$  SE) of BDE-47, -99, -100, -153, -154, -183, -209, BB-153, and HBCD in eggs from two wild and one captive population of peregrine falcons in Sweden.

domly, with solvent runs before and after standard injections to avoid memory effects. The calibration curves were made from standard solutions at 5–9 concentration levels. Compounds were positively identified if the relative retention time (versus the internal standard) differed no more than 0.01 from that of the calibration standards. Peaks less than five times the noise level (three times for BDE-209 and HBCD) were considered below the quantitation limit and are reported as < values. Laboratory blanks were run through the entire procedure at each extraction occasion. All BDE, BB, and HBCD concentrations in blanks were below quantitation limits or less than 1% of the amount in the samples.

## Results and Discussion

All BDE congeners analyzed for, as well as HBCD and BB-153, were detected in both the wild and the captive peregrine falcon eggs, with much higher concentrations in the wild falcon eggs (Table 1). BDE-209 was found in 18 of 21 analyzed eggs (range <20–430 ng/g lipid weight in wild and <7–9 ng/g lipid weight in captive falcons). The different quantitation limits for BDE-209 in wild and captive falcon eggs are due to different sample amounts taken for analysis. BDE-183 was found in all 52 eggs, with much higher concentrations in the two wild populations (range 56–1300 ng/g lw) compared to the captive falcons (range <6–19 ng/g lw). For individual results, see Tables S1–S3, Supporting Information. No temporal trends could be discerned in either the wild or the captive populations. However, this is probably because the number of eggs from different time points were too few and the time period covered (the 1990s) too short.

Statistically significant differences were seen for BDE-99 concentrations between the wild falcon populations, with the southern population having higher concentrations than the northern population (Table 1). There were no statistically significant differences for any other BDE concentrations between the wild peregrine falcons from the northern and southwestern populations, despite them having different diets during breeding (Table 1, Figure 2). However, peregrine falcons as well as many of their prey migrate to wintering grounds along the coasts of southern Europe, where they may be exposed to PBDEs. Studies of sediments from many European river mouths have shown the presence of elevated concentrations of PBDEs, including BDE-209, and PBBs in sediments (25, 26).

When they migrate north, the falcons will continue to be exposed via their diet of migratory birds. Thus, this may indicate that wild falcons are exposed to roughly the same

**TABLE 1. Arithmetic Mean, Standard Deviation (SD), and Geometric Mean (GM) Concentrations (ng/g lipid weight) of Polybrominated Diphenyl Ethers (PBDEs), Hexabromobiphenyl (BB-153), and Hexabromocyclododecane (HBCD) in Eggs from Three Different Peregrine Falcon Populations<sup>a</sup>**

population	year	no. of eggs	BDE47	BDE99	BDE100	BDE153	BDE154	BDE183	BDE209	BB153	HBCD
a) captive	1987–1999	10									
mean			0.83	2.7	2.4	36	4.6	11.6	8.2	40	nd
SD			0.44	0.8	1.1	64	3.3	5.6	0.9	66	
range			(<0.3–1.4)	(1.2–3.8)	(<0.4–4.4)	(7.7–195)	(1.1–10.3)	(<6–19)	(<7–9)	(0.73–170)	(<4–<8)
GM			0.72	2.6	2.2	18	3.6	10.4	8.1	8	nd
b) S Sweden	1992–1999	24									
mean			270	1100	450	1300	240	310	130	99	520
SD			400	1800	620	820	240	290	140	67	840
range			(15–1600)	(140–8000)	(100–2700)	(500–3400)	(57–1100)	(58–1300)	(<20–430)	(26–180)	(79–2400)
GM			140	620	290	1100	190	230	86	77	250
c) N Sweden	1991–1999	18									
mean			360	860	540	1900	410	270	110	110	220
SD			910	2100	1200	3600	1000	210	76	110	210
range			(22–3800)	(110–9200)	(77–5200)	(270–16000)	(50–4400)	(56–700)	(28–190)	(27–370)	(34–590)
GM			96	330	240	1000	180	200	80	82	150
level of significance											
a versus b				<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
b versus c			0.195	0.02	0.318	0.546	0.591	0.823		0.909	

<sup>a</sup> Sample sizes for eggs analyzed for BDE-209 and HBCD were 4 = captive, 7 = S Sweden, and 8 = N Sweden. Differences between populations were tested with the two-tailed Mann–Whitney U-test. BDE-183 values are somewhat overestimated and HBCD values are semiquantitative. BDE-47 = 2,2',4,4'-tetrabromodiphenyl ether; BDE-99 = 2,2',4,4',5-pentabromodiphenyl ether; BDE-100 = 2,2',4,4',6-pentabromodiphenyl ether; BDE-153 = 2,2',4,4',5,5'-hexabromodiphenyl ether; BDE-154 = 2,2',4,4',5,6'-hexabromodiphenyl ether; BDE-183 = 2,2',3,4,4',5,6-heptabromodiphenyl ether; BDE-209 = 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether. n.d. means not detected.

amount of PBDEs and other brominated compounds in their food in both areas and that these may be widespread contaminants in both aquatic and terrestrial bird prey species. However, the statistically significantly higher concentrations of BDE-99 in the southern population indicate that there may also be some differences in congener-specific dietary exposure, possibly due to different congener patterns in aquatic versus terrestrial prey birds. Northern and southern populations of peregrines may also winter in different areas causing a dietary difference, but according to ring-recovery studies there is considerable overlap in wintering-grounds for the two populations (27).

The ΣPBDE concentrations for the lower brominated congeners (BDE-47, -99, and -100) in some of the wild peregrine falcons (maximum of 18000 ng/g lw) are among the highest concentrations seen in wildlife so far. If BDE-153 and -154 concentrations are added, the maximum ΣPBDE concentrations are as high as 39000 ng/g lw (see Tables S2 and S3, Supporting Information). On a wet weight basis, the arithmetic mean concentrations of ΣPBDE, BB-153, and HBCD for the northern population are 230, 6.6, and 53 ng/g. These can be compared to the mean ΣPCB, DDE, and dieldrin concentrations of 12000, 2900, and 140 ng/g ww in eggs ( $n=32$ ) from the same population collected 1991–1994 (P. Lindberg, unpublished results). Thus, the total concentration of the brominated compounds makes up approximately 2% of the total load of measured organohalogen compounds.

The wild falcons had statistically significantly higher PBDE concentrations than the captive falcons (Table 1, Figure 2), which are raised on a controlled diet of chickens. Concentration ranges for the other BFRs in the wild and captive populations are given in Table 1. The largest difference was for BDE-99 where the arithmetic mean was 400 times higher in wild falcon eggs compared with captive falcon eggs.

In several cases, eggs from the same female were collected in different years and analyzed. No clear BDE concentration differences were evident, so means for the eggs from the same female were used in the statistical analyses. One female in the captive breeding population was recruited as an adult from northern Sweden after a wing injury. After four years

in captivity, this female (377-1-1) still had BDE-153 and -154 concentrations that were higher than in the other captive falcons, indicating long half-lives for these congeners. BDE-209 was found in similar concentrations as for the other captive falcons, indicating that this congener may be metabolized more readily as has been seen in humans (28) and rats (29).

The congener patterns of the wild falcons were dominated by the Hx- and PeBDEs, particularly BDE-153, -99, and -100 followed by HBCD (Figure 2). BDE-47, -154, and -183 were present in lower but similar concentrations, followed by BDE-209 and BB-153. The captive population had a somewhat different congener profile than the wild populations, dominated by BDE-153 and BB-153, followed by BDE-183 and -209, then HBCD and BDE-154, with not detectable to very low levels of BDE-47 and low concentrations of BDE-99 and -100. These differences can only be explained by differences in exposure due to diet.

The pattern of PBDE congeners is different in peregrine falcons when compared to previous analyses in piscivorous birds. In guillemot eggs (*Uria aalge*) from the Baltic Sea (30), for example, the dominant congener is BDE-47. The BDE-47, -99, -100, -153, and -154 as well as HBCD concentrations from 1999 were also much higher in falcon eggs (means of 290, 850, 460, 1800, 390, and 250 ng/g lw, respectively) than in guillemot eggs (means of 130, 13, <7, <3, <5, and 150 ng/g lw, respectively).

Some argue that the decaBDE (BDE-209) molecule is so large that it is not bioavailable and therefore cannot accumulate in living organisms. Our study indicates that this is not correct. Eggs from the wild peregrine populations had significantly higher BDE-209 concentrations than the captive population feeding on chickens. This is an indication that this congener is present in the environment, is bioavailable, and taken up in falcons and transferred to eggs. This should not be considered surprising as PCB uptake studies in terrestrial birds such as kestrels (*Falco sparverius*) and ring doves (*Streptopelia risoria*) show high uptake and accumulation of higher chlorinated CB congeners such as Hx-, Hp-, and OcCBs (31, 32). Even 60–70% of CB-209 (DeCB) has



been found to be absorbed in chickens (33). The extent of uptake and transfer of BDE-209 in peregrine falcons is not known and requires further study. Our results also indicate that organisms in the terrestrial environment may be more highly exposed to the higher brominated BDEs, in comparison with aquatic organisms. This requires further study as well.

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## Supporting Information Available

Three tables (S1–S3), one for each falcon population, with concentrations of the individual compounds for each peregrine falcon egg. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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