

TEMPORAL TRENDS OF POLYBROMINATED DIPHENYL ETHERS AND HEXABROMOCYCLODODECANE IN SWEDISH PEREGRINE FALCON (*FALCO PEREGRINUS*) EGGS

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Abstract

A temporal trend study of brominated flame retardants in eggs from peregrine falcon (*Falco peregrinus*), a terrestrial bird of prey, is presented. Eggs collected between 1974 and 2007 were analyzed for the major constituents of the Penta-, Octa- and Decabromodiphenyl ether technical products (BDE-47, -99, -100, -153, -183 and -209), and hexabromocyclododecane (HBCD). Concentrations of BDE-99, -100, -153, -183, -209 and HBCD increased during the first twenty years of this study. After the early 2000s, BDE-99, -100, -153 and -183 concentrations decreased, whereas BDE-209 and HBCD concentrations continued to increase. There is a change in BDE congener patterns over time, with a shift from the dominance of BDE-99 and -47 until late 1980s, to BDE-153 being the predominant congener later on. The Swedish peregrine falcons migrate to southwest Europe during winter and their body burdens of BFRs reflect the general exposure situation in Europe.

Introduction

Temporal trend monitoring is a useful tool in understanding the relationship between levels of contaminants in the environment and their emissions as well as for evaluation of measures taken to reduce emissions. Temporal trend studies from Europe show that tetra- to hexaBDEs started to appear in the environment in the early 1970s and that concentrations increased until about 1985-1995 followed by a stabilisation or decrease after bans^{1,2}. BDE-209 appears in European sediments 10 years later than the PentaBDE congeners. There was a steady increase until the early 1990s when a decrease was seen in German lake sediments³, while no indication of decrease was observed in Swiss lake sediments⁴. HBCD appeared in the European environment in the mid 1980s, generally. Increasing HBCD trends have been observed in wildlife^{1,2} and human milk⁵.

The peregrine falcon (*Falco peregrinus*), a terrestrial bird of prey that preys upon other birds, was close to extinction due to high concentrations of organochlorines and heavy metals in the 1970s⁶. Due to restrictions on these chemicals and a successful breeding programme, the Swedish peregrine falcon population is recovering. In 2004, high levels of PBDEs were found in Swedish peregrine falcon eggs, including the higher brominated congeners BDE-183 and -209, as well as HBCD⁷. Thanks to the long tradition of collecting falcon eggs in Sweden, it was possible to conduct retrospective temporal trend studies of these compounds in a terrestrial bird of prey.

Methods

Addled or unfertilised eggs were collected annually from the population of peregrine falcon in southern Sweden between 1974 and 2007. From the first 20 years of this time series only a few eggs per year were available due to the low breeding success of the peregrine falcons. Samples from 1974 to 1999, as well as 2006, were analysed individually. Individual eggs were analysed to provide a measure of the within-year variation. Between 2000 and 2007, pooled samples containing aliquots from 5-8 individual eggs were analysed. Egg homogenates were liquid-liquid extracted according to methods described in detail elsewhere^{8,9}. Lipid amounts were determined gravimetrically. Internal standards (Dechlorane 603 and ¹³C-BDE-209) were added to an aliquot of the lipids after extraction.

Analysis was done by gas chromatography – mass spectrometry (GC-MS), running the MS in chemical ionisation mode with ammonia as reagent gas, and measuring the negative ions formed (ECNI). The GCs were equipped with DB-5MS fused-silica columns (J&W Scientific), 15 m for BDE-209 and 30 m for tetra-hexaBDEs and HBCD. Detailed information on instrumental settings can be found in Johansson *et al.* (2009)¹⁰. The ions measured were m/z -79 and -81 (bromide ions, tetra-hexaBDEs and HBCD), m/z -484.6, -486.6, -494.6 and -496.6 (phenoxide ions, native and labelled BDE-209), and m/z -237 and -239 for dechlorane. In this study, results for BDEs -47, -99, -100, -153, -183, -209 and HBCD are reported.

To test for significant changes in the individual PBDE-congener and HBCD concentrations over time, log-linear regression analysis was performed. The non-parametric Mann-Kendall trend test was also performed on linear trends. To test for non-linear trend components, a 7-point running mean smoother was applied. Analysis of variance (ANOVA) was used to test this line for significance¹¹.

Results and Discussion

The tetra- to hexaBDEs were present in the falcon eggs already in 1974, whereas BDE-183, -209 and HBCD started to appear in quantifiable levels around 1985 (Figure 1). For BDE-99, -100, -153, -183, -209 and HBCD, significantly increasing linear trends were detected both with the log-linear regression and the Mann-Kendall trend test ($p < 0.05$). BDE-99 and -100 concentrations increased approximately 3-fold from the early 1980s to 1995. For BDE-153 and -183 the concentrations increased approximately 10-fold during the same period. Based on the 7-point running mean smoother, significant non-linear trends were also found for BDE -99, -100, -153, -183 and -209. All PBDEs except BDE-209, showed increasing concentrations until 1995, a leveling off, and then a decrease around 2000-2001. The BDE-209 concentrations continued to increase until 2006 and the yearly increase was 15% per year. For HBCD, the log-linear regression was statistically significant and concentrations are still increasing. The yearly increase is 11% per year, or an increase from about 10 ng/g lipid weight (lw) to 300 ng/g lw over the last 30 years. No temporal trends were detected for BDE-47.

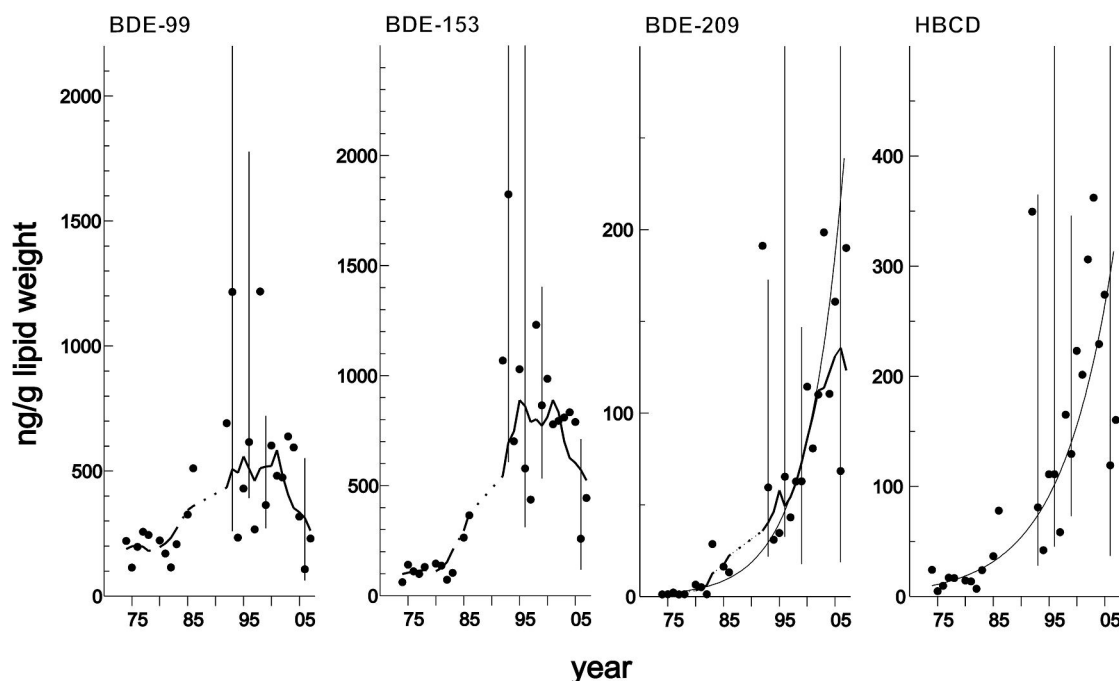


Figure 1. Temporal trends of BDE-99, -153, -209 and HBCD in peregrine falcon eggs from southern Sweden. Concentrations are in ng/g lipid weight. Dots represent the median values and error bars represent 25-75 % percentiles. Log-linear regression (thin line) and 7-point running mean smoother (bold line, drawn where statistically significant $p < 0.05$).

The BDE-99 and BDE-100 temporal trends in falcon eggs agree well with that in breast milk from Swedish mothers (1980-2004) where the increase of tetra-pentaBDEs continued until the mid 1990s and then started to decrease^{5,12}. BDE-99 concentrations in guillemot eggs from the Baltic Sea between 1969 and 2007 show a similar increase, levelling off and decline, but 10 years earlier¹³. Guillemots are piscivorous marine seabirds that are resident in the Baltic Sea, and represent more local emissions to the Baltic Sea, while the concentrations in Swedish peregrine falcons may be more a reflection of the diffuse spread of PBDEs on a European scale.

Comparison of the HBCD temporal trend between peregrine falcons and guillemot shows these to be more similar to each other. The HBCD concentrations increase rapidly and linearly in both species over the same time period, but at a more rapid rate in the falcons, leading to higher concentrations in the falcons in the late 1990s and onwards. There are no signs of concentrations leveling off in either species. These trends differ from that of breast milk from Swedish mothers, where HBCD concentrations have also risen rapidly from 1980 to 2002 but have then leveled off⁵.

For BDE-209, UK peregrine falcon egg concentrations increased from 1975 to 1995 and then decreased significantly¹. This was explained by an increasing consumption of DecaBDE in the UK, which peaked in 1989, and then decreased. Our results also indicate a possible decrease or leveling off of BDE-209 concentrations about 10 years later than in the UK peregrine falcons.

Our data for PBDEs and HBCD can also be compared to those from two other temporal trend studies in peregrine falcons. Similar to our results of a yearly 15% increase in BDE-209 concentrations, increasing BDE-209 concentrations were also shown in peregrine falcons from southern Greenland (6 % per year between 1986-2003)¹⁴, and from different locations in the USA (20 % per year between 1996-2006)¹⁵. Median concentrations of BDE-209 (48 ng/g lw (1874-2007) and 84 ng/g lw (1996-2006) in the peregrine falcon eggs in this study are lower than median concentrations in peregrine falcons from the US (480 ng/g lw) but higher than in falcon eggs from Greenland (11 ng/g lw). The higher median concentrations in US peregrine falcons may be due to the higher market demand for DecaBDE in North America compared to Europe. The increasing trends in all three studies also probably reflect usage patterns, as DecaBDE is still in wide use on both continents. In Greenland falcons, the concentrations of BDE-99, -100, -153 and -154 increased as well, while no significant trends could be detected for BDE-47, -66, -183 and HBCD¹⁴.

Congener pattern changes

The temporal trends for the different BDE congeners leads to a shift in the congener pattern in falcon eggs with time. Eggs from the 1970s contain a higher proportion of lower brominated BDEs, but over time, the higher brominated BDEs become more important. The most rapid proportional increase is for BDE-153, and in the late 1980s it becomes the predominant congener in falcon eggs. This rapid proportional increase could be indicative of a change in the source of exposure to BDE-153, from the PentaBDE product in the 1970s to 1980s to the Octa- and DecaBDE products in the 1990s and 2000s.

The peregrine falcon as monitoring species

The within-year variation in this dataset is large, and may to a large extent be due to the migratory behavior of the birds. Although the peregrine falcons breed within a fairly limited region of Sweden, they (and also their prey) migrate to wintering grounds in other parts of Europe. Peregrine falcon eggs might not, for the above given reasons, be the optimal matrix for these kinds of studies. But this sensitive top predators' history of high contamination load and the presence of higher brominated BDEs (including BDE-209) still makes its eggs a very valuable matrix, as there are currently few species where BDE-209 temporal trends can be followed. The peregrine falcon is a globally occurring species, which makes comparison between continents possible both for spatial studies as well as to follow temporal trends.

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