Congener Patterns of PBDEs in Eggs from Peregrine falcon *(Falco peregrinus)* Breeding in Sweden.

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Introduction

The technical product decaBDE constitutes 80% of the world market demand of brominated flame retardants. The fully brominated BDE-209 has, up until recent years, been assumed not to be biologically available because of the large size and lipophilicity of the molecule. Most previous studies were done in wildlife representing the aquatic food chain. In 2004, Lindberg et al. (2004) found high levels of BDE-209 in eggs of wild peregrine falcon *(Falco peregrinus)*. The pattern of PBDE congeners was also different from earlier studies, with BDE-153 as the dominant congener. Peregrine falcons prey upon other birds and thus can be considered a part of the terrestrial food chain. In other species from the terrestrial food chain, a similar congener pattern has been found (Christensen et al. 2005, Voorspoels et al. 2006, Herzke et al. 2005, Jaspers et al. 2006, Vorkamp et al. 2005). The study by Lindberg et al., included BDEs –47, -99, -100, -153, -154, -183, -209 as well as HBCD in eggs from three different populations of peregrine falcon breeding in Sweden. The current study is based on the same samples, but more PBDE congeners have been quantified to determine if there are congener differences in the different populations due to diet. Our hypothesis is that there will be pattern differences between the two populations that can be differentiated using multivariate data analysis. The southern population preys mainly on terrestrial birds, the northern preys on waders and ducks, and the captive population was raised on domestic chickens and quail. We hypothesize that the higher brominated PBDEs are present to a higher extent in the eggs from the southern population (terrestrial bird diet) compared to the northern population (aquatic bird diet).

Materials and Methods.

Sample extracts from a previous study were used in this study (Lindberg et al. 2004). In the previous study, BDE-47, -99, -100, -153, -154, and -183 were analysed in 52 egg samples and BDE-209 and HBCD were analysed in 21 of the eggs. In this study BDE-209 and HBCD were analysed in the remaining samples and additional analyses of BDE-35, -184, -185, -196, -197, -203, and -207 were performed using GC/MS-ECNI. Ten samples from the captive population, 18 samples from the northern population and 24 samples from the southern population were analysed. The limit of quantification was set to three times the noise level for BDE-209 and for the other congeners to five times the noise level.

PBDE congener patterns were studied with Principal Component Analysis (PCA). Analysis was carried out on concentration data as well as on ratios of each congener to the sum of PBDEs. Before analysis, concentration data were log-transformed to achieve more normally distributed data (Eriksson et al. 1999), mean-centred and scaled to unit variance. Information on BDE congeners in technical mixtures was based on data from LaGuardia et al. (2006).

Results and Discussion.

Figure 1 shows the ratios between the different congeners and the sum of PBDE in the three falcon populations. There is a tendency towards a greater percentage of the higher brominated congeners in the captive population compared to the two wild populations. Some differences are visible in the ratios between the southern and northern populations for BDE-99, -153, -154 and –203 (Fig. 1). Otherwise, it is difficult to see any differences. Thus, PCA was performed on the data in order to see if more subtle differences were apparent.

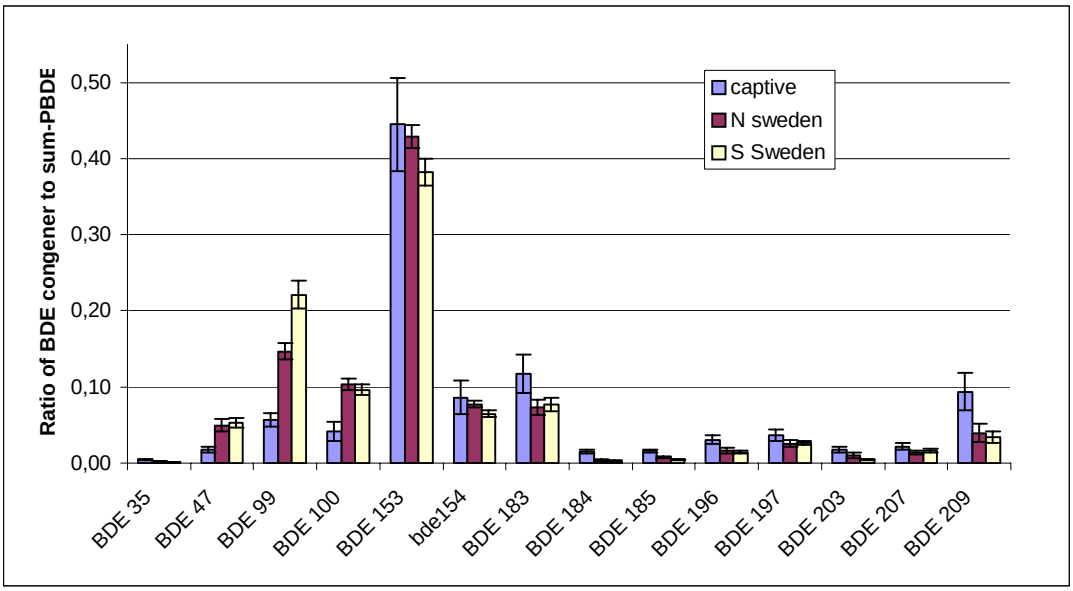

Figure 1. The ratios of the different congeners to the sumPBDE, arithmetic mean ± SE

In the PCA score plot (Fig 2.), the captive falcons separate clearly from the wild falcons. There is some tendency for the falcons in the southern population to be found in the lower quadrants and towards the left quadrant, whereas the northern population falcons are shifted upward and to the right. However, there is no distinct separation between the populations. The loading plot (Fig. 3) shows that some congeners are grouped together. In particular, BDE-47, –99 and -100 representing the PentaBDE technical product, cluster together on the left. The OctaBDE components BDE-183, -184, -185, -196, –197 and –203 and the DecaBDE components BDE-207 and –209 are found on the right side of the plot. BDE-153 and –154 are present in both PentaBDE and in OctaBDE products, and are found in the middle and at the top of the plot. This may be an indication that the falcons are exposed to these congeners via both technical products. The plot also indicates that the different falcons are exposed to different technical PBDE products through their diets.

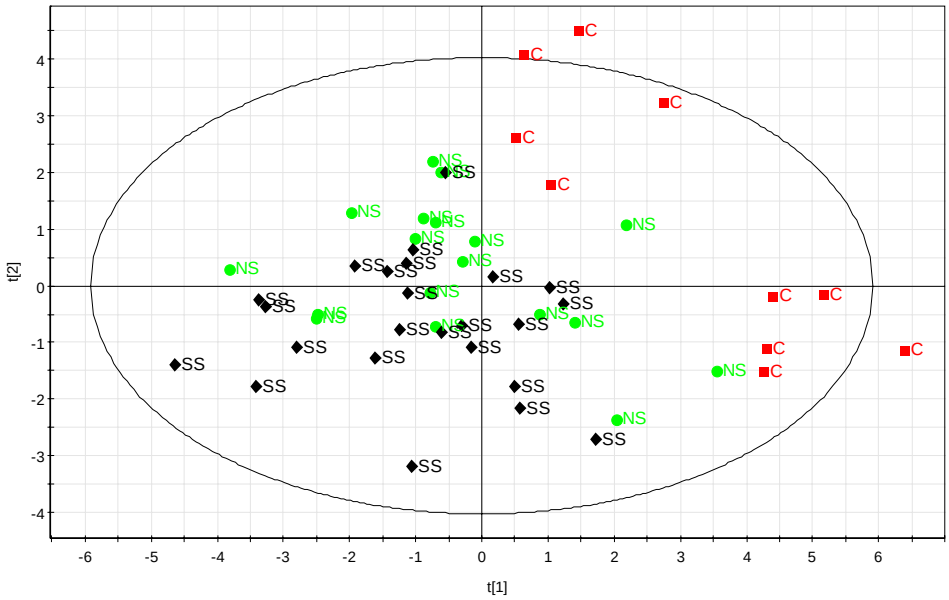

Figure 2. Score plot of the first 2 principal components calculated for the northern (NS), southern (SS) and the captive (C) population of peregrine falcon. R^2= 0.699 and Q^2 = 0.342 for 3 principal components. Ellipse shows Hotelling T^2 (0.05).

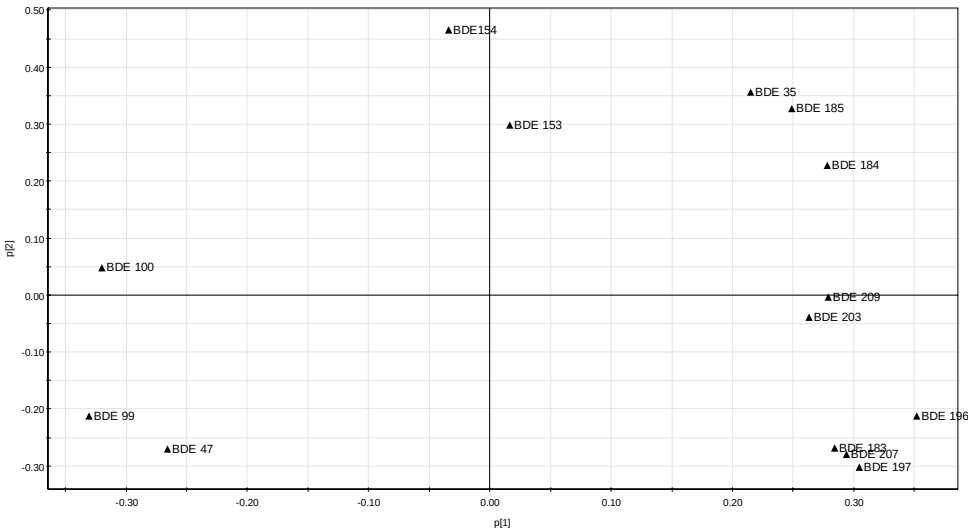

Figure 3. Loading plot for the first 2 principal components of the northern (NS), southern (SS) and the captive (C) population.

Conclusions

The PBDE pattern of the captive population differs from those of the two wild populations, but many of the values for the captive population are under the limit of detection, which makes drawing further conclusions more uncertain. The northern and the southern population cannot be separated although there are some differences. The pattern differences between higher and lower brominated PBDEs cannot be related to the different populations but rather to individual birds. Since peregrine falcons migrate to wintering grounds along the coasts of southwestern Europe and little is known about what they eat during winter, more information about the concentrations of PBDEs in the prey of the falcons, both in nesting areas and wintering grounds is needed. The loading plot indicates that the PBDE patterns in the individual falcons can be traced back to the different technical products Penta-, Octa- and Deca BDE.

References

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