Polybrominated Diphenyl Ethers (PBDEs) in Inner and Outer Blubber Layers in Baltic Grey Seal.

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Introduction.

Earlier studies have confirmed increasing concentrations of DDT compounds as well as polychlorinated biphenyls (PCBs) with age after sexual maturity in male seals but not in females (Addison & Smith 1974, Addison & Brodie 1987) and thereby also higher concentrations among adult males than adult females. However, Baltic grey seal (*Halichoerus grypus*) females of reproductive age studied during the 1980s disclosed higher organochlorine (OC) concentrations than males and also increasing concentrations with age (Blomqvist *et al.* 1992). Most of the studied females were sterile and some of them also severely diseased because of DDT and PCB pollution (Bergman and Olsson 1986, Bergman 1999, Olsson *et al.* 1992). Since then, the concentrations of these contaminants have decreased (Bignert *et al.* 1998) and the seals have recovered and are reproducing normally (Bergman 1999). The present material consists of sexually mature animals sampled after this recovery.

A study on ringed seal (*Phoca hispida*) disclosed significantly higher DDE and PCB concentrations in an outer blubber layer compared to an inner blubber layer on a lipid weight basis indicating different mobilisation of the blubber during seasonal physiological processes such as pregnancy, lactation or moulting (Severinsen *et al.* 2000). They also found significantly higher concentrations in both the inner and outer blubber layers among males compared to females of corresponding age. Kleivane *et al*. (2004) studying female harp seal (*Phoca groenlandica*) found higher concentrations of OC contaminants in the outer blubber layer compared to the inner among fat pre-breeding individuals whereas the opposite was found among thin moulting specimens. In order to study the variation of another halogenated compound in the inner and outer blubber layer, the concentrations of PBDEs were determined in blubber in both male and female grey seal during moulting season in spring and early summer as well as during the forage period in late autumn.

Materials and Methods.

Sampling.

Blubber samples were collected from 32 adult grey seals from the Gulf of Bothnia between 2002 and 2004. Most samples were obtained from hunting (28) and remaining samples (4) from by-caught animals. Thirteen females and eight males were sampled between April and July and four females and seven males between August and December. All animals were between 6-12 years old. All females sampled in the autumn and one female sampled in July were pregnant. Remaining females sampled in the spring showed a corpus luteum in one ovary as a sign of ovulation, meaning that all females in the study were sexually mature. A blubber core through the entire blubber layer was collected and stored at -20°C. Prior to analysis each of the cores was divided into an outer and an inner part where the outer part was close to the skin and the inner part close to the muscle layer.

Chemical Analysis.

The samples were extracted with a mixture of acetone/*n*-hexane and *n*-hexane/diethyl ether and treated with sulphuric acid (Jensen *et al.* 1983). The extracts were injected into a gas chromatograph/mass spectrometer (GC-MS) in electron capture negative ionisation (ECNI) mode. Ammonia was used as

the reaction gas. A 15 m DB-5 MS (J&W Scientific) fused silica column (0.25 mm i.d., 0.25 μm film thickness) was used. The mass fragments monitored were *m/z* 79 and 81 (Sellström *et al.* 2003).

Results and Discussion.

The fat content in the outer layer seems similar in males and females both in spring and autumn and varies between 50-92 %. The fat content of the inner layer was similar to the outer in males during both seasons whereas the fat content of the inner layer among females was significantly higher during autumn (91-97 %) compared to spring (81-92) (unpaired Student's *t*-test: $p<0.05$).

The dominant BDE congener among those measured was BDE-47, with concentrations ranging from 41- 423 ng/g lipid weight. The concentrations of PBDEs seem to be similar in the outer blubber layer among females both in spring and autumn. However, significantly lower concentrations were found in the inner blubber layer for all studied PBDEs during autumn while this only could be seen for the higher brominated compounds BDE-153 and BDE-154 in spring (unpaired respectively paired Student's *t*-test: $p<0.05$) (Figure 1 and 2).

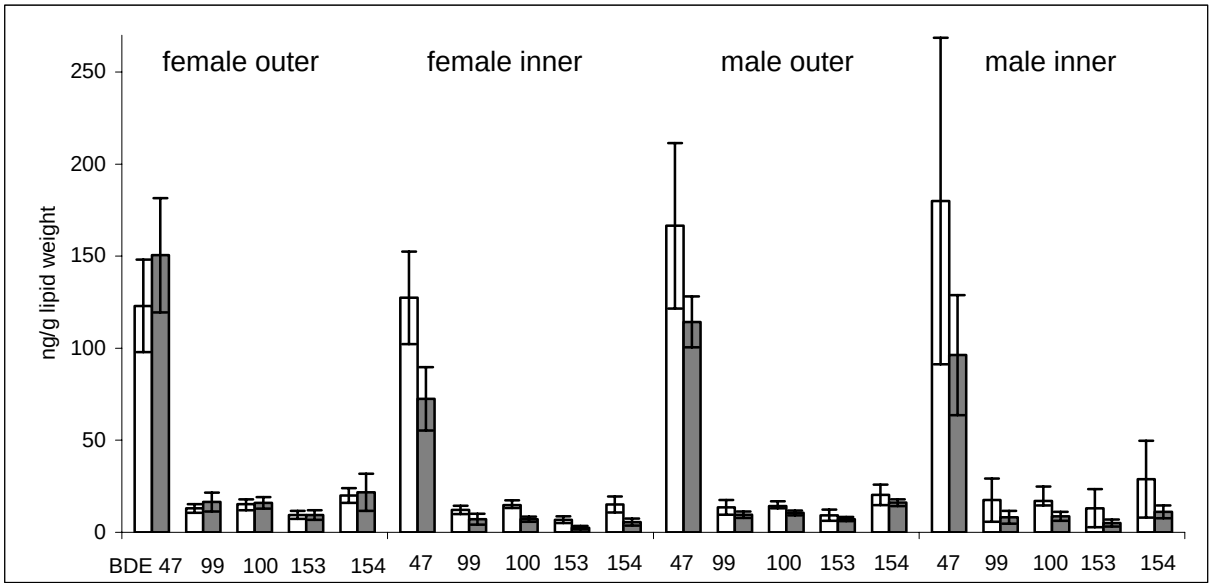

Figure 1. Mean ± 95% confidence interval for concentrations of PBDEs (lipid weight) for grey seal females and males in spring (white bar) and autumn (grey bar), respectively, for both outer and inner layer.

Higher lipid content during the forage period in autumn might partly explain a lower concentration of BDE because of dilution but an additional or complimentary explanation might be the earlier reported transfer of contaminants through lactation. The results support earlier studies indicating a faster mobilisation of the inner blubber layers compared to the outer layers. However, our data on PBDE in grey seal seem different to what was found for OCs in harp seals where higher concentrations were found both in the inner and outer blubber layer in thin moulting females compared to fat pre-breeding females (Kleivane *et al.* 2004).

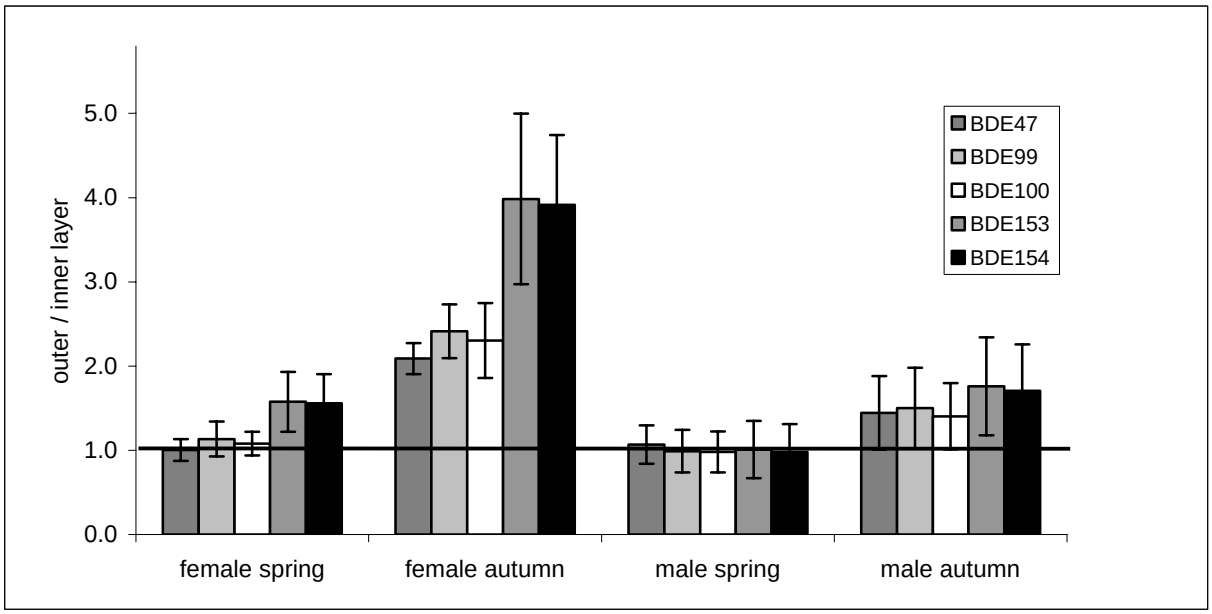

Figure 2. Mean ± 95% confidence interval for ratio of PBDE in the outer blubber layer relative to inner layer for grey seal females and males in spring and autumn, respectively.

For males the concentrations of BDE-47 and BDE-100 in the outer layer are significantly lower in the autumn sample compared to the spring sample (unpaired Student's *t*-test: $p<0.05$) while no such difference was found for the higher brominated BDE-99, 153 or 154. Although the levels in the inner blubber layer seemed lower also in autumn, this was not significant (Figure 1). The differences between the outer and the inner layers were very small both in spring and autumn with statistical significance only for BDE-153 and BDE-154 (paired Student's *t*-test: $p<0.05$) in autumn, which is illustrated by the ratios in Figure 2.

From this figure it is also clear that the variation in concentrations between the inner relative to the outer layers is more evident among females, which again supports the theory of only dilution for males when fat content increases but both dilution and transfer of contaminants through lactation for females.

From the present study some tentative results might be drawn. The significant differences in concentrations between the two sexes of reproductive age for OCs like DDT and PCB in both inner and outer layer in ringed seals found by Severinsen *et al.* (2000) were not seen in grey seal for PBDE in the present study. Furthermore, when OCs tend to increase in both inner and outer blubber layers during periods of lowered foraging (thin females during moulting season)(Kleivane *et al*. 2004), the PBDEs seem to remain more or less constant all the year in the outer layer of both males and females whereas concentrations decreased in the inner layer of females during autumn.

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