DIOXINS IN RINGED SEALS (*Phoca hispida*) FROM THE BALTIC SEA AND SPITSBERGEN

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Introduction

Seals from the Baltic Sea, which is one the most contaminated brackish weater areas in the world, have suffered from reproductive failures since the late 1960s. Reproductive failures and other pathological changes observed in Baltic seals have been connected with their high levels of environmental contaminants such as polychlorinated biphenyls (PCB) (1-4). Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (dioxins) are also detectable in Baltic seals (4-7) and might affect the health status of seals. The concentrations of dioxins have been higher in ringed seals than in grey seals. The levels of dioxins in Baltic seals, however, have been relatively low what one would expect based on their diet (6).

The objective of this study was to measure the concentrations of dioxins in ringed seals (*Phoca hispida*) from the Baltic Sea and to compare levels to those in reference ringed seals from Spitsbergen. Dioxin contents were determined in different tissues of female and male seals. There is not much data on dioxins in other tissues of seals than blubber, so far.

Materials and Methods

The ringed seals were collected from the northern Baltic Sea, the Bothnian Bay, in 1997. The reference seals were collected from Spitsbergen, the Arctic Ocean, in 1996. These seals had been collected for an ongoing study on the ecological, physiological and pathological effects of chlorinated hydrocarbons in the Baltic seals (8). Six female Baltic seals (6-8 years of age), four Baltic male seals (7-21 years), eleven Arctic female seals (2-20 years) and eight Arctic male seals (2-17 years) were investigated here for the content of dioxins. The blubber and liver of each individual were analyzed. The median results of the sum concentration of dioxins (as TCDD equivalents) in these seals have been reported previously (9).

The liver samples (10 g) were freeze-dried and extracted in a Soxhlet device with toluene for 18 h and the blubber samples (5 g) were extracted in an ultrasonication bath after mixing with 10-fold amount of sodium sulphate using hexane and a mixture of hexane:diethyl ether (9). The lipid content of each sample was measured gravimetrically from an aliquot of the extract after evaporating the solvent off by nitrogen.

An aliquot of the extract was spiked with an internal standard mixture of 13C-labelled dioxins (PCDD/PCDFs) and the fat was removed by silica column chromatography (10). Dioxins were separated from PCBs using a column of activated carbon mixed with celite and the dioxin fraction was further purified on an alumina column.

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Analyses were performed by high resolution gas chromatography-mass spectrometry (HRGC-HRMS) utililizing selected ion monitoring mode. The MS instrument (VG 70-250SE) was operated in EI mode using 10,000 resolution and dioxins were separated on a DB-Dioxin column (60 m, 0.25 mm i.d., 0.15 :m film thickness) (10). Laboraroty blank samples were treated and analyzed in a similar way to samples. The concentrations of dioxins were converted to TCDD-equivalents using WHO-TEFs (11).

Results and Discussion

The concentrations of five most abundant dioxins in Baltic seals have been presented in Figure 1. Similarly to previous studies on dioxins in Baltic seals (4-7), 1,2,3,6,7,8-hexaCDD was the dominating congener, whereas 2,3,7,8-tetraCDF dominated in seals from Spitsbergen (Figure 2). Some of the analyzed seals both from the Baltic Sea and Spitsbergen showed elevated concentrations of dioxins. Especially, the concentration of dioxins was elevated in the liver of two Baltic male seals, whereas the dioxin content in the blubber of these seals was at a similar level than in the two other male seals.



Figure 1. The median concentrations of some dioxins and total TEQ of dioxins in the liver and blubber of female and male ringed seals collected from the Baltic Sea in 1997 (lw = lipid weight; 2378-D=2,3,7,8-tetraCDD, 12378-D=1,2,3,7,8-pentaCDD, 123678-D=1,2,3,6,7,8-hexaCDD, 2378-F=2,3,7,8-tetraCDF, 23478-F=2,3,4,7,8-pentaCDF).

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Figure 2. The median concentrations of some dioxins and total TEQ of dioxins in the liver and blubber of female and male ringed seals collected from Spitsbergen in 1996 (for additional information see figure legend for Fig. 1).

The levels of dioxins were much higher in the Baltic seals compared to those in the seals from the background site, the Arctic environment (Figures 1 and 2). The TEQ of dioxins in the blubber was about 35-fould higher in Baltic seals compared to that in seals from Spitsbergen. Dioxin levels are generally declining in the environment due to reduced emissions (12), but the levels in Baltic seals do not significantly differ from those observed in 1980s (6). The levels of dioxins in seals from Spitsbergen, instead, seem to be lower than those in seals collected in 1980s (5,13).

The levels of dioxins were higher in the liver of both female and male seals compared to the blubber (Figures 1 and 2). In the case of PCBs, the contents in the liver and blubber were at a similar level (9). There were differences also between female and male Baltic seals in the dioxin concentration of livers. The median level of dioxins was slightly lower in the liver of females compared to the levels in the liver of males, whereas there were not differences in the blubber between female and male Baltic ringed seals.

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The four-fold higher levels of dioxins in the liver show clearly the strong accumulation of dioxins in the liver tissue, which has earlier been demonstrated in rats (14). Since the levels of PCBs were similar both in the blubber and liver (9), it is likely that PCBs are metabolized more effectively by liver than dioxins or their binding affinity to hepatic proteins (CYP1A) is lower than that of dioxins. The lower level of dioxins in the liver of females could indicate a transfer of dioxins from mother to pup through lactation.

The different levels and patterns of the dominating dioxins in the seals from the Baltic Sea and Spitsbergen indicate that the sources of dioxins are different between these two sites. There are numerous sources of dioxins in the Baltic Sea compared to the Arctic environment, which likely receives dioxins mostly through atmospheric deposition. Compared to the Arctic fish and fish from Swedish west coast, Baltic fish have got much higher levels of dioxins (15).

The elevated levels of dioxins in two male Baltic seals might be due to their exposure to different sources of dioxins than others, but to verify this and to eliminate bias due to contamination occurred during the sample treatment, these samples will be reanalyzed. The dioxin data of seals will also be compared with physiological and pathological changes. Elevated concentrations of dioxins were recently reported in a starved ringed seal (7). Blood of the seal individuals studied here will be analyzed for the level of dioxins in the future.

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