PCDD/Fs, PCNs, PBDEs AND PCBs IN FOOD SOURCES OF BALTIC SEALS

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Introduction

Polybrominated diphenyl ethers (PBDE) and polychlorinated naphthalenes (PCN) have gained more attention as envinronmental pollutants besides polychlorinated biphenyls (PCB) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF) during recent years. PBDEs are structurally similar to PCBs and have had a wide use as fire retardants for several decades [1]. PCNs, that are structurally similar to the notorius PCDD/PCDFs, were previously produced and used for similar purposes as PCBs [2].

The Baltic Sea has been one of the most polluted water areas in the world since the 1970s. The heavy pollution load of the Baltic Sea has affected the Baltic fauna. For example ringed and grey seal populations declined dramatically in the 1970s [3], and have shown a slow recovery since then. The major source of contaminants in the Baltic seals is most likely the diet. Baltic ringed and grey seals feed roughly at the same trophic level of the food web [4-6]. However, there are differences in the contaminant burden between the seals [7]. Recent studies have shown that especially the Baltic ringed seals still are suffering from high concentrations of pollutants, such as PCBs and DDT compounds [7].

One of the main food sources of the Baltic ringed seals has been herring (*Clupea harengus*) [4,5]. In the Bothnian Bay, young ringed seals feed on stickleback (*Gasterosteus aculeatus*), smelt (*Osmerus eperlanus*), eelpout (*Zoarces viviparus*), fourhorn sculpin (*Onconottus quadricornis*) and whitefish (*Coregonus lavaratus*), whereas young grey seals feed mainly on whitefish and herring [6].

The main aim of this study was to investigate the levels and congener profiles of PCDD/PCDFs, PCNs, PBDEs and PCBs in food sources of the Baltic seals. Data on contaminants in the diet could be one explanation to the observed differences of contaminant levels and profiles between Baltic ringed and grey seals.

Materials and Methods

The study material consisted of the following eight species: salmon (*Salmo salar)*, whitefish, herring, stickleback, smelt, eelpout, fourhorn sculpin, and Saduria (*Saduria entomon*). All samples were caught by the Finnish Game and Fisheries Research Institute from the river Kalajoki, in the Bothnian Bay area, at the end of June or in July in 2001. Ten or more individuals of each species were collected and were pooled to one sample. Each pool contained both adult females and males, except for the salmon pool that consisted of one-year old males.

For analyses of contaminants, the whole fish or muscle tissue of all individuals in each pool were homogenised. Herring, whitefish, smelt, fourhorn sculpin and stickleback samples consisted of whole fish, whereas the muscle tissues of eelpout and salmon were analysed. In addition, salmon liver was analysed. Homogenised samples were freeze-dried and extracted with toluene. The lipid content was determined gravimetrically and the extract was purified by column chromatography. PCDD/PCDFs and PCBs were isolated and analysed as previously described [8]. Briefly, the extract was purified using three columns: silica gel impregnated with sulphuric acid column (fat removal), carbon mixed with Celite column (separation of PCDD/PCDFs from PCBs) and alumina column (final purification). For the analyses of PCNs, an aliquot was taken from the sample after the silica column, and the aliquot was further purified on an alumina column, similarly as for PCBs and PBDEs. Alumina cleanup of PCBs, PBDEs and PCNs was performed on a column of activated alumina (0.6 g) where the impurities were first eluted with two ml of hexane. Compounds of interest were then collected with 18 ml of 20% dichloromethane in hexane.

All samples were analysed for 17 PCDD/PCDFs, 16 PCNs, 14 PBDEs and 38 PCBs. All analyses were performed using high-resolution gas chromatography-high-resolution mass spectrometry (Hewlett Packard 6890-VG 70-250 SE or Micromass Ultima). Analyses were performed in electron impact ionisation mode using selected ion monitoring mode with a 10,000 resolution. PCDD/PCDFs and PCBs were separated on a DB-Dioxin column (60 m x 0.25 mm i.d. x 0.15 mm), and PBDEs and PCNs on a DP-5 column (60 m x 0.25 mm i.d. x 0.15 mm). The limit of determination (LOD) of PBDE congeners was 0.05 ng/g lw. LODs of PCDD/PCDFs, PCNs and PCBs varied between 0.5 and 5 pg/g lw, between 5 and 20 pg/g lw and between 0.1 and 1 ng/g lw, respectively.

Results and discussion

The levels of PCBs were the highest in all species (lipid weight (lw) results in Figure 1). Depending on the species, PBDE level was between 1/8 and 1/30, and PCN level between 1/240 and 1/300 of that of PCBs. The load of PCDD/PCDFs was between 1/3 and 1/16 of that of PCNs.

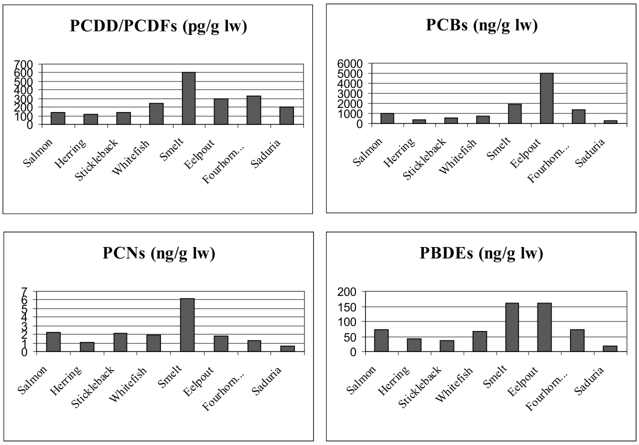

Figure 1. PCDD/PCDFs, PCNs, PBDEs and PCBs in different food species of Baltic seals.

The highest sum concentrations of PCDD/PCDFs and PCNs were measured in smelt feeding on amphipods, whereas the highest load of PCBs was measured in eelpout, also feeding on amphipods. The highest content of PBDEs was measured in smelt and eelpout. The lowest levels of PCNs, PBDEs and PCBs were measured in Saduria (an isopod feeding on dead matter), whereas the lowest PCDD/PCDF content was in herring feeding on plankton. Whitefish and stcikleback, other plankton eating species, showed a little bit higher content of PCDD/PCDFs, PCNs and PCBs than herring. A trophic transfer of the studied compound groups was observed in the benthic food chain consisting of fourhorn sculpins and Saduria.

Changes in the food chain were also observed for the composition profiles of the studied compounds like in the case of PCDD/PCDFs (Figure 2). 2,3,4,7,8-PeCDF, 2,3,7,8-TCDF and OCDD were the three dominating PCDD/PCDFs in Saduria, whereas OCDD did not accumulate in the fourhorn sculpin that feeds on the isopods. Compared to Saduria, the proportion of 2,3,4,7,8-PeCDF was clearly higher in fourhorn sculpin indicating the higher persistency of this congener compared to 2,3,7,8-TCDF. 2,3,4,7,8-PeCDF dominated also in herring, whitefish, eelpout and smelt, whereas 2,3,7,8-TCDF dominated in salmon and stickleback. The high persistency of 2,3,4,7,8-PeCDF was seen in the liver of salmon.

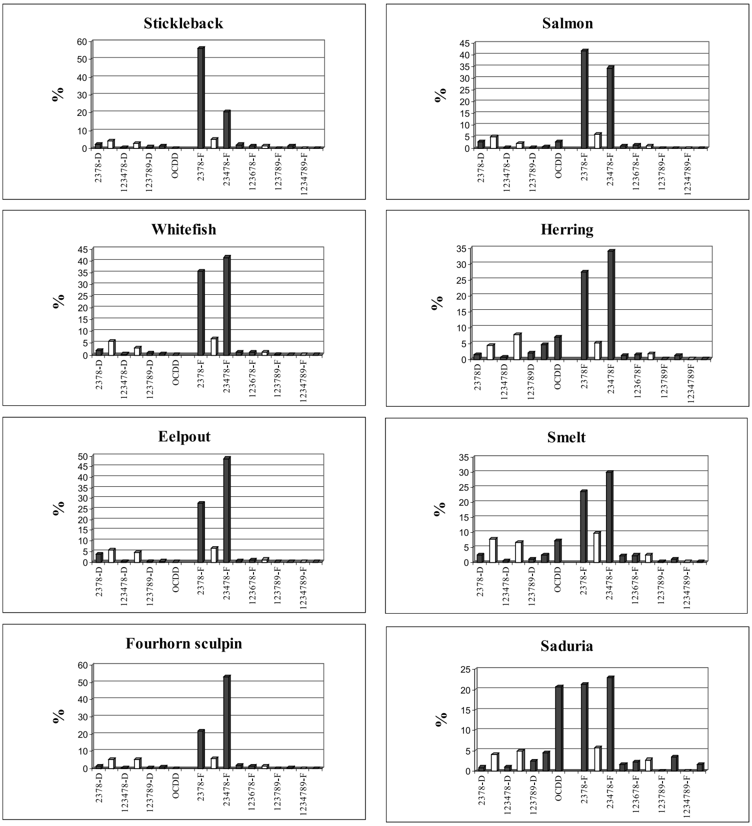

Figure 2. Relative composition of PCDD/PCDFs in different food species of Baltic seals.

In contrary to PCDD/PCDFs, the PCB profiles of Saduria and fourhorn sculpin were near to each other. The profiles of the PCBs were most similar among the studied contaminant groups in all samples, PCB 153 being the most dominant congener in all species. There were, however, some species differences between the PCB profiles. For example, PCBs 101 and 187 were low in Saduria and the fourhorn sculpin, but abundant in the species feeding on plankton (stickleback, whitefish and herring).

Of PBDEs, similarly to PCBs, one congener, PBDE 47, was the most dominant in all samples. PBDE 47 was the only PBDE that biomagnified in the food chain from Saduria to fourhorn sculpin. PBDE 99 was the second dominant PBDE in Saduria, as well as in herring, whitefish and in salmon, but in eelpout, smelt, and stickleback the proportion of PBDE 99 was lower than that of PBDE 100.

In the case of PCNs, 1,3,5,7-PeCN dominated in all species, except in fourhorn sculpin, where 1,2,3,4,6,7-/1,2,3,5,6,7-HxCN was the most dominant PCN analysed. Changes in the food chain of Saduria and fourhorn sculpin were also observed for PCNs. In Saduria, and in the species feeding on plankton 1,3,5,7-TeCN was the second dominating PCN.

Based on the profiles of the studied compounds, the species could be divided into three groups A-C. In group A, consisting of Saduria, smelt and herring, 2,3,4,7,8-PeCDF was the major PCDD/PCDF, but the level of 2,3,7,8-TCDF was near to that of 2,3,4,7,8-PeCDF (Figure 2). OCDD was the third or fourth major PCDD/PCDF in this group. Of PCNs, 1,2,3,5,7-PeCN dominated and 1,3,5,7-TeCN was the second highest PCN in this group. PBDEs 99, 100, 153 and 154 were abundant PBDEs in addition to PBDE 47.

2,3,4,7,8-PeCDF was the dominating congener also in group B consisting of fourhorn sculpin, eelpout and whitefish, but the level of OCDD was low. Of PCNs, 1,2,3,5,7-PeCN and 1,2,3,4,6,7-/ 1,2,3,5,6,7-HxCN were the dominating PCNs in fourhorn sculpin and eelpout, whereas PCN profile in whitefish resembled that in herring. The proportion of PBDE 99 was low, except in whitefish.

In group C that consisted of stickleback and salmon, 2,3,7,8-TCDF dominated, instead of 2,3,4,7,8-PeCDF. Similarly to Saduria, smelt and herring in group A, 1,2,3,5,7-PeCN dominated and 1,3,5,7-TeCN was the second highest in stickleback and salmon. The proportions of higher chlorinated, 1,2,3,4,5,6,7-HpCN and 1,2,3,4,5,6,8-HpCN, instead, were lower compared to group A. PBDEs 99, 100, 153 and 154 were other abundant PBDEs.

The connecting factor between the species in each group could be similarities in their food sources. Based on similar PCDD/PCDF profiles, salmon could have stickleback in its diet. Herring and whitefish, both feeding on plankton, showed similar PCN and PBDE profiles. The different profiles of PCDD/PCDFs, PCNs and PBDEs between smelt and eelpout, both feeding on amphipods, refers that their diet is different or that they have different accumulation/ metabolism. The low proportion of PBDE 99 in fourhorn sculpin and eelpout refers to higher metabolism of PBDE 99 in these species. On the other hand, only muscle were analysed in the case of eelpout.

Based on the results, the diet could explain the differences observed in the contaminant levels and profiles between Baltic ringed and grey seals. If we assume that the diet of adult seals is similar to that of young seals in the Bothnian Bay, the intake of contaminants of ringed seals in ten times higher than that of grey seals.

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