Levels of persistent organic pollutants in Baltic herring

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Introduction

The Baltic Sea has a long history of being one of the most polluted brackish water areas in the world. Baltic herring (*Clupea harengus* L.) that plays a significant role in the diet of both human and Baltic seals is a good indicator of pollution of the Baltic Sea. Herring of the Gulf of Bothnia are considered to be stationary fish as they have a low migratory behaviour. Migration among young herring in the Gulf of Finland is also low, whereas older herring migrate even to the southern Baltic Sea [1]. The growth of herring in the Gulf of Finland has retarded since the 1980's [2].

Monitoring of organochlorine compounds such as PCBs has been performed in the Baltic Sea since the late 1960's. This monitoring has shown a continuous decline of polychlorinated biphenyls (PCB) [3]. In 1990's, the data of herring did not reveal any clear decline in the concentrations of PCBs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF, dioxins) [4]. There is less data on levels and trends of other pollutants such as toxaphene, polychlorinated napthalenes (PCN) and polybrominated diphenyl ethers (PBDE) in Baltic herring from different areas of the Baltic Sea. PCNs have been used for similar purposes as PCBs and PBDEs are widely used as flame retardants.

The main aim of this study was to investigate by herring analyses the contamination of different sites along the coast of Finland. We aimed to see whether polluted and less polluted sites along the coast of Finland were reflected in the herring data. Besides, dioxins and PCBs, toxaphene, DDT compounds, PBDEs and PCNs were analysed.

Methods and Materials

Baltic herring collected from 10 locations of the Baltic Sea in 1999 were included in the study. The herring were caught during most vigorous spawning season (beginning of May to mid-June) in 1999. The numbering of the sampling sites was based on the previous publication [4].

The weight (w) and length (l) of each individual fish were measured and a condition factor (Cf) was calculated [4]. The age of each herring was estimated using data from ICES [5] (herring weight as function of age). The herring were analysed in the form they are sold for human consumption. Cleaned herring (head, fins and gut removed) were pooled according to sampling site and herring size. Herring from each sampling site were combined into two pools representing small and large herring. Herring below 18.5 cm were considered small and over that large. The two pools of herring from Korsnäs (site 4) consisted both of small and large herring.

The pooled sample was freeze-dried and Soxhlet extracted using toluene or toluene and a mixture of hexane, acetone and petroleum ether. The fat content was determined gravimetrically after evaporating solvents to dryness. An aliquot of the extract was purified for analyses using column chromatography as described earlier [6]. The lipids were removed on silica gel impregnated with sulphuric acid and the isolation of PCDD/PCDFs from PCBs and other compounds was performed on carbon mixed with Celite. DDT compounds, PBDEs and PCNs were analysed from an aliquot cleaned up on alumina [6] after 1-g silica column (44% H_2SO_4 v/w). For analyses of toxaphene, an aliquot of PCB fraction from carbon-Celite cleanup step was purified on Florisil as earlier [7].

The extracts were analysed for 17 PCDD/PCDFs, 33 PCBs, three toxaphene indicator compounds (Parlar Nos 26, 50 and 62 [8]) and total toxaphene. Total toxaphene was quantified by comparing to technical toxaphene. In addition, large herring were analysed for DDT compounds (*o,p'*- and *p,p'*-isomers of DDE, DDD and DDT), 15 PBDEs and 16 PCNs. Of the dioxins, toxic congeners were studied and the analysed PCBs included toxic PCBs (non-*ortho*-PCBs). ^{13}C-labeled standards were used as internal standards. The laboratory reagent and equipment blank samples were treated and analyzed by the same method as the actual samples.

All analyses were performed using high-resolution gas chromatography-high-resolution mass spectrometry (HRGC-HRMS). Analyses were performed with VG 70-250 SE or Micromass Ultima 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 μm), and other compounds on a DP-5 column (60 m x 0.25 mm i.d. x 0.15 μm).

Results and Discussion

The sum concentrations of PCDD/PCDFs, PCBs, and total toxaphene in small and large herring from different locations along the Finnish Baltic Sea coastline are presented in Figure 1. The concentrations of PCBs and dioxins per lipid weight were quite similar to those reported earlier for herring collected from the Gulf of Bothnia [9,10].

There were no significant differences in the sum concentrations of PCDD/PCDFs and PCBs in small herring between the sampling sites. This indicates that these pollutants are quite evenly distributed in zooplankton, major herring prey species in the Baltic Sea locations investigated. Higher levels of PCBs have been reported in herring from the southern part of the Baltic Sea [11].

In contrary to dioxins and PCBs, the exposure of herring to toxaphene was clearly lower in the Gulf of Finland (especially in sites 8 and 10) compared to the Gulf of Bothnia (Figure 1). The sum of toxaphene indicator compounds consituted approximately half of the total toxaphene load in the Gulf of Bothnia. It seems that toxaphene levels in Baltic herring have decreased from those in 1970s [12]. Up to 13 µg/g lw of toxaphene were measured in herring caught off from Gotland in 1978.

Based on the analyses of DDT and PCNs in large herring (Figure 2), the Gulf of Finland might be less polluted with PCNs than the Gulf of Bothnia, whereas DDT is more evenly distributed contaminant. DDT levels measured here were similar to those reported for herring (13-14 cm) collected from the Bothnian Bay in 1991 [10]. The mean length of large herring from the Gulf of Bothnia was 17 cm [4].

PCN levels measured here were similar to those reported earlier for herring from the Gulf of Bothnia [13]. Higher levels of PCNs have been measured in herring from the southern part of the Baltic Sea (Karlskrona) [10]. According to the study of Lundgren et al. [13], there are no year variations of PCN levels in herring.

The difference between small and large herring was clear in the area of the Gulf of Bothnia (sites 1, 2, 3, 5, and 6), whereas there were no great differences in the concentrations of dioxins, PCBs and toxaphene between small and large herring in the Gulf of Finland (sites 8, 10, and 11). The higher exposure of large herring to PCBs and PCDD/PCDFs in the Gulf of Bothnia has been explained by their different feeding characteristics compared to those of small herring [4]. In the Gulf of Finland both small and large herring feed mainly on zooplankton. In the Gulf of Bothnia, large herring feed relatively more on crustaceans and small fishes. The ages of small herring from both the Gulf of Bothnia and Gulf of Finland were quite similar (between 4 and 6 years), whereas large herring from the Gulf Finland were older than those from the Gulf of Bothnia (9-10 years vs. 5.5-9 years) [4]. The age of herring for human consumption is usually 3-6 years or older.

The congener profiles were quite similar between sampling sites with few exceptions. The five dominating dioxins in all herring were 2,3,4,7,8-PeCDF, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,7,8-PeCDD and 1,2,3,6,7,8-HxCDD. The contribution of 1,2,3,4,6,7,8-HpCDF, a typical PCDD/PCDF to chlorophenol formulation Ky-5, to total dioxin load was the highest in herring from site 11 that is located nearest to the River Kymijoki. However, there is no statistical evidence for significant contribution of the River Kymijoki as a source of Ky-5 related dioxins in herring [4].

The relative contributions of toxaphene compounds were also different in herring from the Gulf of Finland compared to herring from the Gulf of Bothnia (Figure 3). This might indicate that the sources of toxaphene in the Gulf of Finland are different from those in the Gulf of Bothnia.

This study revealed no clear point sources for most studied organochlorine pollutants, except possibly for toxaphene and PCNs.

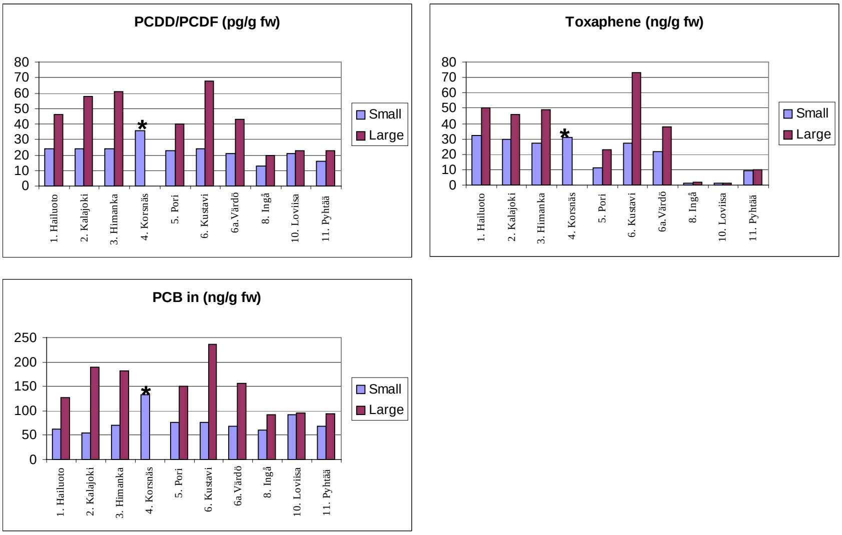

Figure 1. PCDD/PCDFs, PCBs and toxaphene in small and large herring from different locations of the Finnish Baltic Sea coastline (* = site 4 results mean of small and large herring).

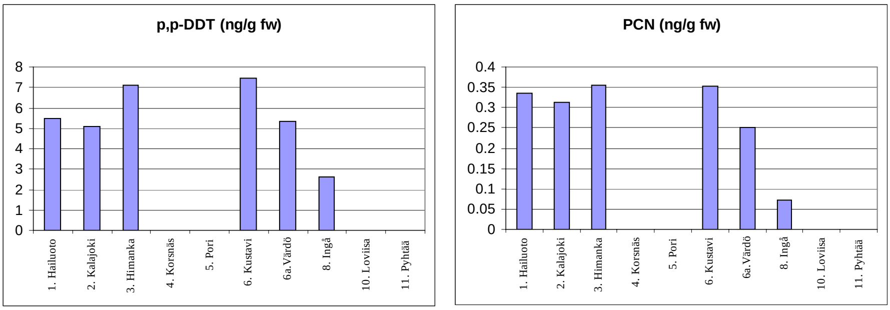

Figure 2. *p,p'*-DDT and PCNs in large herring from different locations of the Finnish Baltic Sea coastline.

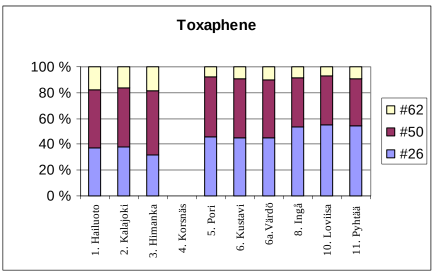

Figure 3. Contribution of toxaphene compounds in small Baltic herring from different locations of the Finnish Baltic Sea coastline.

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References

1 Parmanne, R. (1990). Finn. Fish. Res. 10, 1-48.
2 ICES (2001). Report of the Baltic fisheries assessment working group. April 18-27, Gdynia, Poland.
3 Bignert, A., Olsson, M., Persson, W., Jensen, S., Zakrisson, S., Litzén, K., Eriksson, U., Häggberg, L., Alsberg, T., 1998. Environmental Pollution 99, 177-198.
4 Kiviranta, H, Vartiainen, T, Parmanne, R, Hallikainen, A, Koistinen, J (2003) Chemosphere 50, 1201-1216.
5 ICES (1998) Report of the Baltic herring age-reading study group. February 23-27, Riga, Latvia.
6 Koistinen J., Nyman M., Helle E. and Vartiainen T. (2002). Organohalogen Compounds 57, 157.
7 Koistinen, J, Paasivirta J, Vuorinen, P (1989) Chemosphere 19, 527-530.
8 Vetter, W, Oehme, M (2000) Chapter 8 in New Types of Persistent Halogenated Compounds. The Handbook of Environmental Chemistry Vol. 3, Part K, Springer.
9 Asplund, L, Jansson, B, de Witt, C, Bergek, S, Hjelt, M, Rappe, C, Odsjö, T, Olsson, M (1990) Organohal. Compd. 1, 405-408.
10 Strandberg, B, Bandh, C, van Bavel, B, Bergqvist, P-A, Broman, D, Näf, C, Pettersen, H, Rappe, C (1998) The Science of the Total Environment 217, 143-154.
11 Järnberg, U., Asplund, L, de Witt, C, Grafström, A-K, Haglund, P, Jansson, B, Lexen, K, Strandell, M., Olsson, M, Jonsson, B (1993) Environ. Sci. Technol. 27, 1364-1374.
12 Jansson, B, Vaz, R, Blomkvist, G, Jensen, S, Olsson, M (1979) Chemosphere 4, 181-190.
13 Lundgren, K, Ishaq, R, van Bavel, B, Broman, D, Tysklind, M (2003) Organohal. Compd. 62, 399-403.