Spatial and seasonal variation of the dioxin and PCB content in herring from the northern Baltic Sea

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Introduction

PCBs and many other persistent organic pollutants show declining trends in the Baltic Sea as a result of actions taken[1]. For polychlorinated-*p*-dioxins (PCDDs) and polychlorinated-dibenzofurans (PCDFs), the situation is different. The levels of the total TCDD toxic equivalents (TEQ) in guillemot eggs and herring sampled within the National Swedish Monitoring Programme have been constant during the last two decades[2]. It seems that the central part of the Baltic Sea, the southern Bothnian Sea (Figure 1), is one of the most polluted regions since herring sampled in that area showed higher levels than herring from other Baltic areas[3]. The dioxin content of fat fish from the Baltic often exceeds the prescribed maximum limits[4,5], and therefore Sweden and Finland are currently only allowed to sell on the domestic market. The future situation may be even worse sincein short the dioxin-like PCBs will also be included in the risk assessment.

In the 1980s, the dioxin emissions from combustion processes and pulp and paper industry were in the focus, and consequently strong measures were taken to reduce their emissions. Other potential sources have received less attention. These include leakage from contaminated soils and sediments, accumulation by river transport, drainages from big cities and long-range air deposition. Recently, Environmental Chemistry at Umeå University compiled a dioxin source inventory on behalf of the Swedish EPA[6]. In the survey, potential source areas were identified. Many of these are located along the Baltic coast.

The purpose of the current study was to investigate spatial and seasonal variation of the dioxin and PCB content in herring sampled along the northern Baltic Sea coast, which includes many of the potential source areas. We also aimed to map out risk zones for dioxins and dioxin-like PCBs on the basis of the results and available toxicological data.

Materials and Methods

During 2004, herring samples were collected at 31 locations along the Swedish coast in the Baltic Sea (Figure 1). The majority of the fish were caught during May-June (n=27), while a few were taken in September-November (n=4). From each location, muscle samples of 15 herring individuals were pooled. Length and weight of the herring were 20±1.1 cm and 52±7.2 g. From the pooled samples, a total of 30 g muscle was analyzed.

The sample preparation has been described earlier[7]. In short, the fish muscle was homogenized with dehydrated Na_2SO_4 and extracted with acetone:*n*-hexane and *n*-hexane:diethylether. A multilayer silica column eluted with *n*-hexane was followed by a carbon AX21/Celite column to purify and fractionate the extracts. The carbon column was eluted with dichloromethane:*n*-hexane and toluene. Fraction 1 contained the mono-*ortho* and poly-*ortho* PCBs and fraction 2 the non-*ortho* PCBs and the PCDD/Fs. The last clean up step was a miniaturized multilayer silica column. ^{13}C-labelled congeners of all 2,3,7,8-substituted PCDD/Fs and all target PCBs were used as internal standards.

The instrumental analysis was carried out by gas chromatography-high resolution mass spectrometry (GC-HRMS). A 60 m DB5MS capillary column with an i.d. of 0.32 mm was connected to a double focusing magnet sector mass spectrometer (Waters, Autospec), which was operating in EI+ selected ion monitoring mode. Samples were splitless injected at an injector temperature of 280^{o}C. For fraction 1, the temperature program for the oven was 170^{o}C for 2 min, 3^{o}C min^{-1} to 300^{o}C, hold for 5 min and for fraction 2, 190^{o}C for 2 min, 3^{o}C min^{-1} to 300^{o}C, hold for 6 min. Other instrumental conditions were as follows: helium carrier gas at a constant flow of 1.2 mL/min; transfer line temperature 275 ^{o}C; ion source temperature 250^{o}C.

For the 27 spring-summer samples, the spatial correlation structure was studied using sample variogram. The variogram shows the semivariance/s^2 (where s^2 is the total variance) plotted versus the distance (Figure 2). The semivariance is defined by: $\gamma(h) = \frac{1}{2n}\sum_{i}^{n-h}(x_i - x_{i+h})^2$, where x_n -x_{n+h} is the difference between two values a distance *h* apart (see e.g.[8]). Assuming a constant spatial autocorrelation throughout the investigated area, the variograms were further used to find appropriate parameters for extrapolating the results into generalized maps. The concentrations in each 2.5 km grid cell in the investigated area were estimated using scaled inverted exponential distance weighting, i.e.neighbour sample concentrations were weighted (w_i) inversely proportional to the distance r_i to the centre of current grid cell according to: $w_i = (1 - r_i / r_{max})^a$,with the exponent *a* set to 4 and the maximum radius r_{max} set to 75 km. It was furthermore decided that at least to samples within this radius were required to form a weighted mean value in the grid cell.

Results and discussion

The samples were divided into categories based on sampling location and sampling season (Table 1). This kind of grouping did not show any significant spatial differences, while large differences were found between spring-summer and fall samples.

Table 1. Concentrations ± 1SD (pg/g fresh weight) expressed as WHO-TEQ. For location of the sampling areas, see Figure 1.

	Spring-summer samples			Fall samples		
pg/g fresh weight	Bothnian Bay (BB) (n=4)	Bothnian Sea (BS) (n=19)	Baltic Proper (BP) (n=4)	Bothnian Bay (BB) (n=2)	Bothnian Sea (BS) (n=1)	Baltic Proper (BB) (n=1)
PCDD/F TEQ	4.7 ± 0.85	5.2 ± 1.4	4.2 ± 1.7	1.1 ± 0.16	0.82	1.5
PCB TEQ	2.3 ± 0.31	2.7 ± 0.58	2.5 ± 0.50	0.63 ± 0.11	0.75	1.4
Total TEQ	7.1 ± 1.2	7.9 ± 0.58	6.7 ± 2.2	1.7 ± 0.27	1.6	2.9

Despite the fact that herring of the sampled size may migrate considerably[9], the variogram showed spatial auto correlation in the range of about 100 km (Figure 2). The relatively large differences between spring-summer and fall samples, also for concentrations expressed on fat weight, indicates fairly fast changes in the equilibrium between water and fish muscle and that the measured concentrations are representative of the sample region during the sampling season. Assuming this, generalized maps using inverted distance weighting up to 75 km were produced (Figure 3). The maps clearly indicate elevated risk for human consumption in the southern parts of the Bothnian Sea. The estimated levels in the Bothnian Bay are less reliable due to the low number of samples in the north. Large areas show concentrations above the prescribed maximum for dioxin residues (4 pg TEQ/g w.w.). The herring samples were taken from muscle tissue without skin and subcutaneous fat. However, herring is normally consumed with the skin implying a fat content and corresponding dioxin and PCB concentrations at least 1.5 times higher than the concentrations in this investigation. On the other hand, the 27 spring-summer samples show concentration about 2-6 times higher compared to the few (n=4) fall samples taken. The fall situation is thus expected to be noticeably better.

It should be stressed that Figure 3 is based on fresh weight concentrations to reflect the risk of human consumption. Since the average fat content in herring muscle varies along the coast, the distribution based on fat weight differs somewhat from the one presented here. A map based on fat weight (not shown) implies that the northern parts of the Baltic Proper show higher concentrations, thus moving the centre of the ´hot spot' area somewhat southwards, but the lower concentrations in the middle of the Bothnian Sea remain low.

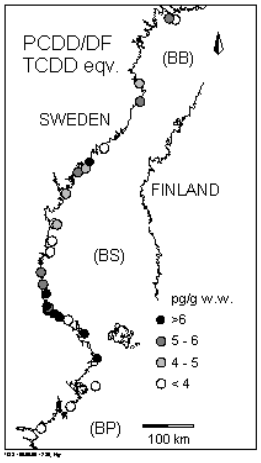

Figure 1. Concentrations of PCDD/Fs (pg TEQ /g w.w.) in herring muscle. Grey and black dots indicate levels above the prescribed maximum limits for dioxin residues. BB: Bothnian Bay; BS: Bothnian Sea; BP: Baltic proper

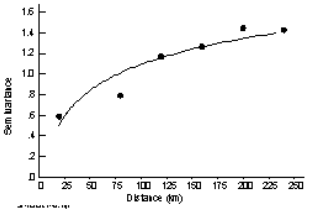

Figure 2. Sample variogram, the PCDD/F TEQ semivariance/s^2 plotted versus distance.

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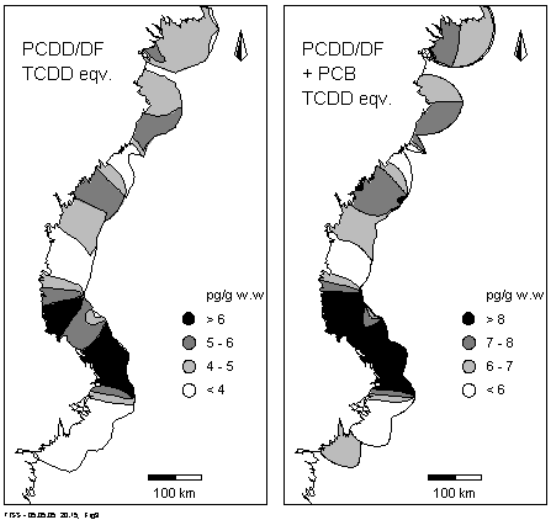

Figure 3. Extrapolated generalized maps showing estimated risk for human consumption. The maps are based on dioxin and PCB concentrations of herring caught during the spring-summer season.

References

1. Bignert A., Olsson M., Persson W., Jensen S., Zakrisson S., Litzén K., Eriksson U., Häggberg L. and Alsberg T. (1998) *Environ. Pollut.* 99: 177-198.

2. Bignert A., Asplund L. and Willander A. (2004) Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota. pp.1-132. Report to the Swedish EPA.

3. Olsson M., Bignert A., deWitt C. and Haglund P. (2002) Bottniska viken 2002, Årsrapport från den marina miljöövervakningen. Dioxiner - ett särskilt problem för Bottenhavet. 35-39. Umeå Marina Forskningscentrum (UMF).

4. Council regulation amending commission regulation (EC) setting maximum levels for certain contaminants in foodstuffs. EC No 2375/2001. The Council of the European Union.

5. Commission recommendation on the reduction of the presence of dioxins, furans and PCBs in feedingstuffs and foodstuffs (2002/201/EC). The Commission of the European Communities.

6. Bergqvist P.-A., Tysklind M., Marklund S., Åberg Å., Sundqvist K., Näslund M., Rosén I.-L., Tsytsik I. and Malmström H. (2005) Kartläggning av utsläppskällor för oavsiktligt bildade ämnen: PCDD/F, PCB och HCB. MK2005:01, 1-241.

7. Danielsson C., Wiberg K., Korytar P., Bergek S., Brinkman U.A.T. and Haglund P. (2005) *J. Chromatogr. A*, in press.

8. Davis J.C. (1986) Statistics and Data Analysis in Geology, Wiley & Sons, New York, ISBN 0-471- 08079-9

9. Parmanne R. (1990) *Finn. Fish. Research* 10: 1-48.