SPATIAL VARIATION IN DIOXIN CONCENTRATIONS IN HERRING (*CLUPEA HARENGUS*) AND SPRAT (*SPRATTUS SPRATTUS*) WITHIN THE BALTIC SEA

Miller A[1*], Bignert A[1], Cantillana T[2], Aune M[2], Nyberg E[1], Kiviranta H[3]

[1]Department of Contaminant Research, Swedish Museum of Natural History, Frescativägen 40, 114 18 Stockholm, Sweden. [2]Swedish National Food Agency, P.O. Box 622, SE – 751 26, Uppsala, Sweden. [3]National Institute for Health and Welfare, Box 95, FI-70701, Kuopio, Finland.

E-mail contact: Aroha.Miller@nrm.se

1. Introduction

Fish are one of the main sources of dioxins (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) in humans. High dioxin levels in fish from the Baltic Sea have caused concern for many years due to their impact on the environment and human health[1], especially as some fish species from this region are frequently consumed by humans. Concentrations in Baltic herring (*Clupea harengus*), but very rarely in sprat (*Sprattus sprattus*), occasionally exceed the established maximum limit set by the European Commission for human food consumption[2] of 3.5 pg WHO_{05}-TEQ/g w.w. (∑PCDDs+PCDFs) and 6.5 pg WHO_{05}-TEQ/g w.w. (∑PCDDs+PCDFs+DL-PCBs) (1881/2006 EC). Exceptions have been granted to both Sweden and Finland to allow fish from the Baltic region with dioxin concentrations higher than the maximum human consumer levels to be placed on the domestic market only, provided that consumers are informed of the dietary recommendations. Within International Council for the Exploration of the Sea (ICES) regions 24, 25 and 27, all herring < 17 cm length are considered to be below the maximum human consumer concentrations. Herring > 17 cm length caught from regions 24, 27 and parts of 25 (fig. 1), can also be sold to other EU countries as long as the region is indicated on all packaging (SFS 2011:1494; LIVSFS 2011:19)[3, 4]. Nevertheless, dioxin concentrations can vary depending on where in the Baltic region fish are caught. The National Food Agency (NFA) and the Swedish Museum of Natural History (SMNH) have together collected data on dioxin concentrations in both herring and sprat throughout the Baltic Sea region. To determine whether herring and sprat from different locations within the Baltic Sea are below maximum human consumption guidelines for dioxins, and therefore marketable to other EU countries, we examined data on dioxin concentrations for these two species, caught from various ICES regions.

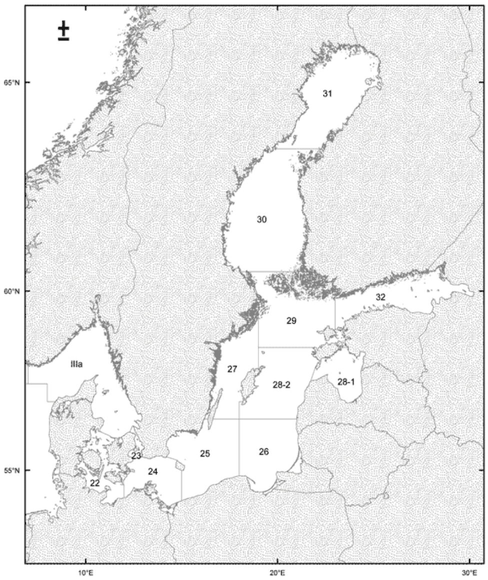

Figure 1. Map of ICES regions in the Baltic Sea. Only regions 24 – 31 were included in the following data.

2. Methods

Sample Preparation

Both herring and sprat were caught from several locations within the Baltic Sea, herring from ICES regions 24 – 31, and sprat in ICES regions 24 – 29 as they typically do not occur in the two northern most regions (30 and 31) (both species sampling include region 28-2, not 28-1, or 32; 10 of 12 samples of sprat came from region 29-S, a less contaminated area compared to 29-N) (fig. 1). Herring was caught in 2009 – 2011 from various months each year. Sprat was caught in various months throughout 2010 only. Month of capture varied as both SMNH and NFA contributed fish for this project.

Herring and sprat were prepared at NFA for dioxin and PCB analyses. Biological measurements (length, weight) were taken. Fat percentage was calculated during dioxin analysis. Herring muscle tissue and skin were sampled. For sprat, the heads, intestines and tail fin were removed. Samples were homogenised and then 100 g of homogenised tissue was sampled. A total of 119 pooled herring samples, and 34 pooled sprat samples were taken (table 1). Each pooled sample consisted of between 4 to 56 individuals (herring) or 53 to 124 individuals (sprat), depending on weight. Total number of fish sampled per ICES region is given in table 1.

Table 1. Summary of herring and sprat samples throughout the Baltic Sea region.

ICES Region	Species	No. pooled samples	Total No. individuals per region
24	herring	9	87
	sprat	2	113
25	herring	20	329
	sprat	12	1012
26	herring	7	119
	sprat	2	169
27	herring	20	540
	sprat	5	472
28	herring	20	450
	sprat	10	1020
29	herring	12	297
	sprat	3	243
30	herring	26	597
31	herring	5	132

Dioxin Analyses

Extraction, clean-up and analysis of PCDD/Fs and PCBs were carried out according to validated methods at the National Institute for Health and Welfare (THL) in Kuopio, Finland[5]. The pooled samples were analysed for the seventeen chloro-substituted PCDD/Fs, twelve dioxin-like PCBs (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) and six non dioxin-like PCBs (marker or indicator PCB 28, 52, 101, 138, 153 and 180).

Statistical Analyses

The PCDD/F and dl-PCB levels are presented as toxic equivalents (TEQ) using the toxic equivalency factors (TEF) set by the WHO in 2005. Herring and sprat were length adjusted, herring to 17 cm (average consumer size, and because herring < 17 cm should comply with maximum human consumption concentrations) and 20 cm (herring >17 cm are preferred for surströmming (fermented herring), and are worth more money to the fishermen[6]); and sprat to 13 cm (average consumer size) and 17 cm (to be a comparable size to herring) using the following equation:

$$Y_{adj}=Y_{obs}+ß(x_m-x_{obs})$$

where Y_{obs} are the observed concentrations, ß is the beta value from the regression, x_m is the length you want to adjust to (e.g., here, 17 and 20 cm for herring), and x_{obs} are the observed lengths. This relationship is based on a regression calculated for each species between dioxin concentration and length. These adjusted values, and their 95% confidence intervals, are presented on maps of the Baltic Sea, by ICES region.

Principal component analysis (PCA) was performed on the proportions of PCDD, PCDF and dl-PCB -TEQ and CB153 concentrations relative to the sum of PCDD/F+dl-PCB for unadjusted data, to study possible geographical gradients in PCDD/F+DL-PCB patterns, and to distinguish differences between herring and sprat. The percentage of PCDD, PCDF and dl-PCB TEQ and CB153 relative to the sum of PCDD/F+dl-PCB was calculated and log-transformed prior to the PCA analysis. Before the PCA scores were plotted, they were centered and scaled to 100%. The eigenvector loadings were added to the PCA plot as vectors.

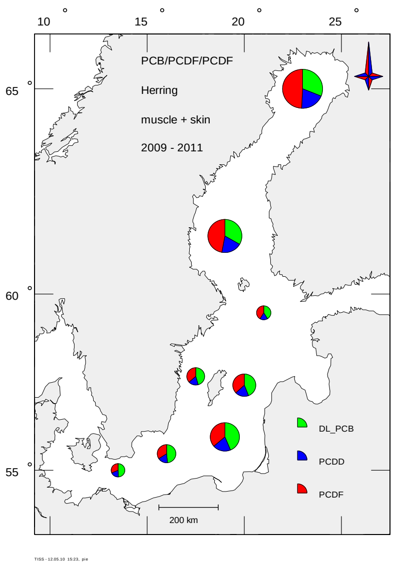

Figure 2. Map of Baltic Sea region showing relative contribution to total TEQ of PCDDs (blue), PCDFs (red) and dl-PCBs (green) in herring. Size of circles indicates relative concentration.

3. Results and Discussion

For herring, PCDFs or dl-PCBs contribute the most to TEQ, while PCDDs contribute the least (figure 2). TEQ_{2005} values are lowest in the south (region 24), increase moving north, and are highest in the Bothnian Bay (region 31). Region 26 has higher $TEQ_{PCDD/F}$ and $TEQ_{PCDD/F+dl\text{-}PCB}$ values compared to the other southern sites.

Sprat $TEQ_{PCDD/F}$ values remain relatively low through all sampled regions, with the exception of region 26 where it is higher (2.78 pg/g w.w.). This trend is also reflected in the $TEQ_{PCDD/F+dlPCB}$ values. However, the lowest value is seen in region 29, the northern most region sampled for sprat, and this coincides with the highest fat content (16.1%) (table 2). Sprat from this region were sampled in autumn, whereas the other sprat were sampled between winter – spring, which may explain the higher fat percentage. The dominant source of dioxin pollution to the Baltic Sea has been attributed to atmospheric deposition[7, 3], with industrialized areas along the coastline likely contributing to localized variation. The south - north gradient seen in herring may be explained by location (e.g., lower salinity and temperatures in northern areas affecting diet), or fish biology, while elevated concentrations seen in region 26 may be due to local source points e.g., pulp/paper mills or other industry.

Table 2. Arithmetic mean TEQ_{2005} values (pg/g w.w) and fat % for herring and sprat from each ICES region.

ICES Region	Herring			Sprat		
	PCDD/F TEQ_{2005} pg/g w.w.	PCDD/F+dlPCB TEQ_{2005} pg/g w.w.	Fat %	PCDD/F TEQ_{2005} pg/g w.w.	PCDD/F+dlPCB TEQ_{2005} pg/g w.w.	Fat %
24	1.06	2.09	10.3	1.49	3.72	8.6
25	1.48	2.88	5.6	1.85	3.85	8.9
26	2.82	5.02	5.9	2.78	5.45	8.3
27	1.6	2.94	4.8	1.9	4.11	9.6
28	2.19	3.92	5	2.2	4.3	8.1
29	1.54	2.61	6.7	1.31	2.69	16.1
30	3.62	5.43	7.2			
31	4.21	6.12	5.5			

When examining $TEQ_{PCDD/F +dl\text{-}PCB\ 2005}$ values for herring length adjusted to 17 cm and 20 cm (standard consumer size, and the preferred size for surströmming, respectively), the same south – north gradient is observed (fig. 3). In herring adjusted to 17 cm, more regions are below 6.5 $pgWHO_{05}$-TEQ g/w.w. (∑PCDDs+PCDFs+DL-PCBs) compared to herring adjusted to 20 cm. Dioxin levels are known to be age and therefore size (length, weight) related, with older/larger fish having higher concentrations compared to younger/smaller fish[8, 9, 5].

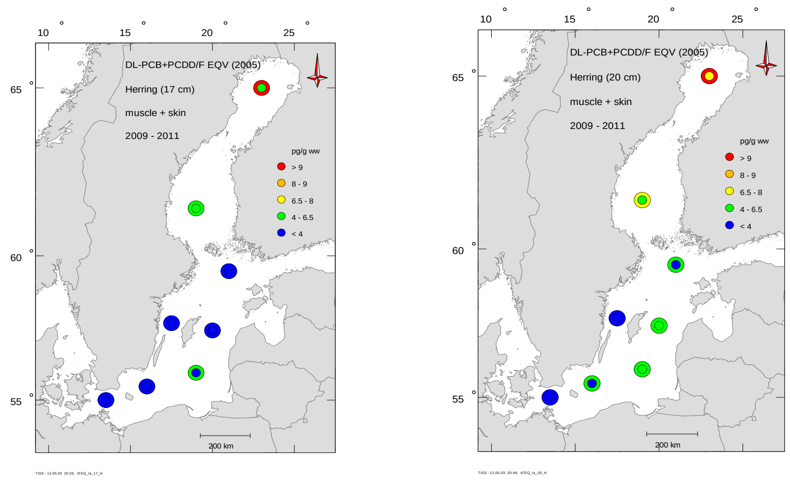

Figure 3. Map of the Baltic region. Circles represent sampled herring, length adjusted to 17 cm (left), and 20 cm (right) from each of the ICES regions (see figure 1). Small inner circles show the mean $TEQ_{PCDD/F+dl\text{-}PCB\ 2005}$ values, while larger outer circles depict the 95% confidence interval around these mean values.

Herring from the Bothnian Bay (region 31) exceed the maximum limit for human food consumption in 20 cm adjusted herring. For 17 cm adjusted herring, the mean concentration in region 31 is lower than the maximum limit, but the CI is still higher. Location is probably instrumental in explaining dioxin concentrations here. More fresh water and less salt water input means reduced herring growth rates[10] (i.e., lack of growth dilution) due to a different diet to herring in other areas of the Baltic, implying longer exposure time for the same size fish. A slower turnover of sediments and water (residence time of Baltic Sea water ranges from 25 – 35 years[11]) and less net loss of dioxins could also contribute. Increasing riverine fluxes of organic matter (OM) over the last decades[12] may play a role, since OM functions as a carrier for POPs from land to sea.

For herring 17 cm or smaller, regions 24, 25, 27, 28 and 29 are completely below maximum consumer limits. Region 26 is below maximum consumer limits, but there is a risk of higher dioxin concentrations in herring. For 20 cm herring, regions 24 and 27 are below maximum consumer limits. Mean concentrations in regions 25 and 29 are also below maximum limits, although there is a risk of higher dioxin concentrations in herring, when the confidence intervals are considered.

Sprat adjusted to 13 and 17 cm from region 26 have higher $TEQ_{PCDD/F +dl\text{-}PCB\ 2005}$ values than the other regions examined (fig. 4). Sprat at 13 cm length from regions 24 – 29 are below maximum consumer levels, except for the CI for region 26. The PCA (fig. 5) shows that southern sites form a separate group to northern sites (light blue shapes), and sprat are more strongly influenced than herring by dl-PCBs with the inclusion of CB153.

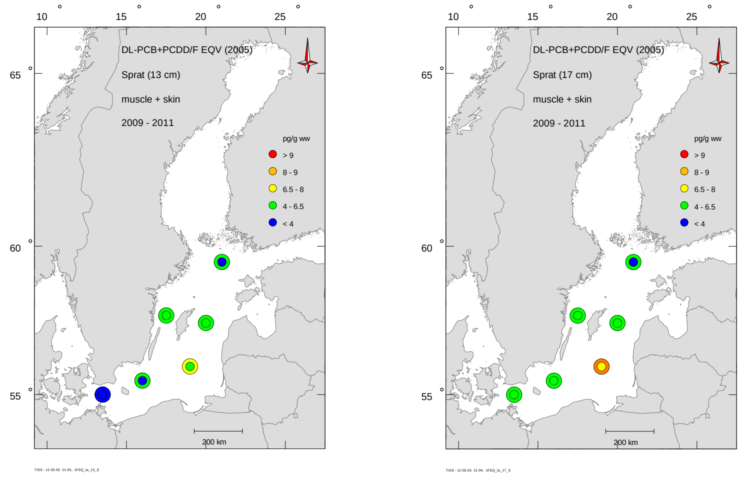

Figure 4. Map of the Baltic region. Circles represent sampled sprat, length adjusted to 13 cm (left), and 17 cm (right) from each of the ICES regions (see figure 1). Small inner circles show the mean $TEQ_{PCDD/F+dl-PCB\ 2005}$ values, while larger outer circles depict the 95% confidence interval around these mean values.

Herring of 17 cm and 20 cm length or smaller from regions 24, 25, 27, 28 and 29 are below the maximum limit for human food consumption of 6.5 pg WHO_{05}-TEQ g/w.w. (∑PCDDs+PCDFs+DL-PCBs). Herring of 20 cm length from regions 30 and 31 still occasionally exceed the maximum consumption limit, and it is therefore recommended that herring from these regions are not allowed to be sold outside of the domestic market.

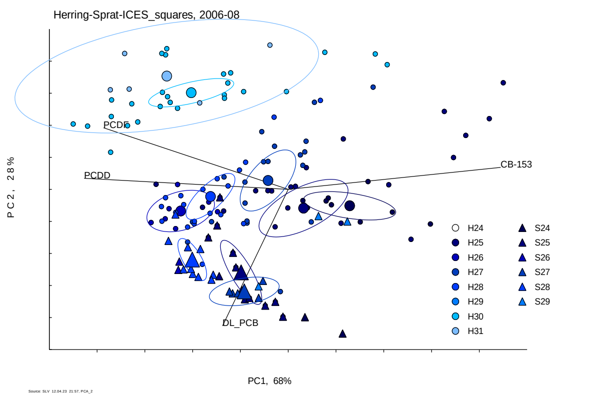

Figure 5. Principal component Analysis showing the proportions of PCDD, PCDF and dl-PCB TEQ, and CB153 concentrations relative to the sum of PCDD/F+dl-PCB for unadjusted data, for both herring (circles) and sprat (triangles).

4. Acknowledgements

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5. References

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