TEMPORAL VARIATION IN PCDD/F CONCENTRATIONS IN GUILLEMOT EGGS (*URIA AALGE*) AND HERRING (*CLUPEA HARENGUS*) WITHIN THE BALTIC SEA AND AT THE SWEDISH WEST COAST

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1. Introduction

High dioxin levels in biota from the Baltic Sea have caused concern for many years due to their impact on the environment and human health[1]. Environmental monitoring of different biota has been conducted by a number of EU countries, including Sweden, to follow temporal changes in dioxins[2]. Within the Swedish National Marine Monitoring Programme, guillemot eggs (*Uria aalge*) and herring (*Clupea harengus*) are collected to monitor spatial and temporal trends in dioxins and furans (PCDD/Fs).

Guillemot are suitable for monitoring dioxins in the Baltic Sea as most do not migrate further than the southern part of the Baltic Proper during the winter season. They feed mainly on sprat (*Sprattus sprattus)* and herring (*Clupea harengus*). Guillemot breed for the first time at 4 - 5 years of age. Eggs hatch after about 32 days. The egg content is high in fat (11 - 13%), and is thus appropriate for dioxin analysis. Normally, guillemot lay just a single egg per breeding season, but if this egg is lost another may be laid. It has been shown that guillemot eggs that are laid late tend to contain significantly higher concentrations of organochlorines compared to eggs laid early[3], and therefore only early laid eggs are analysed for dioxins. Ten guillemot eggs, collected between weeks 19 – 21 (22), are analysed for dioxins each year.

Herring is a pelagic species that feeds mainly on zooplankton. It becomes sexually mature at about 2 - 3 years of age in the Baltic Sea, and at 3 - 4 years of age on the Swedish west coast. Herring muscle tissue is fat and therefore appropriate to use for dioxin analyses. Herring is the most commonly used indicator species for monitoring contaminants in biota within the Baltic Monitoring Programme in the HELCOM convention area. It is the most dominant commercial fish species in the Baltic. It is important not only for human consumption, but also for several other predators in the marine environment, such as guillemot. Various regulations and conventions have been implemented to reduce dioxin emissions e.g., the Stockholm Convention and the Convention on Long Range Transboundary Air, which are among the most important for the control and reduction of sources to the environment. Previously, a tentative Quality Standard (QS) in biota for secondary poisoning for 2,3,7,8-TCDD of 1.2 pg/g wet weight (w.w.), was suggested by the European Commission (EC)[4]. In early 2012, the QS was re-evaluated and it was recommended to use the maximum level for dioxins and furans in foodstuffs of 3.5 $pg_{WHO05\text{-}TEQ}$/g w.w.. However, here we focus on the earlier threshold level of 1.2 pg/g w.w., as we believe this gives greater environmental protection. To examine dioxin concentrations in herring in relation to the suggested target level of 1.2 pg /g w.w., and whether dioxin concentrations have changed over time, we present temporal data on dioxins in guillemot eggs and in herring from the Swedish National Marine Monitoring Programme.

2. Methods

Sample Preparation – Guillemot eggs

Guillemot eggs are collected from St Karlsö, Gotland, Sweden (fig. 1). Length, width and total weight of eggs are recorded. Egg contents are removed (blown out). Embryo tissue is separated from the yolk and white, which are homogenised. Weight of the empty, dried eggshell is recorded. Egg shell thickness is measured at the blowing hole using a modified micrometer. Thirty grams of the homogenised egg content is prepared for dioxin analyses.

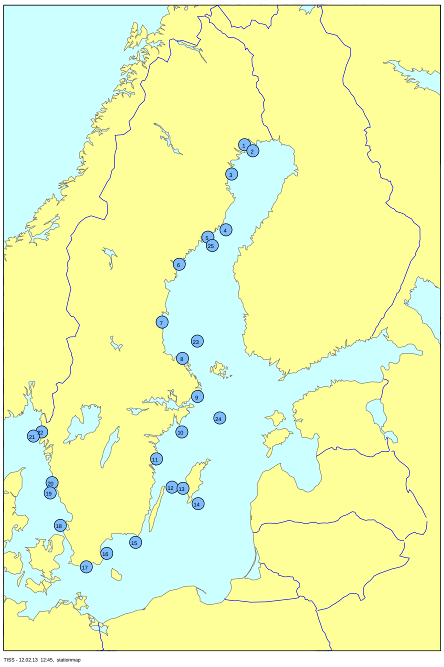
Sample Preparation – Herring

Herring samples are collected each year from seventeen sites along the Swedish coast: Rånefjärden, Harufjärden, Kinnbäcksfjärden (Bothnian Bay), Holmöarna, Örefjärden, Gaviksfjärden, Långvindsfjärden, Ängskärsklubb (Bothnian Sea), Lagnö, Landsort (northern Baltic Proper), Byxelkrok, Abbekås, Hanöbukten, Utlängan (southern

Baltic Proper), Kullen, Fladen (Kattegat) and at Väderöarna (Skagerrak) (fig. 1). Herring are also collected from two sites in the open sea, the Baltic Proper and the Bothnian Sea. Age determination is conducted using their scales. Analysed specimens are female, between 2 - 5 years. Total body weight, liver weight, total length and maturity of gonads are recorded. The number of herring sampled has varied over the years. In some years, 7 - 15 individuals were pooled at each site, while in other years 8 - 10 individual fish were analysed from each site. Dorso-lateral herring muscle tissue of approximately 10 g per specimen/pool was removed under strict laboratory protocols, and sent for analysis.

Dioxin Analyses
Analyses are carried out at the Department of Chemistry, Umeå University. The extraction method is described by [5], the clean-up method by [6], and the instrumental analysis (GC-HRMS) by [7]. The laboratory participates in the annual FOOD intercalibration rounds, including laboratory reference material (salmon tissue) with each set of samples.

Statistical Analyses
One of the main purposes of the monitoring programme is to detect trends. Log-linear regression analyses are performed for the *entire investigated time period* and also for the *most recent 10 years* for longer time series. The slope of the line describes the yearly percentage change. A slope of 5% implies that the concentration is halved in 14 years, whereas a slope of 10% corresponds to a similar reduction in 7 years, and 2% in 35 years. Suspected outliers are marked with a red cross in the time series.
Values reported that are below the quantification limit are substituted using the reported LOQ divided by the square root of 2.



Evaluation against threshold level
The levels of PCDD/Fs in herring muscle was evaluated against the QS for 2,3,7,8-TCDD in biota (secondary poisoning) of 1.2 pg/g w.w. The toxic equivalence concept has been used converting the concentrations into toxic equivalents (TEQ), which are based on the assumption that all 2,3,7,8-substituted PCDDs and PCDFs have the same mode of action. The dioxin-like PCBs (dl PCBs) are excluded in this evaluation due to lack of analytical data. Toxic equivalency factors (TEFs) for humans and wild life from 1998 are used[8].

Figure 1. Sampling sites of within the Swedish National Marine Monitoring Programme. 1) Rånefjärden, 2) Harufjärden, 3) Kinnbäcksfjärden, 4) Holmöarna, 5) Örefjärden, 6) Gaviksfjärden, 7) Långvindsfjärden, 8) Ängskärsklubb, 9) Lagnö, 10) Landsort, 11) Kvädöfjärden, 12) Byxelkrok, 13) St.Karlsö, 14) SE Gotland, 15) Utlängan, 16) V. Hanöbukten, 17) Abbekås, 18) Kullen, 19) Fladen, 20) Nidingen, 21) Väderöarna, 22) Fjällbacka, 23) Bothnian Sea offshore site, 24) Baltic Proper offshore site, 25) Bonden.

3. Results and Discussion

Temporal Variation
In guillemot eggs, significant decreasing trends are observed for TCDD, TCDF and total PCDD/Fs ($pg_{WHO98\text{-}TEQ}$/g l.w.) during the period 1970 - 2010 (fig. 2). This is most likely a reflection of the restrictions put in place to reduce dioxin emissions. However, contrary to TCDDs, TCDFs show no decreasing trend since the early1990s, which may explain why the trend levels off for total PCDD/Fs during the last 20 years (fig. 2). A broad range of primarily PCDFs were produced in chloralkali industries, which produced Cl_2 on site for the pulp industries[9]. Sludge from these plants were often stored at local dump sites, which may now leak dioxins.
At Ängskärsklubb, which had very high levels at the start of the sampling period, a significant decreasing trend in dioxin concentrations in herring is seen (fig. 3, 4). This trend is probably due to the long time that monitoring has been conducted here (since 1979), the high concentrations seen at the start of the monitoring period, as well as restrictions to decrease dioxin emissions taking effect. A significant decreasing trend was also seen at Fladen (lipid weight basis) (fig. 4). Fladen is on the Swedish west coast, and environmental conditions are more similar to open ocean conditions e.g., salinity, which influences zooplankton community composition and thus herring diet[12] and growth rates. Export of dioxins to the open ocean is a major net loss mechanism for dioxins in coastal environments[13, 12], and may also influence dioxin loss here. There are no significant changes in TCDD-

equivalent concentrations over time in herring muscle at Harufjärden and Utlängan, either on a wet weight or a lipid weight basis (fig. 3, 4). This may be due to the shorter monitoring period in these areas (since 1990 and 1988 respectively), but is more likely related to environmental conditions e.g., lower salinity and lower temperature influencing herring diet[10], and causing slower growth rates, and/or slow water turnover decreasing net loss of dioxins from the system[14]. Between 2000 – 2007, an increasing trend was observed at Harufjärden (fig. 4), but the very low levels of TCDD-equivalents in herring from 2008 – 2009 eliminate that trend. The low levels of TCDD-equivalents cannot be explained by fat content, weight or length (these parameters were normal) so further investigations are needed.

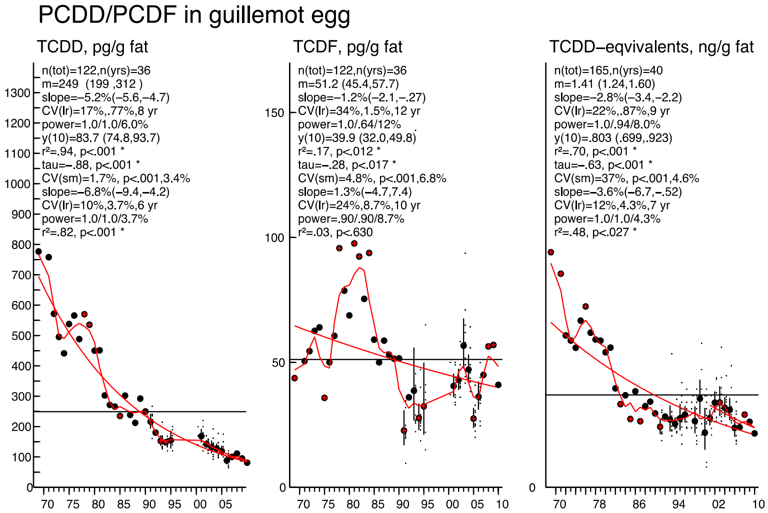


Figure 2. TCDD, TCDF (pg/g l.w.) and PCDD/Fs in TCDD-equivalents ($ng_{WHO98-TEQ}$ /g l.w.) concentrations in guillemot eggs from Stora Karlsö (time series starting in 1970). Dots with red crosses indicate suspected outliers, because they are further from the regression line than expected from the residual variance around the line.

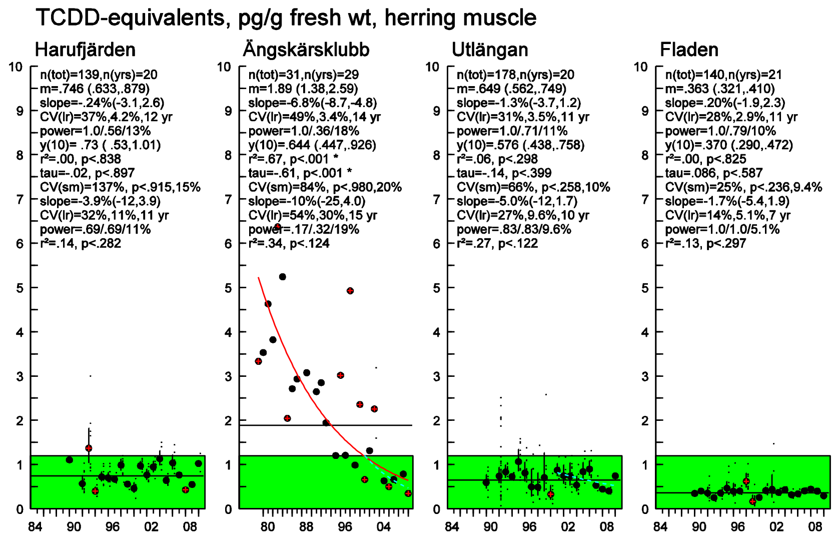


Figure 3. PCDD/F concentrations in TCDD-equivalents ($pg_{WHO98-TEQ}$/g w.w.) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (time series starting in 1990, 1979, 1988 and 1990 respectively). The green area denotes the levels below the suggested target value for PCDD/Fs in fish (secondary poisoning). Dots with red crosses indicate suspected outliers, because they are further from the regression line than expected from the residual variance around the line.

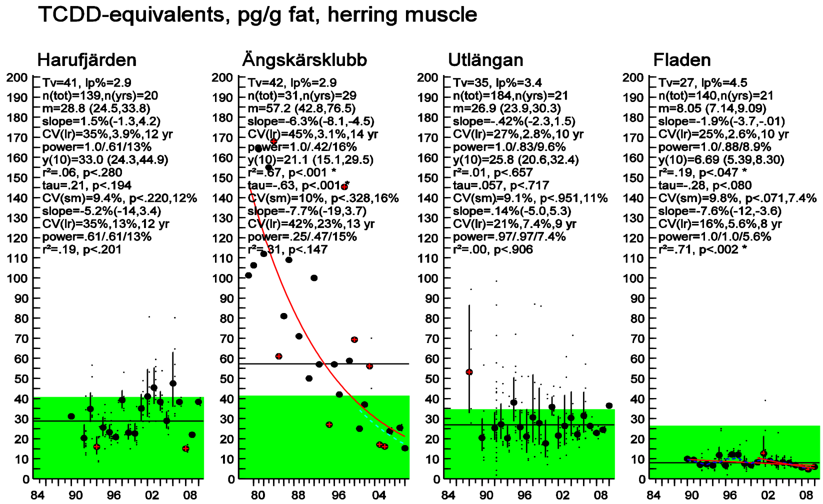


Figure 4. PCDD/F concentrations in TCDD-equivalents (pg$_{WHO98\text{-}TEQ}$/g l.w.) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (time series starting in 1990, 1979, 1988 and 1990 respectively). The green area denotes the suggested target value (recalculated to lipid weight) for PCDD/Fs in fish (secondary poisoning). Dots with red crosses indicate suspected outliers, because they are further from the regression line than expected from the residual variance around the line.

Evaluation against threshold level

All time-series are close to the suggested target value for fish (protection of predators against secondary poisoning, 1.2 pg/g w.w.) except for Fladen on the Swedish west coast, which is about four times lower than the suggested target level (fig. 3, 4). If the toxic equivalents from the dl-PCB where added to the PCDD/Fs, the sum of these together would probably exceed the QS of 1.2 pg/g w.w. at all Baltic sites.

Data from this monitoring programme indicates that additional efforts are required to further reduce dioxin emissions to the Baltic, so that these emission reductions can be reflected in biota, to better protect the environment, and human health.

4. Acknowledgements

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5. References

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