Tracing of the PCDF/PCDD contamination from the Frierfjord area along the Norwegian south coast

Martin Schlabach[1], Jon Knutzen[2], Birger Bjerkeng[2] and Georg Becher[3]

[1] Norwegian Institute for Air Research (NILU), P.O. Box 100, 2007 Kjeller, Norway
[2] Norwegian Institute for Water Research (NIVA), P.O. Box 173 Kjelsås, N-0411 Oslo, Norway
[3] National Institute of Public Health, P.O. Box 4404 Torshov, N-0403 Oslo, Norway

Introduction

Until 1989-90 Frierfjorden, S. Norway, was the recipient of large amounts of polychlorinated dibenzofurans/dibenzo-p-dioxins (PCDF/PCDD). Calculated according to the international or the nordic model (1,2) for toxic equivalency factors (TEFs), which in this case give little difference, the yearly discharge was about 300-500 g Toxic Equivalents (TEQs, cf. 3). About 65 % of $\sum$TEQ in the magnesium factory waste water came from 2,3,7,8-substituted HxCDF, in particular 1,2,3,6,7,8-HxCDF and 1,2,3,4,7,8/9-HxCDF (close to 30 % each, cf.4). After 1990 the direct load was reduced to 1-3 g TEQ/year in 1992-1996.
In spite of the strongly decreased load dioxin levels in organisms have remained high after an initial improvement in 1991-1992 (5). Furthermore, there has been strong indications that the influence from this contamination still may be traced southward along the Skagerrak coast (6), as it was during the original loading (7). The goal of the present study is to assess this problem on the basis of results from a study of PCDF/PCDD in hepatopancreas of edible crabs *(Cancer pagurus)* at assumed reference localities, including Skagerrak sites (8). Supplementary analysis of mussels to the same objective (still transport of dioxins in the surface water of the coastal current ?) is in progress.

Materials and Methods

As part of a registration of micropollutants in seafood, pooled male crabs have been sampled at 11 stations along the Norwegian south and west coast. Along with other components the samples were analysed for PCDF/PCDD and non-ortho PCB as described in detail in (8).

Linear regression methods and principal component analysis (PCA) are used to identify the influence of the Frierfjord dioxin discharge along the Skagerrak coast. PCA is a projection method for extraction of the systematic variations in a data set. PCA reduces the original data set into a model with a few dimensions (principal components). PCA can be used to find patterns in the data. i.e. groups of samples that are special (classification) and it can be used to find the most important variables.

Results and Discussion

The proportion of total TEQ in crabs from 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF show a geographical pattern that may indicate remaining influence from the former discharge. Figure 2 shows the proportions on log scale versus the distance along the coast from the outlet of the Frierfjord.

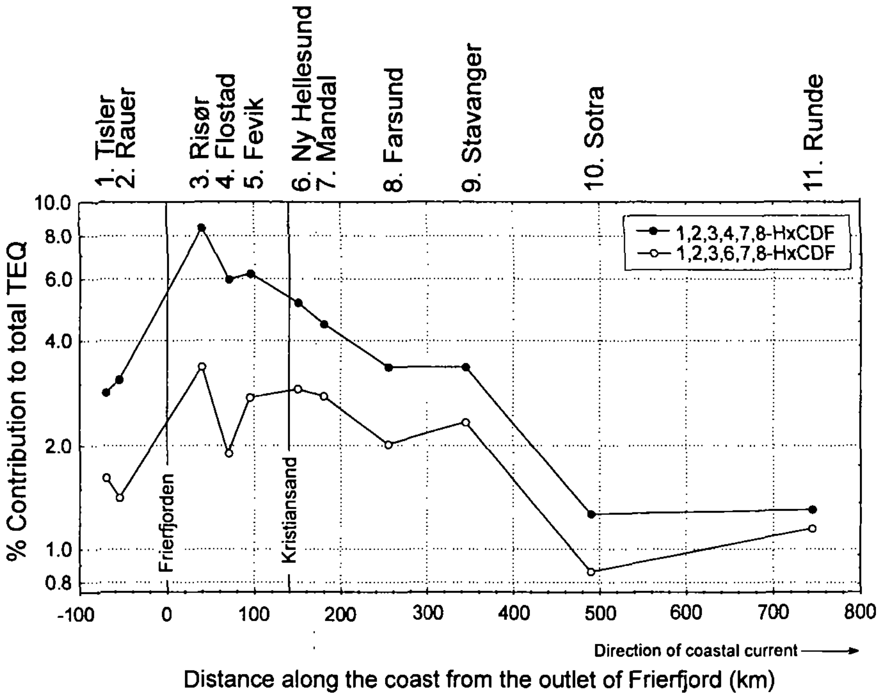

Figure 1: Contribution of 1,2,3,4,7,8- and 1,2,3,6,7,8-HxCDF to total TEQ for the different samples.

Moving in the direction of the coastal current (left to right in the plot), there is an increase around the mouth of Frierfjord in the relative contributions of 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF. The highest values at Risør are about 1/3 and 1/10 of the proportions in the original discharge from the magnesium factory, with a gradual exponential decrease (linear on log scale) along the coast, particularly for the first component. Both the maximum value and the exponential decrease with distance along the coast from Risør to Stavanger are clearly consistent with a remaining influence from the former Frierfjord discharges.

For 1,2,3,4,7,8-HxCDF there is a strongly significant regression with distance along the coast from Risør to Sotra, following the relation $\%_{1,2,3,4,7,8\text{-HCDF}} = 8.86 \cdot e^{-0.00365 \cdot km}$, with a nominal significance level $p= 0.000066$. A simulation study with 1000 random samples of y values for the actual x values shows that the real significance level is 28 times the nominal, i.e. the probability of finding such a strong regression in some subset of consecutive stations by accident is still only $p=0.0018$. Regression on the points from Risør to Stavanger has $p=0.0014$.

In this case all the points included in the regression have higher values than any excluded point, and simulation shows that the real significance level for such an outcome is about equal to nominal significance. Thus the exponential reduction along the coast from Risør to Stavanger appears to be quite significant.

Figure 2 below shows absolute values (ng/kg) of TEQ from 1,2,3,4,7,8-HxCDF versus TEQ from other components than 1,2,3,4,7,8-HxCDF or 1,2,3,6,7,8-HxCDF. Station 3 to 9 (Risør – Stavanger) closely follow a relation $TEQ_{1,2,3,4,7,8\text{-HxCDF}} = 0.0188 \cdot TEQ_n^{1.491}$ (R^2=0.984), i.e. with decreasing relative contributions for lower total TEQ. This would be consistent with reduction in TEQ with distance being due to longer transport times, coupled to a faster decay rate for 1,2,3,4,7,8-HxCDF than for the other components. Sotra and Runde have as high absolute TEQ as Farsund and Stavanger, but the relative contributions from 1,2,3,4,7,8-HxCDF are lower than would be expected given the total levels. The upstream localities also deviates the same way. The general picture is the same for 1,2,3,6,7,8-HxCDF, but here Flostad also deviates somewhat from the regression.

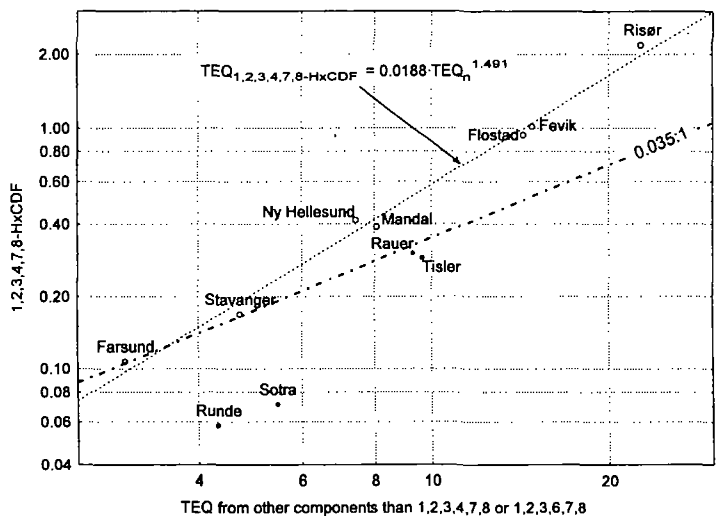

Figure 2: TEQ of 1,2,3,4,7,8-HxCDF versus TEQ of other compounds than 1,2,3,4,7,8- and 1,2,3,6,7,8-HxCDF.

A log-linear covariance analysis of the model

$$TEQ_{1,2,3,4,7,8\text{-HxCDF}} = c_i \cdot TEQ_n^{\alpha}$$

with different group levels c_i for station groups (Tisler, Rauer), (Risør – Stavanger) and (Runde, Sotra) show differences between groups that are significant at better than p=0.00003. This may be taken as indicating that the influence from PCDF/PCDD that have previously been discharged to Frierfjord extends to the Stavanger area.

Principal component analysis

The data-set consist of 11 samples with the concentration of 15 2,3,7,8-chlorinated PCDD and PCDF congeners (1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF were mostly below the detection limit and were removed completely from the data set). In order to compare the dioxin profiles of the samples and not the differences in concentration, the data set was normalised.

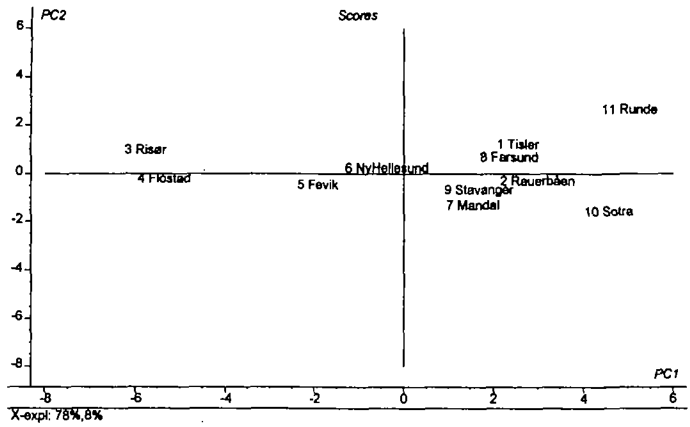

Figure 3: Scores plot of the principal component analysis of PCDF/PCDD results of crab samples from the Norwegian south and west coast.

Principal component 1 (PC1) can explain more than 75% of the variance between the samples. The scores plot in figure 2 shows that the stations from Risør down to Ny-Hellesund (downstream from the Frierfjord area) form a distinct separate group with a negative PC1. The rest of the samples with exception of Sotra and Runde are grouped very closely.
Hereby, the principal component analysis confirms the conclusion from the linear regression statistics about the influence of dioxin from the Frierfjord emissions down to Ny-Hellesund. However, due to the lower concentrations it was not possible to identify the typical pattern further downstreams.

Acknowledgement
The basis for this study has been sponsored by the Norwegian Food Control Authority (SNT) and the Norwegian Pollution Control Authority (SFT)

References

1. NATO/CCMS. North Atlantic Treaty Organisation/Committee on the Challenge of Modern Society, *Report No. 176*, **1988**.
2. Ahlborg U G; *Chemosphere* **1989**, 19, 603.
3. Knutzen J and Oehme M; *Chemosphere* **1989**, 19, 1897.
4. Knutzen J and Oehme M; *NIVA-report 2189*, **1988**, ISBN 82-577-1477-1 (in Norwegian).
5. Knutzen J and Oehme M; *Organohalogen Compounds* **1993**, 12, 203.
6. Knutzen J, Biseth Aa, Brevik E M, Egaas E, Green N W, Schlabach M and Skaare J U; *NIVA-report 3834-98*; **1998**, ISBN 82-577-3414-4 (in Norwegian, Engl. summary).
7. Oehme M, Bartonova A and Knutzen J; *Environ. Sci. Technol.* **1990**, 24, 1836.
8. Knutzen J, Becher G, Schlabach M and Skaare J U; Manuscript submitted to Dioxin'98.