

DO HISTORICAL DEPOSITS IN SEDIMENTS CONTRIBUTE TO PCDD/F-LEVELS IN BIOTA? – A FIELD STUDY

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Introduction

Levels of PCDD/Fs in biota in the Baltic Sea frequently exceed established levels for human consumption, especially in the southern Bothnian Sea^{1,2}. While the main source of PCDD/Fs is generally regarded to be atmospheric deposition^{3,4}, the elevated levels in the southern Bothnian Bay indicates that there may be additional sources. Olsson et al.⁵ suggested that ongoing pollution from cellulose industries may be an important source. Here we report results from a field study investigating the role of historical deposits in sediments outside forest industries and their possible contribution to PCDD/F levels in biota.

Materials and methods

In 2009-2011, 2378-substituted PCDD/Fs were sampled in sediments, benthic fauna and perch (*Perca fluviatilis*) outside a number of forest industries (Östrand, Ortviken, Iggesund, Norrsundet, Korsnäs, Karlholm and Hallsta) and at reference sites (Norbergfjärden, Axmarfjärden, Gräsö and Vålarö; see Karlsson et al.⁶ for geographic details and analytical methods). 3-8 surface sediments were sampled in each area. Benthic fauna consisted of various species including *Marenzelleria sp.*, *Chironomus sp.*, *Macoma baltica* and *Saduria entomon*. In perch we prepared pooled muscle homogenates from 10 individuals (15-20 cm length). Perch is considered to be non-migratory and hence reflecting the local contamination of pollutants including PCDD/Fs. One of the pulp mills, Norrsundet, was closed down in December 2008 allowing us to study the development of PCDD/F contamination following the termination of the effluent discharge.

Results and discussion

Average concentrations of 17 congeners of PCDD/F in each coastal area are shown in **Figure 1**. In the diagram, hexa and hepta chlorinated congeners are pooled together. The highest sum concentrations were measured outside the mills Norrsundet, Karlholm and Hallsta. Outside Norrsundet, which was an ECF bleached kraft mill, concentrations of several congeners were elevated. Outside Karlholm (a board factory) and Hallsta (a TMP mill) primarily highly chlorinated congeners such as OCDD and HpCDD were elevated.

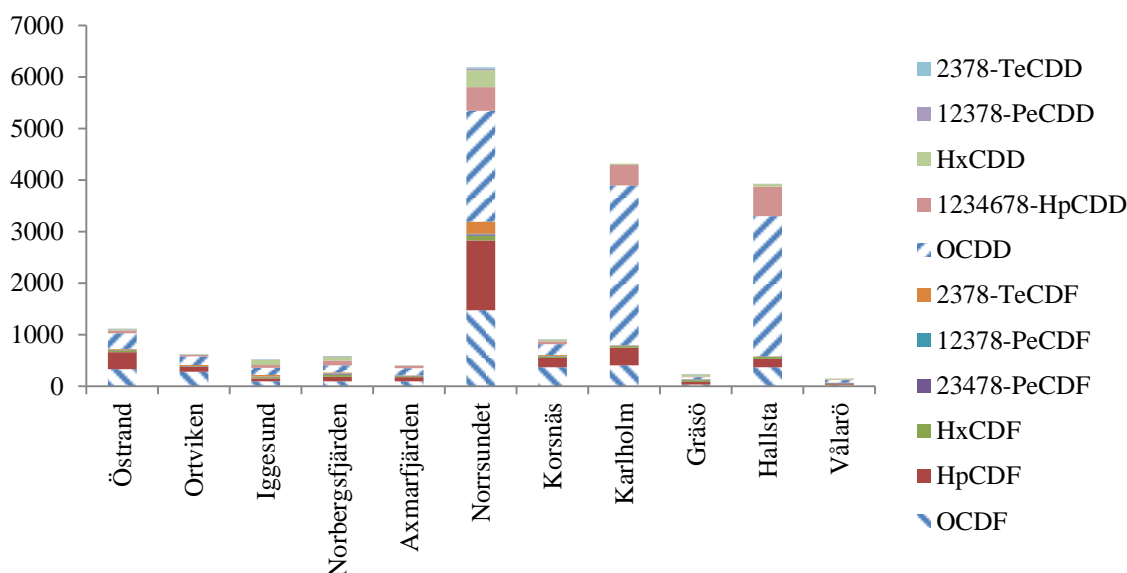


Figure 1 Average PCDD/F levels (pg/g dw) in sediment from the different coastal areas.

Average concentrations of 17 congeners of PCDD/F in perch from the different coastal areas are shown in **Figure 2**. The highest levels were measured outside kraft mills Norrsundet and Iggesund. The levels, however, were far below recommended levels for human consumption.

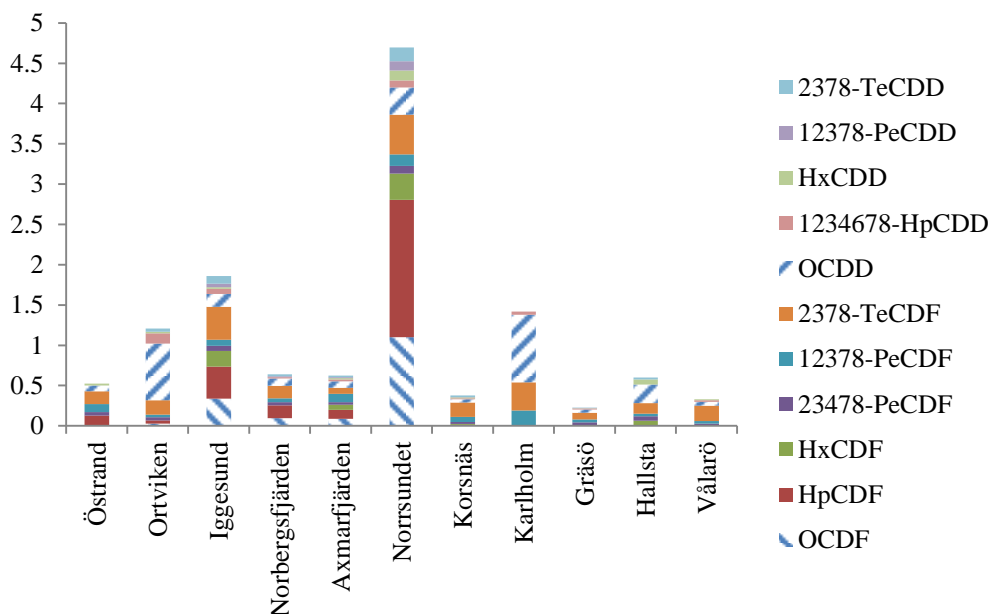


Figure 2 Average PCDD/F levels (pg/g ww) in perch from the different coastal areas.

For total PCDD/F concentration, there is no apparent connection between levels in sediment and fish. Statistical correlations for individual congeners are shown in **Table 1**. Correlations were positive for all detected congeners, but considerably smaller for congeners typical for ambient air deposition (HpCDD, OCDD, PeCDF⁷). High correlations were found for congeners traditionally associated with chlorine bleaching (TeCDD, TeCDF) and tetrachlorophenol⁸. In **Figure 3** the decreasing levels of PCDD/Fs with distance from the Iggesund pulp mill is shown. However, as shown in the right hand figure, levels of 23478-PeCDF actually increase with distance from the pulp mill indicating that the mill is not a source for this specific congener.

Table 1 Statistical correlation (*r*-values) between sediment and perch for individual congeners. Number of data in brackets. Blank spaces indicate less than three samples above detection limits.

2378-TeCDD	0.83 (7)	2378-TeCDF	0.70 (11)
12378-PeCDD	0.90 (6)	12378-PeCDF	0.37 (11)
123478-HxCDD		23478-PeCDF	0.39 (10)
123678-HxCDD	0,81 (9)	123478-HxCDF	0.77 (5)
123789-HxCDD		123678-HxCDF	0.75 (3)
1234678-HpCDD	0.26 (9)	123789-HxCDF	
OCDD	0.59 (11)	234678-HxCDF	
		1234678-HpCDF	0.95 (7)
		1234789-HpCDF	
		OCDF	0.94 (6)

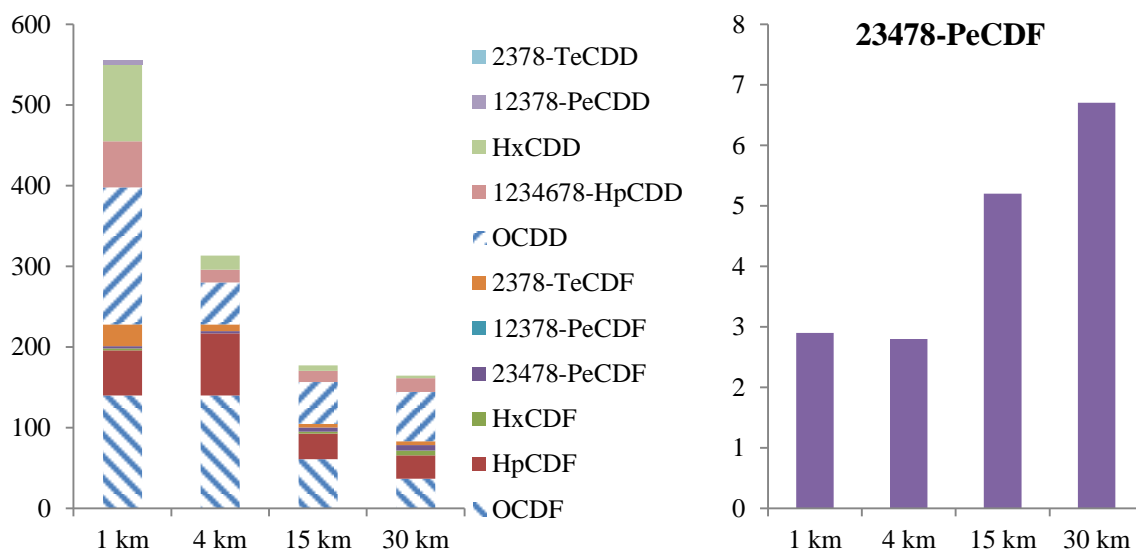


Figure 3 Measured levels (pg/g dw) in surface sediments of all 2378-substituted PCDD/Fs (left) and 23478-PeCDF in a gradient outside Iggesund pulp mill.

The occurrence of elevated PCDD/F levels in both sediment and perch in several locations may either reflect a common source affecting both matrices, or an influence of the sediments on the levels in fish. Very high levels in benthic fauna (**Figure 4**) indicate that there exists a path from the sediments to the food web.

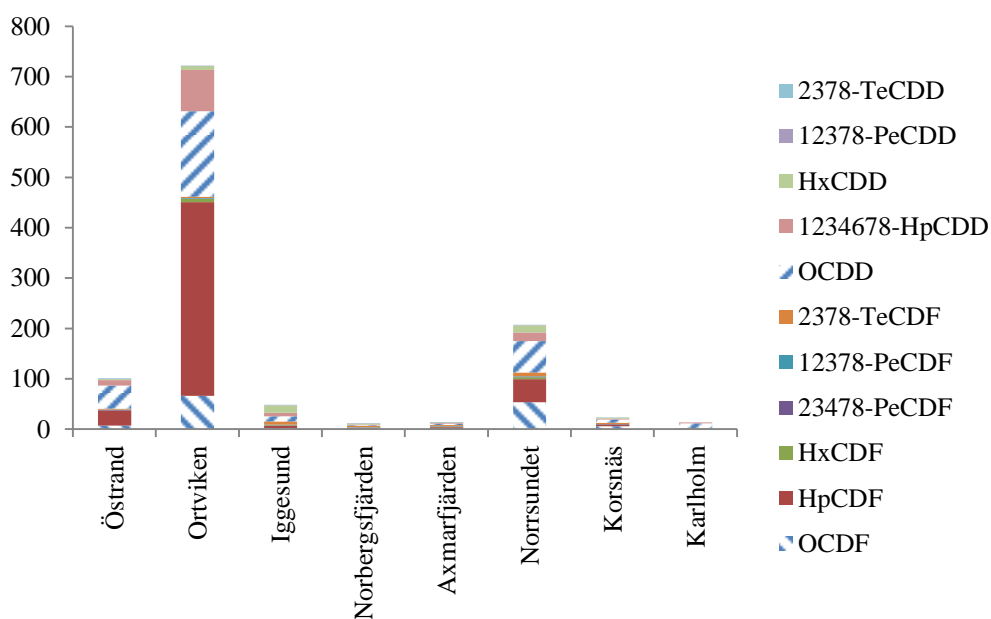


Figure 4 Average PCDD/F levels (pg/g ww) in benthic fauna from the different coastal areas.

Another indication of an ongoing influence from the sediments is the development of PCDD/F levels in perch outside the Norrsundet mill after the termination of effluent discharge in December 2008. As shown in **Figure 5** there is an apparent decrease of HpCDF and OCDF in perch after 2009, but the toxic congeners reflected in the toxicity measured as WHO-TEQ (including 2378-TeCDD and 12378-PeCDD) do not decrease after the mill was closed down. Since the age of the fish in the samples should be around three years this result indicates that there is another source than the mill affecting the fish, and we argue that this source should be the sediments.

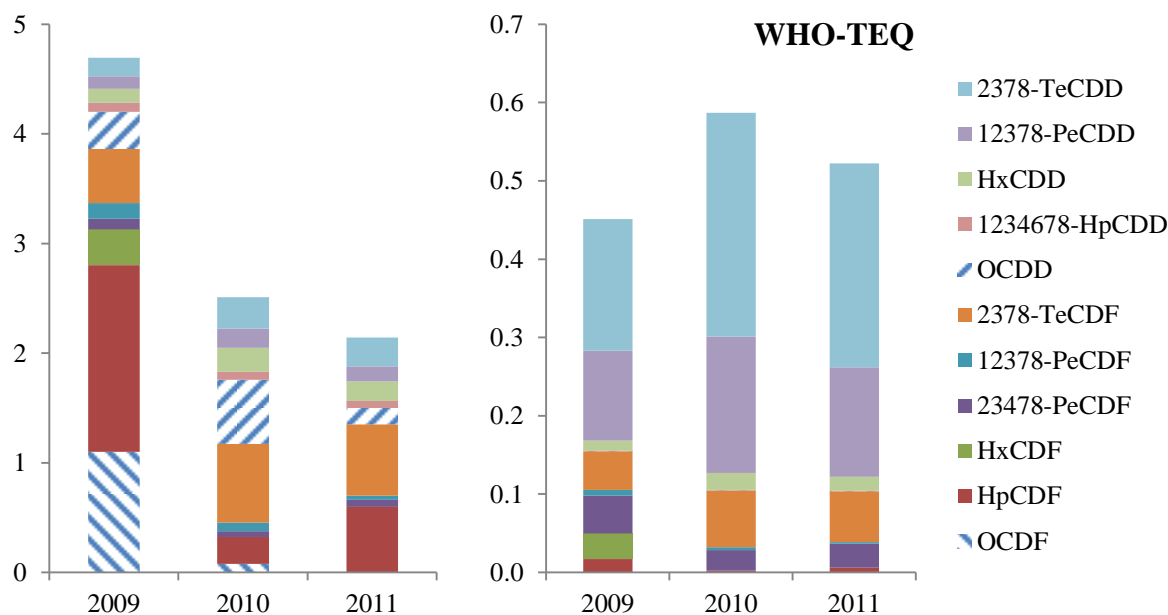


Figure 5 Time series 2009-2011 of PCDD/F in perch (pg/g ww) measured as total concentration (left) and WHO-TEQ (right).

We conclude that historically deposited PCDD/Fs, specifically congeners associated with chlorine bleaching of kraft pulp, appear to influence levels found in biota. This conclusion is strongly supported in Norrsundet where the mill was closed down just before this field study was carried out. However, other studies indicate that pollution of PCDD/F from pulp mills have declined dramatically since chlorine bleaching was replaced with other bleaching methods in the 1980's and 1990's^{6,9}, so the elevated levels of PCDD/Fs found in fish outside other pulp mills may also be partly attributed to historical deposits in the sediments.

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