Dioxin concentrations in sediments of the Baltic Sea - A preliminary survey of existing data

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Introduction

The Baltic Sea region is one of the most contaminated areas with persistent organic pollutants (POPs) including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (dioxins). The high load of dioxins in Baltic fish has lead to restrictions of the use of contaminated fish for human consumption. Uncertainties about sources, geographical distribution of these contaminants, the pathways of bioaccumulation and possible ecotoxicological and human health effects are of concern. POPs may enter the Baltic Sea from atmospheric deposition, riverine input and point sources along the coast. The ultimate sink for the majority of the compounds is the open sea and coastal sediments, although some fraction enters the food chain.

Analysis of sediment has been widely used to study regional and temporal trends of dioxin pollution in freshwater and oceans and the Baltic Sea has been one of the most studied sea areas for dioxin-like compounds as well. Only a fraction (unknown) of the analytical results have been published in scientific papers, however. Here we present regional distribution of certain congeners of dioxins in surface sediments and in six sediment cores from the Baltic Sea. New data is compared with data on earlier Finnish sediment surveys [1,2,3,4]. Some data from published papers [5,6,7,8],and unpublished data from the Kattegat Sound[9] is also given for reference. The purpose of this paper is to:

1. get an "draft" picture of regional distribution (possible hot spots, major regional differencies) along the Finnish-Swedish-Danish-German coastal and open sea sites in the Baltic
2. study differences in congener distributions (source identification)
3. study temporal changes in sediment profiles
4. identify major areas with gap of data
5. call for more data (both published and grey literature as well as new sediment surveys)

Material and Methods

Surface sediment samples along the Finnish coast and one sediment profile from the previously poorly studied Bothnian Bay was sampled in 2002-2003. Samples were collected from known sedimentary areas both near the coast and offshore with pistonless corers with an inner diameter from 9.0 to 13 cm. All the sites were sliced in the field to 2 cm slices and the surface (0-2cm, 2-4 cm) and deep (35-50cm) samples as well as one profile were analyzed for dioxin concentrations.

For reference data from published scientific literature is given (see above). When comparing the results note that the sediments were collected during a long time frame (1988-2003) and the concentrations at surface (and conc. change in profile) reflect the concentration at the time of sampling. P18 and Iggesund /Swedish sediments were taken earlier (late 1980's) than Finnish/Danish/German (mid 1990's-2003).

Results and Discussion

The basic interest of the authors was to study the contribution of identified point sources in Finland on sediment dioxin levels and to compare that with other regions. For this purpose we focus on certain point source-identified congeners. This was also feasible, because not all toxic congeners have been included in some reports. Furthermore, two of the selected congeners 2,3,4,7,8-PeCDF, and 2,3,7,8-TCDF are the main congeners in Baltic fish (Baltic herring, salmon) with alarmingly high dioxins exceeding the maximum level for edible fish (4 pg/g) set by EU in some individuals.

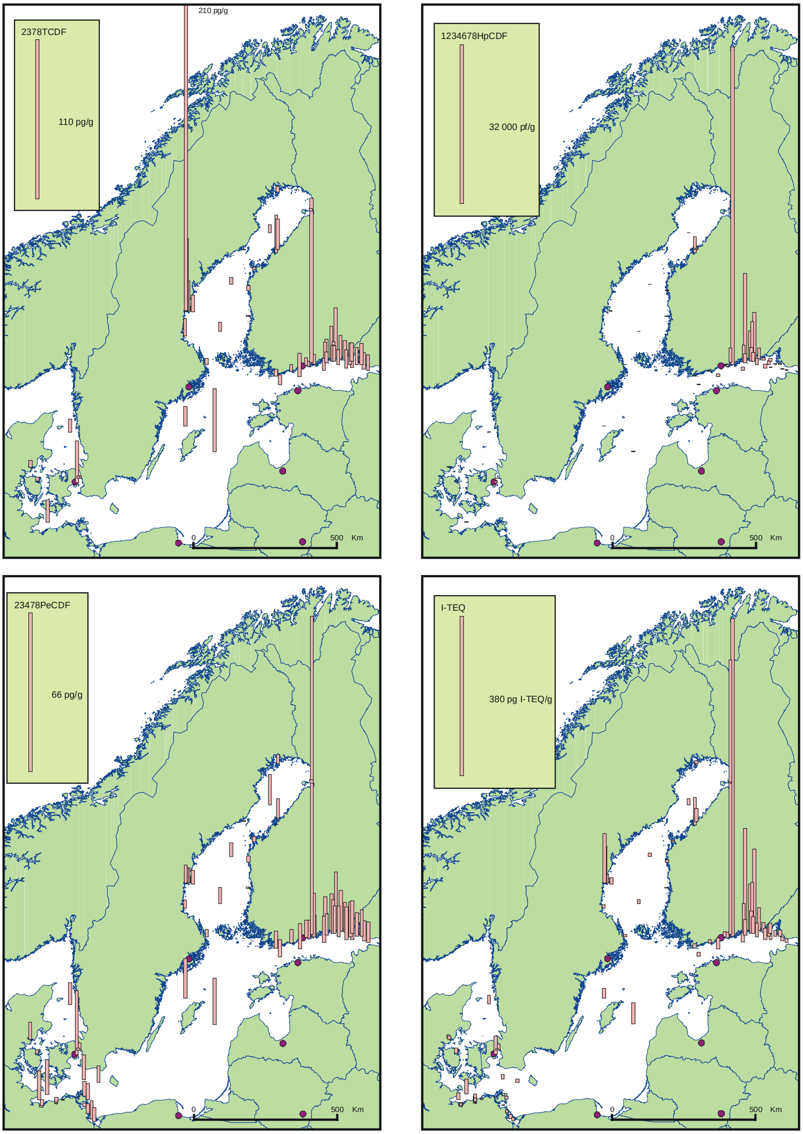

Figure 1. Spatial distribution of PCDD/Fs as concentrations of selected congeners (2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDF, 2,3,4,7,8-PeCDF) and as I-TEQ in surface sediments in the Baltic Sea (for references see text).

Regional distribution

The spatial distribution of dioxins in surface sediments of the Baltic Sea is presented in Figure 1. Clearly highest dioxin levels have been reported near identified point sources along the Finnish coast of the Gulf of Finland (Isosaari et al. 2000, Isosaari et al. 2002, unpublished data from Regional Environment Center). These three sources are the vinyl chloride monomer (VCM) production plant at Sköldvik, the chlorophenol (Ky-5) production along the Kymijoki River and a possible sawmill source (Ky-5 product) near Emäsalo. All these sources have been closed but a continuous transport of old contaminated sediments from Kymijoki river (44 g I-TEQ in 2001) is still a major source of dioxins to the Gulf of Finland[10]. Two of these point sources have emitted specially 1,2,3,4,6,7,8-HpCDF and one (VCM plant, Sköldvik) 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF as well. The main congener in Sköldvik (OCDF) is not shown because of its low concentration in all other sites excluding this one. Note that in Sköldvik and in Emäsalo peaks occur in near vicinity of the source only.

Other identified point sources are located along the Gulf of Bothnia in the vicinity of pulp mills at Iggesund (Sweden)[5] and Pietarsaari (Finland)[1] and emerge only to some extent as I-TEQ, but specially in TCDF (Iggesund).

Note that for 2,3,4,7,8-PeCDF which is most abundant congener in fish, there is only one anomalously high concentration at Sköldvik sewage outlet, but no further. Notably high PeCDF concentrations (17 – 41 pg/g d.w.) compared to many of the coastal sites have been reported at Gotland deep (BY15)[2] and north-west from Gotland (P18)[6] (Fig. 1). Interestingly 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD have been shown to be the main congeners contributing to I-TEQ of dioxins in atmospheric emissions from most anthropogenic sources[11], in air and in deposition[12].

There is no indication of any major dioxin load from St. Petersburg area (Fig. 1). No data was available from the eastern coast of the Baltic Sea (Poland, Kaliningrad, Lithuania, Latvia, Estonia).

Sediment profiles

Figure 2 shows the locations and table 1 the concentrations of selected PCDD/PCDF congeners at surface layer, at concentration maximum and at deeper sediments (14-40 cm) of six sediment cores.

Figure 2. Location of identified local dioxin sources and sites for sediment profile samplings at different studies.

For I-TEQ and for most of the congeners maximum concentrations occur deeper than at surface at all sites. This indicates a general decrease in anthropogenic input of dioxins to the Baltic Sea. The highest concentrations and drop in I-TEQ occur at the Gulf of Finland (sites K15, LL3a, JML1b) (58-75% reduction) with the exception of AKL (22%) that locates at the river Kymijoki estuary. Note that in most of the profiles the historical background (before 1900's) was not found and that the surface in P18 reflects years 1982-1988 whereas in other profiles mid or late 1990's.

Table 1. Concentrations of some PCDD/PCDF congeners in sediment profiles (pg g^{-1}, dw) and I-TEQ of PCDD/PCDFs (pg I-TEQ g^{-1}, dw) (S=surface, M=maximum, D= deep sediment).

Site	Sedim. disk	**1234678-HpCDF**	**12378-PeCDD**	**23478-PeCDF**	**2378-TCDD**	**2378-TCDF**	**OCDF**	**OCDD**	**toxic sum**	**I-TEQ**
K15	S	7 570	9.94	9.40	1.41	12.16	6 450	155	14 529	116
	M	28 500	53.95	27.27	3.61	18.66	23 100	699	53 958	473
	D	763	1.17	4.34	0.28	3.36	2 040	17	2 870	16.1
AKL	S	17 095	7.31	7.44	1.74	13.16	17 492	394	35487	242
	M	23 265	5.29	6.99	1.17	5.11	32 979	253	56965	311
	D	103	0.00	0.00	2.45	0.74	30	47	210	6.3
LL3a	S	733	3.47	10.95	0.36	7.85	778	102	1740	22.8
	M	2 660	9.14	17.72	0.61	13.07	2 470	134	5540	61.2
	D	442	1.41	6.32	0.19	4.91	430	24	959	12.9
JML1b	S	105	1.52	7.10	0.49	6.44	95	92	365	9.7
	M	274	5.01	16.25	0.79	13.20	231	149	824	23.5
	D	8	0.90	1.38	0.23	1.75	19	13	57	2.4
SR5	S	38	1.79	6.59	0.47	6.01	59	73	237	8.4
	M	51	2.58	9.76	0.67	8.21	88	94	329	12.2
	D	2	0.15	0.61	0.22	0.46	5	4	17.5	1.0
P18	S	98	3.47	16.40	1.00	13.10	73	273	656	22.2
	M	106	5.23	19.90	0.55	15.70	190	273	876	27.9
	D	3	0.19	0.86	0.06	0.78	9	12	38	1.3

The surface, maximum and "deep" sediment still exhibit high concentration of 1,2,3,4,6,7,8-HpCDF and OCDF up to LL3a indicating a wide dispersion of Ky-5 in the Gulf of Finland . The profiles of sites K15 and AKL having contaminated by Ky-5 differ clearly from the profiles of other sites. The effect of Ky-5 is also seen in the middle of the Gulf of Finland at LL3a and probably also at site JML1b (Table1, Fig. 3).

The congeners most abundant in fish (2,3,4,7,8-PeCDF, TCDF) do not differ either in surface or at maximum in the Gulf of Finland compared to other profiles (Table 1). Interestingly, the lowest concentrations for both of these congeners were found in the middle of the Bothnian Sea (SR5), i.e. within the area of highest concentrations in Baltic Herring of certain weight or age. At all sites far from point sources or coasts (JML1b, SR5 and P18) 2,3,4,7,8-PeCDF is the congener with the highest percentage from the total toxicity (28-40 % from I-TEQ) at all depths.

Although OCDF and OCDD form the majority of total dioxins in open sea sites they do not contribute much to the overall toxicity. The five other selected congeners (2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD and 1,2,3,4,6,7,8-HpCDF) account for more than 50 % of the total toxicity in all cases (Fig 3.)

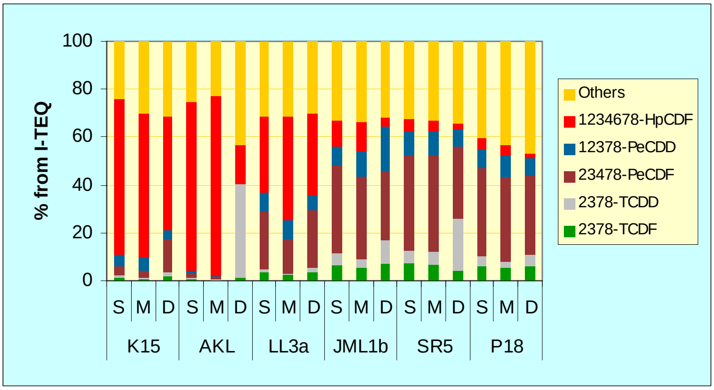

Figure 3. Congener patterns at different sediment profiles. (See table 1 and figure 2 for explanations)

Conclusions

The survey confirms the importance of Kymijoki-derived and highly chlorinated PCDF-congeners to the total toxicity in sediments in the Gulf of Finland. The findings do not support that any of the known point source would significantly influence to those congeners that are most abundant in fish. Instead, regional distribution indicates that atmospheric deposition may act as a major source for those congeners and especially for 2,3,4,7,8-PeCDF.

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