TRENDS OF PCDD/FS IN COASTAL AND OFFSHORE BALTIC SEA SEDIMENT CORES COVERING THE 20th CENTURY

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Introduction

The Baltic Sea is heavily polluted by polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), and consequently the concentrations of these toxic compounds in Baltic biota frequently exceed the European Union maximum tolerable limit for food and feed[1,2,3]. Increased emissions of PCDD/Fs from industrial and other sources were observed in the 1970's[4]. Accordingly, Kjeller and Rappe reported on the trends of dioxins in a sediment core from the central subbasin, for the years 1882 through 1985[5]. According to this study, the peak concentration was observed in the layer that corresponds to late 1970's (total PCDD/Fs =1800 pg/g). Since then, the levels gradually decreased, and by 1985, the concentrations were reduced by 19%. However, no extensive study has been conducted on the deep sediment layers to better understand the trend of the levels in the sediments over time. In this study, the historical records of dioxins from a large number of costal and offshore sites throughout the Baltic Sea are reported.

Materials and Methods

Nine sediment cores were sampled from accumulation bottoms near the coast (Figure 1 A-H): Seskarö Bay, Gussö Bay, Kallholm Bay, Nordmaling Bay, Nätra Bay, Svartvik Bay, Sandarne Bay, and two in Lövsta Bay, using a Gemini corer (a twin-barrel Niemistö Corer). Similarly, six sediment cores were sampled from offshore sites (Figure 1 J-O): Northern Bothnian Bay, Northern Bothnian Sea, Southern Bothnian Sea, Baltic Proper, Arkona Basin and Northern Bornholm Basin. The coastal and offshore cores were sliced in 2 cm and 3 cm disks respectively. The dating of the disks were made using ^{137}Cs and ^{210}Pb radioactivity measurements and by studying the laminated structure of cores sampled in anoxic areas. Sample preparations were made using Soxhlet extraction followed by clean-up using multilayer silica and activated carbon columns based on the method reported by Sundqvist et al. 2009[2]. PCDD/Fs were chromatographically separated using a DB-5 column and measured by GC-HRMS. The levels reported here are the sums of all *tetra*-*octa*-CDD/Fs.

Figure 1. The nine coastal and six offshore sampling sites in the Baltic Sea.

Results and Discussions

In all of the sediment cores, peak levels and subsequent reductions in recent layers were observed, although the extent of reductions for the various sites differed (Figure 2, Table 1). Three of the coastal cores showed exceptionally high peak concentrations (G, H1, H2; Table 1). This area, the northern Baltic coast of Sweden, is known to have a long record of cellulose related industrial activities, which has been associated with emissions of PCDD/Fs. Significant reductions from peak levels were observed for all sites, although the decline for Gussö Bay was less pronounced. This site was chosen as a reference site because of the lack of known point sources in the area.

Levels of PCDD/Fs in five of the six offshore sediment cores were reported earlier together with suggestions of possible sources and estimations of their contributions[6]. The peak concentrations in the off-shore cores were found to occur on average 12 years later than those of the coastal sites (Figure 3, Table 2). Further, the reduction from peak levels was generally smaller than in the coastal cores. It was also observed that in regions where the coastal sites had extremely high peak levels, the offshore sites had higher peak levels than the other offshore sediment cores studied. These observations clearly indicate that coastal emissions of hydrophobic pollutants eventually will impact large areas including offshore regions by slow post-depositional lateral transport of sediments.

Table 1 Peak concentrations (sum *tetra*-*octa*-CDD/F) and percentage of reduction from peak to lowest concentration in the nine coastal sediment cores.

Site		Peak concentration		Lowest concentration		% reduction	Figure
		year/depth	Conc. (pg/g dw)	year/depth	Conc. (pg/g dw)		
A	Seskarö Bay*	1965-1968	3 900	2008-2010	200	94	2A
B	Gussö Bay*	1990-1994	630	2006-2010	430	31	2B
C	Kallholm Bay*	1982-1986	5 000	2006-2010	1 200	77	2C
D	Nordmaling Bay	1980-1984	1 400	2006-2010	580	57	2D
E	Nätra Bay	1975-1978	1 700	2007-2010	420	75	2E
F	Svartvik Bay	1969-1972	1 700	2000-2004	180	89	2F
G	Sandarne Bay	1966-1969	14 000	2007-2010	1 700	88	2G
H1	Lövsta Bay 1**	38-40 cm	47 000	0-2 cm	7 400	84	2H1
H2	Lövsta Bay 2**	38-40 cm	17 000	4-6 cm	2 400	86	2H2

*The dating of these sediment cores is uncertain and is based on observations of laminated sediment layers resulting in estimates of average sedimentation rates **No dating available

Table 2 Peak concentrations (sum *tetra*-*octa*-CDD/Fs) and percentage of reduction from peak to lowest concentration in the six offshore sediment cores.

Site		Peak concentration		Lowest concentration		% reduction	Figure
		years/depth	Conc. (pg/g dw)	years/depth	Conc. (pg/g dw)		
J	Northern Bothnian Bay	1992-1996	1 100	2005-2008	530	52	3J
K	Northern Bothnian Sea	1984-1986	860	2005-2007	450	47	3K
L	Southern Bothnian Sea	1992-1995	590	2007-2008	430	27	3L
M	Baltic Proper	1985-1987	2 700	2001-2003	1 700	36	3M
N	Arkona Basin	1982-1987	1 200	2002-2004	890	24	3N
O	N. Bornholm Basin	3-6 cm	1 900	0-3 cm	1 100	39	3O

In the coastal sediment cores, the levels of PCDD/Fs (total *tetra*- through *octa*-substituted congeners) increased significantly during early 1970's in most of the cores (Table 1). Since then, the levels were reduced with on average 75% (range 31-94%), which is attributed to the emission reduction efforts that was made at regional as well as international levels since early 1970's (e.g. the ban of chlorophenol use and reduced air emission levels). Recent coastal sediment layers in the northern Baltic Sea generally have lower concentrations of PCDD/Fs than at the southern sites. However, since the sites were selected only to represent different sources, no major conclusion can be drawn from this observation.

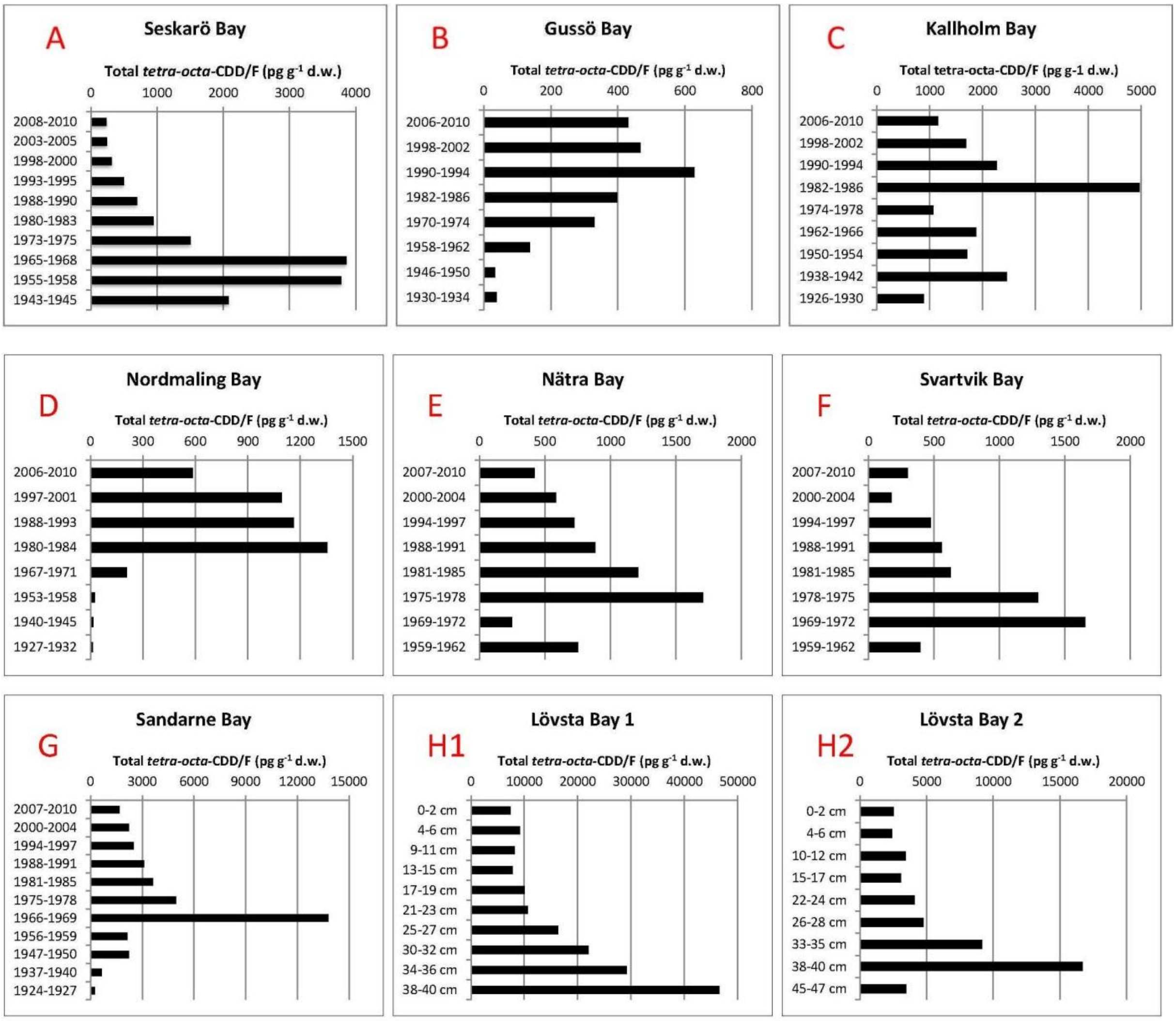

Figure 2. Trends of PCDD/Fs (sum *tetra*-*octa*-CDD/F) in coastal sediment cores of the Baltic Sea.

At the offshore sites, levels were reduced from peak levels with on average 37% from peak levels (range 24-52%). The levels of PCDD/Fs in recent layers of the offshore sites were found to be similar to the levels in recent layers of the coastal sites in far northern part of Baltic Sea. The magnitude of the general decrease from the 1990's agrees fairly well with modeled values for the atmospheric deposition of PCDD/Fs into the Baltic Sea, which recently was assessed to have declined by 50% from beginning of 1990's to mid of 2000's[7].

Although implemented emission reduction efforts have significantly reduced the levels of PCDD/Fs and other POPs in the Baltic Sea, a continuation of the existing and additional efforts are required in order to effectively reduce the levels of PCDD/Fs and also dioxin-like compounds in the Baltic Sea. The BalticPOPs research program, which aims to examine the underlying causes for the high and stable levels of PCDD/Fs in Baltic fish, will eventually suggest management strategies that will help Europe to take a further step towards the specific targets of EUSBSR PA3 (European strategy for the Baltic Sea Region – Hazardous compounds), viz. concentrations of hazardous substances close to natural levels and all fish safe to eat.

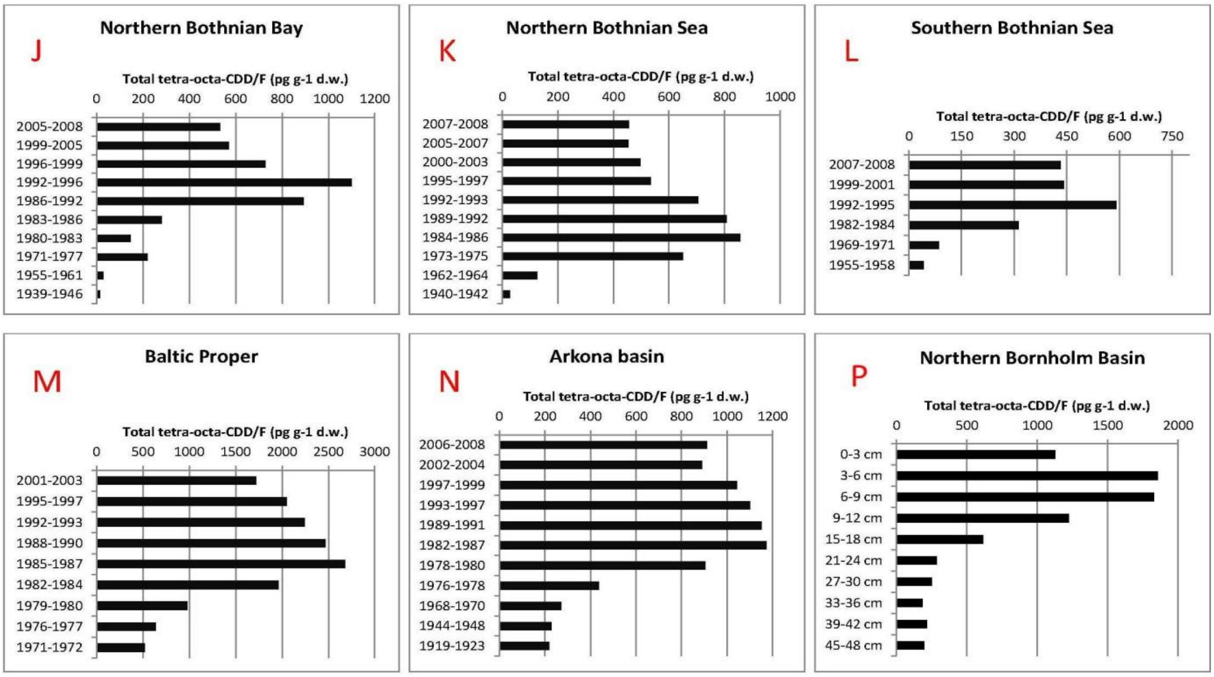

Figure 3. Trends of PCDD/Fs (sum *tetra-octa*-CDD/F) in offshore sediment cores of the Baltic Sea.

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