CONCENTRATIONS AND CONGENER PATTERNS OF PCDD/FS IN SURFACE SEDIMENT, SETTLING PARTICULATE MATTER, WATER AND FISH FROM THE SOUTH BOTHNIAN SEA, SWEDEN

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Abstract

This study focused on PCDD/F contamination along the Swedish coast of the southern Bothnian Sea, a heavily polluted area of the Baltic Sea. Data from earlier studies of surface sediment, perch, viviparous blenny and herring were analyzed together with new data for settling particulate matter (SPM) and sea water. PCDD/F pollution in surface sediment and SPM in the southern Bothnian Sea were similar both in respect to pattern and levels. The highest levels were 170 000 and 33 000 pg/g TOC in sediment and SPM respectively, and the congener pattern was dominated by OCDD, OCDF and 1,2,3,4,6,7,8-HpCDF. The dissolved concentrations in water were estimated by analysis of passive samplers of low density polyethylene (LDPE) type. The water pollution pattern was extremely different and showed complete domination of 2,3,7,8-TCDF. The fish showed species specific differences in the fractions of the two dominating congeners, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF. All species did, however, show an increase in the fraction 2,3,4,7,8-PeCDF as compared to the pattern in passive water samplers.

Introduction

In the southern Bothnian Sea, both sediment and fish show elevated levels of PCDD/Fs as compared to other areas along the Swedish coast of the Baltic Sea[1,2,3]. This is an area with high abundance of industries connected to the cellulose industry. In the present study, PCDD/F levels of settling particulate matter (SPM) and passive water samplers (low density polyethylene; LDPE) were analyzed together with results of surface sediment, perch, viviparous blenny and herring from earlier studies[1,2,3]. Samples were collected along transects from the industries and at a reference station. All matrices were, however, not sampled at all locations. The aim was to get an overview of the pollution situation in different matrices in the southern Bothnian Sea both concerning levels and pollution patterns. Furthermore, it was of interest to understand the flow paths of PCDD/Fs from sources via the water and aquatic biota to human exposure.

Materials and Methods

Sampling. Surface sediments (top 2 cm) were sampled using a core-sampler (Gemini type). Prior to subsampling, the cores were visually inspected. Perch (*Perca fluviatilis*) and Viviparous blenny (*Zoarces viviparous*) were collected by local fishermen in autumn 2004[2]. Skin and bone were removed and the muscle tissue was kept frozen until analysis. Baltic herring (*Clupea harengus membras*) was collected during the period May-July 2004[1]. Each herring sample, consisted of 15 individuals. LDPE and samplers for SPM were deployed for approximately 6 months. The number of samples (*n*) included for each matrix are listed in Table 1.

Extraction and clean-up. Sediments and SPM were air dried prior to extraction. The extraction and clean-up has been described previously[3]. Fish samples were homogenized together with sodium sulphate and extracted at room temperature with acetone:hexane followed by diethyl ether:*n*-hexane. LDPEs were gently shaken in 100 ml *n*-hexane for 3 days. ^{13}C-labelled internal standards (all 2,3,7,8-chlorine substituted congeners) were added prior to extraction. The clean-up for fish samples has been described in detail by Danielsson *et al.*[4]. The fractionation column and the miniaturized multilayer silica column described for sediment were used also for LDPE. Tetradecane was added as a keeper and ^{13}C-labelled recovery standards were added prior to instrument analysis.

Instrumental analysis. The instrumental analysis was carried out by gas chromatography-high resolution mass spectrometry (GC-HRMS). A 60 m DB5 capillary column (J & W Scientific, Agilent Technologies, USA; i.d. 0.25 mm; film thickness 0.25 µm) or a 60-m DB5MS capillary column (J & W Scientific, Agilent Technologies, USA; i.d. 0.32 mm; film thickness 0.25 µm) was used. Samples were splitless injected and helium at a constant flow was used as carrier gas. The MS was operated in EI+ selected ion monitoring mode at an electron energy of 36 eV and a resolution of 10 000.

Identification of PCDD/F was performed based on retention times and isotope ratio of the two most intense ions. Losses during sample preparation were adjusted for according to the isotope dilution method. Only the results of 2,3,7,8-substituted congeners were investigated in the present study. The following congeners may co-elute with other PCDD/Fs in deposition, water, SPM and sediment samples: 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF. Reported data for these are therefore maximum values. Two hexachlorinated dioxins (1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD) were not satisfactorily separated and were therefore reported as sum levels of both congeners (Figure 2).

Results and Discussion

Concentrations in the different matrices are presented in Table 1. Sediment samples showed levels from 550 pg/g TOC at the reference station to 170 000 pg/g TOC at the most polluted location. SPM were sampled rather close to industries and no marine reference station was included. In sediment and SPM, the concentrations decreased with distance from the industries (Figure 1). The pollution was also dependent on the water flow directions as can be seen in the left picture, where the sediment sample taken in most close proximity to the industry is shielded by an island and therefore showed a substantially lower concentration than the sample north of the industry. The highest concentration in SPM (33 000 pg/g TOC) was found in close proximity to one of the pulp industries. Ten LDPE samples were included in the study and showed concentrations from 7.0 and 18 pg/g sampler. For this type of water samplers, sampler-water partitioning constants (K_{MW}) for PCDD/Fs are not yet available. However, recently partitioning constants for 14 PAHs were determined (Cornelissen *et al* unpublished). Concentrations of PCDD/F in water were estimated through extrapolation of the K_{MW} using log K_{OW} of the PAHs and PCDD/Fs (Table 1). The concentrations are also given per gram sampler. Perch and viviparous blenny, which are rather lean fish (0.7% and 1.2% fat), showed concentrations approximately 10 times lower than the fattier herring (4.3% fat). In Table 1, concentrations are expressed on lipid weight basis which cancel out the variation in bioaccumulation which is due to variation in lipid content.

Table 1. Number of samples and measured concentrations of 2,3,7,8-substituted PCDD/Fs in sediment, settling particulate matter, water (LDPE), perch, viviparous blenny and herring.

	Sediment	**SPM**	**Water (LDPE)**	**Perch**	**Viviparous blenny**	**Herring**
	pg/g TOC (d.w.)	pg/g TOC (d.w.)	fg/L[a] (pg/g sampler)	pg/g l.w. (w.w.)	pg/g l.w. (w.w.)	pg/g l.w. (w.w.)
n	18	10	10	15 (individuals)	13 (individuals)	10 (pooled samples)
Sum 2378-PCDD/F	550 – 170 000 (18-23 000)	6 700 – 33 000 (380-3 500)	2.1-4.1[a] (7.0 – 18)	51 – 630 (0.38-3.7)	78-260 (0.80-3.1)	190 – 460 (11-20)

[a] Semiquantified using experimental K_{MW} data for 14 PAHs (Cornelisson *et al* unpublished data)

The pollution pattern of 2,3,7,8-substituted PCDD/Fs in sediment and SPM was dominated by three congeners: 1,2,3,4,6,7,8-HpCDF, OCDF and OCDD (Figure 2). In fish, on the other hand, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF were the most abundant congeners. In perch and viviparous blenny, the fraction 2,3,7,8-TCDF in relation to total concentration was generally higher than the fraction of 2,3,4,7,8-PeCDF and in herring a clear dominance of 2,3,4,7,8-PeCDF was observed. In LDPE, 2,3,7,8-TCDF constituted over thirty percent of the total PCDD/F levels and the distribution between the other congeners were fairly even. The estimated water concentrations showed a pattern even more dominated by 2,3,7,8-TCDF (Figure 2).

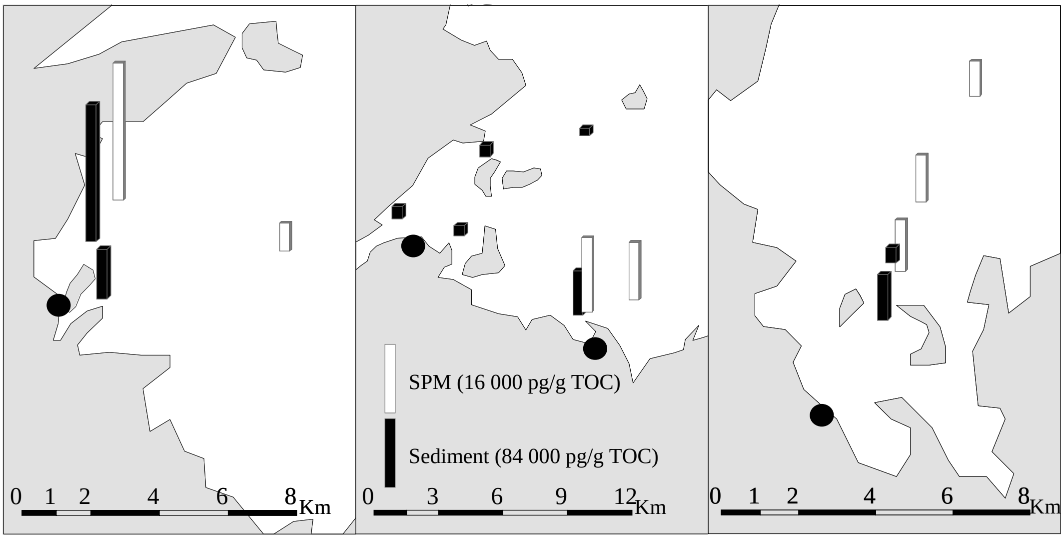

Figure 1. Sum PCDD/F in sediment and SPM in connection to four industries (indicated with black dots).

The relationship between 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF has previously been discussed for herring[1]. The herring samples presented here are part of another study where a negative correlation (r^2=0.75, p<0.001) was found between the fractions of these two congeners (expressed as fraction of the total concentration). The reason for this correlation is not known, but was suggested to be the result of different source contributions and/or different biological half-lives of the congeners. There are indications that 2,3,4,7,8-PeCDF is more recalcitrant than most other 2,3,7,8-substituted PCDD/Fs[5]. A significant correlation was also found between the ratio of 2,3,4,7,8-PeCDF/2,3,7,8-TCDF and the TEQ-levels for herring (r^2=0.43, p<0.001). Also for perch samples, a significant and negative correlation was found between the fractions of 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF (r^2=0.28, p<0.05). However, no correlation with the TEQ was observed. No significant correlations were found for viviparous blenny. In sediment a positive correlation is indicated between the fraction 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF. Sampled fish species in the current study were of approximately the same age. Thus, the pattern differences indicate species specific feed, metabolic capacity or metabolic selectivity. Finally, all species showed accumulation of 2,3,4,7,8-PeCDF as compared to the LDPE (Figure 2), which supports the hypothesis of pattern shift as a result of biotransformation, whether it be in the fish or the feed.

Passive water samplers, like LDPE, sample the dissolved fraction of PCDD/Fs, which explain the large shift in the pattern in LDPE on one hand and in sediment and SPM on the other hand. In fact, the pollution pattern of PCDDs in sediment and SPM showed similarities with the pattern in LDPE, but with a clear shift towards the highly chlorinated, less water soluble, congeners. The same trend was seen for PCDFs. However, the results must be interpreted with caution since the patterns in different matrices vary between location, primarily for sediment and SPM. For comparison with a background level sediment, the pollution pattern in an offshore sample (app. 100km from shore; 6 800 pg/g TOC; 220 pg/g d.w.) from the southern Bothnian Sea is also shown in Figure 2. The offshore sediment showed clear similarities to the average pattern in coastal sediments. Average pollution patterns in wet and dry deposition as well as atmospheric pattern from the Swedish west was also included[6]. In both atmospheric samples and deposition, a clear dominance of OCDD was observed. The difference in pollution pattern between atmosphere/deposition and SPM/sediment indicates that the southern Bothnian Sea is not only receiving airborne PCDD/F but also inputs from local pollution sources. The elevated concentrations in sediment observed in connection with potential point sources do, however, decrease rapidly with distance.

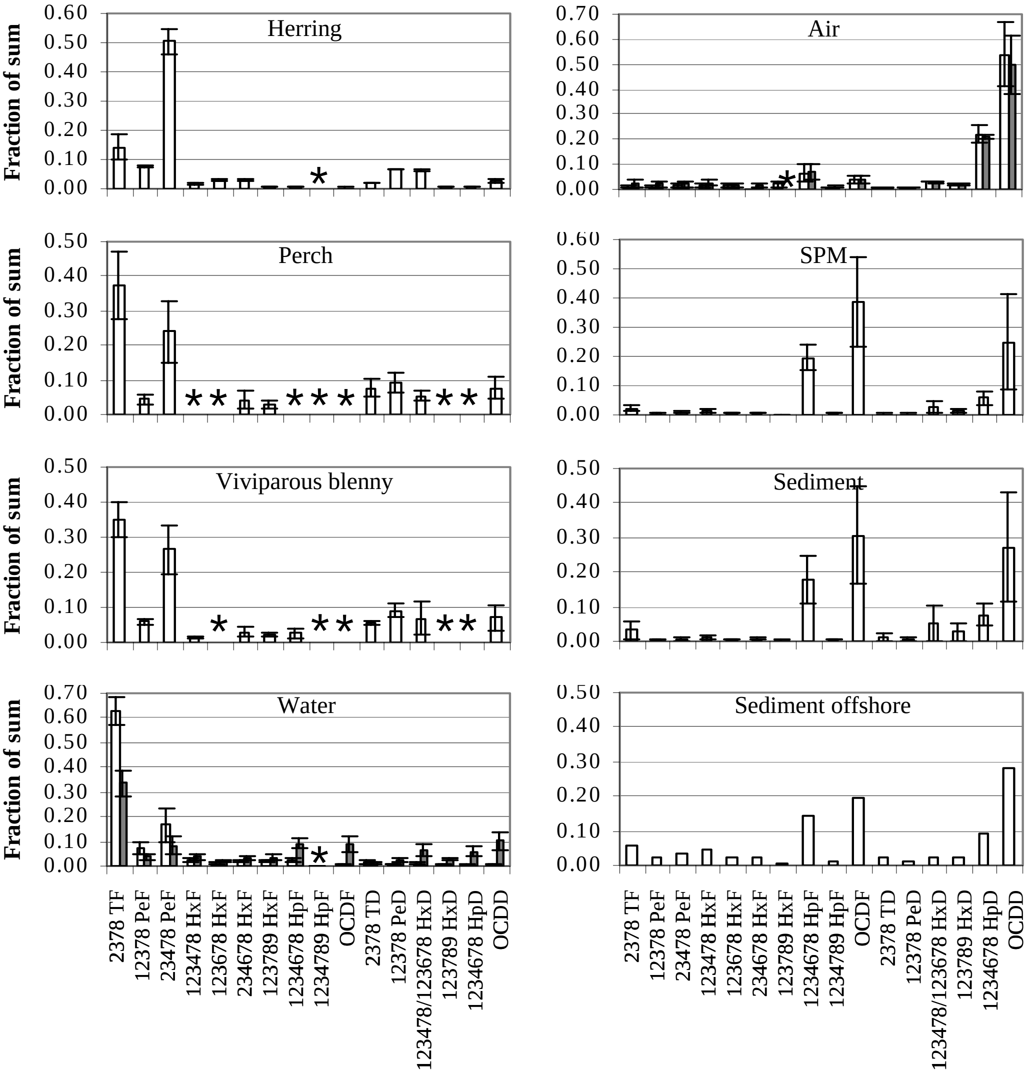

Figure 2. PCDD/F patterns (one stdev) in different matrices in the Bothnian Sea: herring, viviparous blenny, perch, water (white bars: estimated water profile; grey bars: profile in LDPE), SPM and sediment and air (white bars: wet and dry deposition; grey bars: atmospheric pattern) from the Swedish west coast[6]. Asterisks indicate that more than half of the observations were below detection limit (values were set to zero).

Acknowledgements

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