SPATIAL DISTRIBUTION AND PROFILES OF DIOXINS IN SURFACE SEDIMENT FROM THE BALTIC SEA

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Introduction

Many persistent organic pollutants exhibit declining trends in the Baltic Sea environment[1]. For polychlorinated-*p*-dioxins (PCDDs) and polychlorinated-dibenzofurans (PCDFs), the situation is different. Samples of guillemot eggs and herring analyzed within the National Swedish Monitoring Program have shown constant levels since the 1980s. Fat fish from the Baltic Sea often exceeds the limit of maximum PCDD/F residues established by EU, and at present, Sweden and Finland are only allowed to sell on the domestic market until 2011[2,3]. Thus, there must be significant sources of PCDD/Fs, which contribute to the elevated levels in the Baltic Sea and it is of great importance to investigate the origin of the contaminants.

Combustion processes and pulp and paper industry were in focus during the 1980s, and strong measures were taken to reduce their emissions. Other potential sources received less attention. These include leakage from contaminated soils and sediments, accumulation by river transport, drainages from big cities and air deposition. Recently, Environmental Chemistry at Umeå University compiled a PCDD/F source inventory on behalf of the Swedish EPA[4]. In the survey, so-called "hot

Figure 1. Sediment sampling locations in the Baltic Sea and sum PCDD/F concentrations (each bar unit equal 5 ng/g d.w.). The highest value has been decreased 4 times for clarity (TISS, Thematic Images and Spatial Statistics).

spots" were identified. Many of these are located along the Baltic coast. Once a pollution source has been identified, it is vital to get an understanding of the local distribution around the source as well as to determine the characteristic fingerprint of the source in order to investigate the importance of the source as a contributor to the total PCDD/F load of the Baltic Sea. It has been shown that congener-specific information is far more effective for source identification than conventional information, which usually is given for 2,3,7,8-substituted congeners only and the sum of congeners in the homologue groups[5]. Background contamination in off-shore sediments generally show low concentration variability, while sediments close to shore are more heterogeneous and demands a finer sampling grid[6].
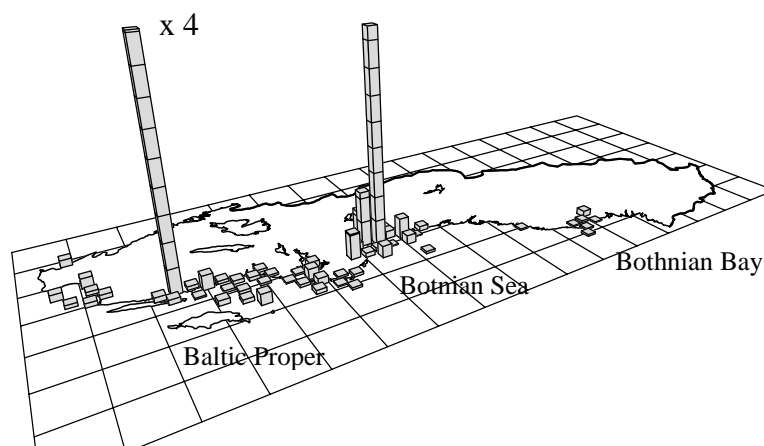
The aim of the present study was to determine concentrations and comprehensive congener patterns of PCDD/Fs in surface sediment in order to understand the distribution of recent PCDD/F pollution in the Baltic Sea. All sediments in this study were taken in the Baltic Sea and efforts were made to sample near potential sources as well as offshore.

Materials and Methods

Sampling locations and sampling techniques. A total of 60 surface sediment samples and one sediment trap sample were taken along the Swedish coast in the Baltic Sea (Figure 1). Most of the samples were sampled aboard the ship S/V Ocean Surveyor (Geological Survey of Sweden, SGU). Accumulation bottoms were located using hydro-acoustic methods and the sediments were inspected with a video camera prior to sampling to ensure undisturbed sediment. The remaining samples were sampled from R/V Lotty (Umeå Marine Sciences Center, UMSC). The sediments were all sampled using a Gemini corer or box-core and before subsampling, they were

visually inspected. Each subsample consisted of the upper 1-2 cm of the sediment. All samples were frozen directly after sampling and kept in a freezer until analysis. Most of the samples were taken at sites with possible or known contamination of PCDD/F.

Extraction and clean-up. The sediment samples were either freeze dried or air dried in a chemical hood prior to analysis. After drying, the samples were homogenized with a Waring commercial blender and thereafter they were put into cellulous extraction thimbles and placed in 100 ml Soxhlet-Dean-Stark. Prior to extraction, ^{13}C-labelled internal standard were added. The samples were extracted with toluene for at least 15 hours. For measurement of dry weight, subsamples of 0.5 to 4 g were dried at 130°C over night. Loss of ignition (%) was determined by heating the subsamples to 550°C for 4 hours and used as a measure of the organic carbon content of the sediments. Prior to clean up, tetradecane (40-50 μl) was added as a keeper and the toluene was evaporated.

The clean up and fractionation procedure included four column sets and one step to remove interfering sulphur from the extracts. The first column (i.d.=1.6 cm, L=30 cm) was packed (from the bottom) with glass wool, 3g KOH-silica, 3g neutral silica, 6g 40% (w.w.) H_2SO_4-silica and 3g Na_2SO_4. The column was rinsed with two times the adsorbent volume using *n*-hexane and eluted with 60 ml *n*-hexane. After evaporation, activated copper was added to the samples until the reaction with sulphur ceased. The second column was identical to the first. The fractionation was performed on the third column, which consisted of a mixture of AX21 carbon (7.9%) and Celite. This column was described in detail by Danielsson *et al.*[7]. The column was eluted with 40 ml dichloromethane:*n*-hexane and 40 ml toluene. Fraction 1 contained the mono-*ortho* and poly-*ortho* PCBs and fraction 2 the non-*ortho* PCBs and the PCDD/Fs. Tetradecane (40μl) was added to fraction 2 and the samples were evaporated. The last clean up step was a miniaturized multilayer silica column[7]. Prior to instrument analysis, ^{13}C-labelled recovery standards were added.

Instrumental analysis. A comprehensive congener specific analysis was performed and concentrations for a total of 74 congeners (11 TCDD, 11 PCDD, 6 HxCDD, 2 HpCDD, OCDD, 15 TCDF, 12 PeCDF, 11 HxCDF, 4 HpCDF, OCDF) were determined among which some co-eluted. 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; filmthickness 0.25 μm) was connected to a double focusing magnet sector mass spectrometer (Waters, Autospec), which operated in EI+ selected ion monitoring mode. Samples were splitless injected (3 μL, split opened after 2 min) at an injector temperature of 280°C. The temperature program for the oven was 190°C for 2 min, 3°C min^{-1} to 292°C, hold for 5 min, 10 °C min^{-1} to 325 °C. Other instrumental conditions were as follows: helium carrier gas at a constant flow of 1.2 mL/min; transfer line temperature 275 °C; ion source temperature 250°C; resolution 10 000; electron energy 36eV.

For each compound, the two most intense ions in the molecular ion cluster were recorded. Identification was performed based on retention times and isotope ratio of the monitored ions. The sum of the peak areas of the monitored ions was used for quantification and losses during sample preparation were adjusted for according to the isotope dilution method. A quality assurance (QA) sample was analysed together with every 30 samples and the result was compared to levels obtained from analyses conducted during several years.

Results and Discussion
The median concentration (95th percentile) of sum-PCDD/F was 0.78 (6.1) ng/g d.w. (5.8 (41) ng/g org C). The range of concentrations is rather large (0.041-180 ng/g d.w.) and the highest values were found at two hot-spots located in the Bothnian Sea and Baltic Proper, respectively (Figure 1). One of the hot-spots was located outside a pulp and paper industry and the other in connection with a ceased copper industry. Other locations with elevated concentrations were pulp and paper industries, Stockholm city, a chipboard industry and a metal industry. As expected the lowest concentration was found at a reference point far from potential sources. The elevated PCDD/F concentrations near the pulp and paper industries are in accordance with the study by Olsson *et al.*[8] who measured PCDD/Fs and other POPs in perch and viviparian blenny at the same coordinates as in the present study. Olsson *et al.*[8] identified a local impact from PCDD/Fs outside the studied pulp industries and the chipboard industry, all located in the southern Bothnian Sea. In a study by Bignert *et al.*[9] significantly higher levels in herring from the southern part of the Bothnian Sea as compared to the northern part were found, also suggesting that this area require further attention.

A Principal Component Analysis (PCA) was preformed on comprehensive congener specific data normalised to sum-PCDD/F (individual congener concentration divided by sum-PCDD/F). This kind of normalisation eliminates differences in concentration levels and other sample specific properties like organic matter content,
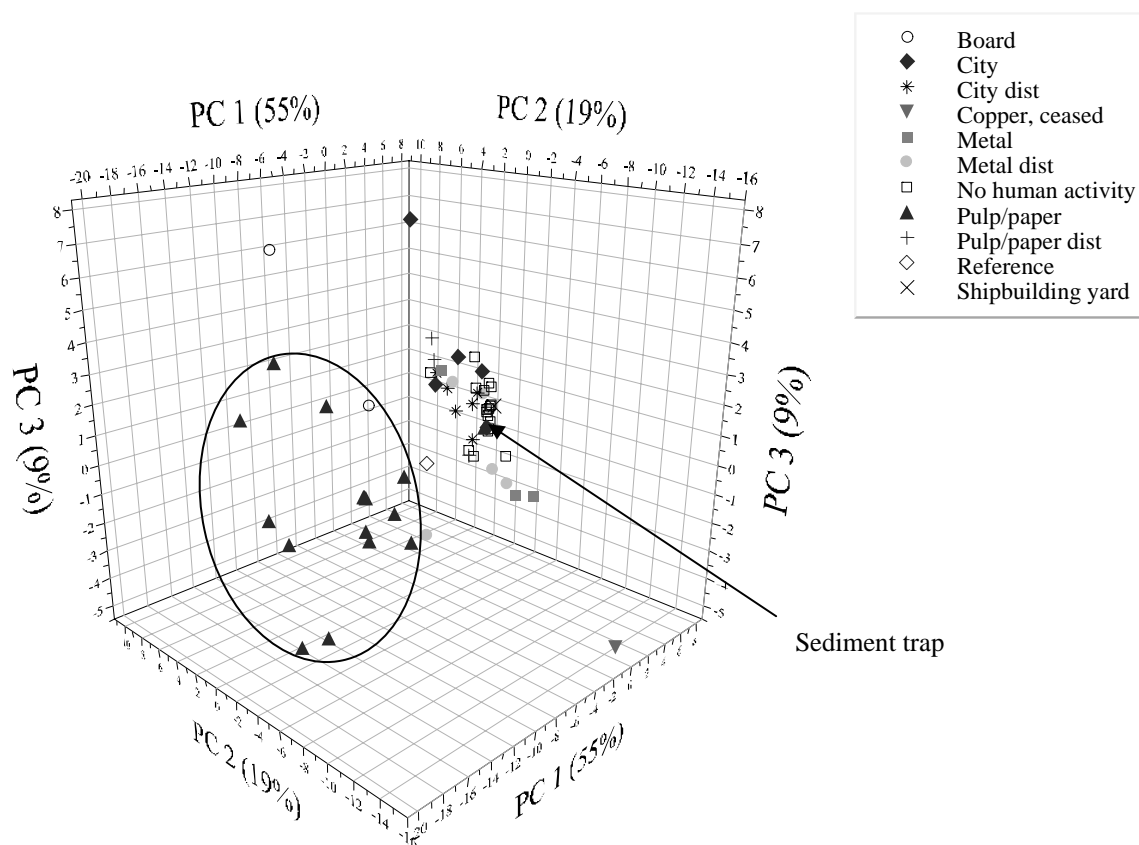
Figure 2. Three-dimensional PCA score plot showing the profile similarities between the sediment samples. The samples are marked according to human activities in the area (see legend). Samples taken close to pulp and paper industries are surrounded with an ellipse.

thus focusing exclusively on the differences in pollution pattern. The first three principal components (PCs) explained 83% of the variance in the data. The samples taken near pulp and paper industries form a group (marked with an ellipse) indicating that the pollution fingerprint from these locations are similar and differs from other samples (Figure 2). However, looking at homolog profiles, two different patterns for pulp and paper industries were found (Figure 3). One is dominated by penta- and hexa-CDD, while the other is clearly dominated by hepta- and octa-CDF. The chipboard industry showed similarities to pulp and paper industries when looking at the congener pattern but is separated due to the domination by octa-CDD. Samples taken further from pulp and paper industries (pulp/paper dist) did not exhibit the same fingerprint as samples taken closer to the industries. Sediment samples taken outside one specific metal industry formed another group in the PCA, whereas sediment from other metal industries showed a somewhat different fingerprint. The ceased copper industry, which showed high levels of PCDD/F, also showed a specific fingerprint dominated by highly chlorinated furans, and it was therefore clearly separated from the other sampling sites in the PCA-plot. Sediments taken in connection with large cities could not be separated from the samples taken in areas without any specific human activities and the homolog profiles were dominated by octa-CDD. The sediment trap probably represents atmospheric deposition and it can be assumed that objects near this data point in the PCA-plot are insignificantly affected by local pollution sources (Figure 2).

In a survey on previously existing sediment data, Verta *et al.*[10] concluded that the major source of toxic PCDD/Fs in herring and salmon in the Baltic Sea is probably atmospheric deposition. The next step of the present study is to apply a multivariate statistic tool (receptor modelling) which has been developed to apportion sources using pollution patterns.

The conclusions drawn from our study are that highly contaminated sediments can be found close to point sources along the Swedish coast in the Baltic Sea and that different activities have produced different pollution patterns of PCDD/F, which is in accordance with earlier studies in the Baltic Sea[11]. It is, however not possible to

conclude whether the concentrations and profiles found derive from recent emissions or if it is leakage from previous contaminations in the sediment brought to the surface via bioturbation and redistribution of sediments.
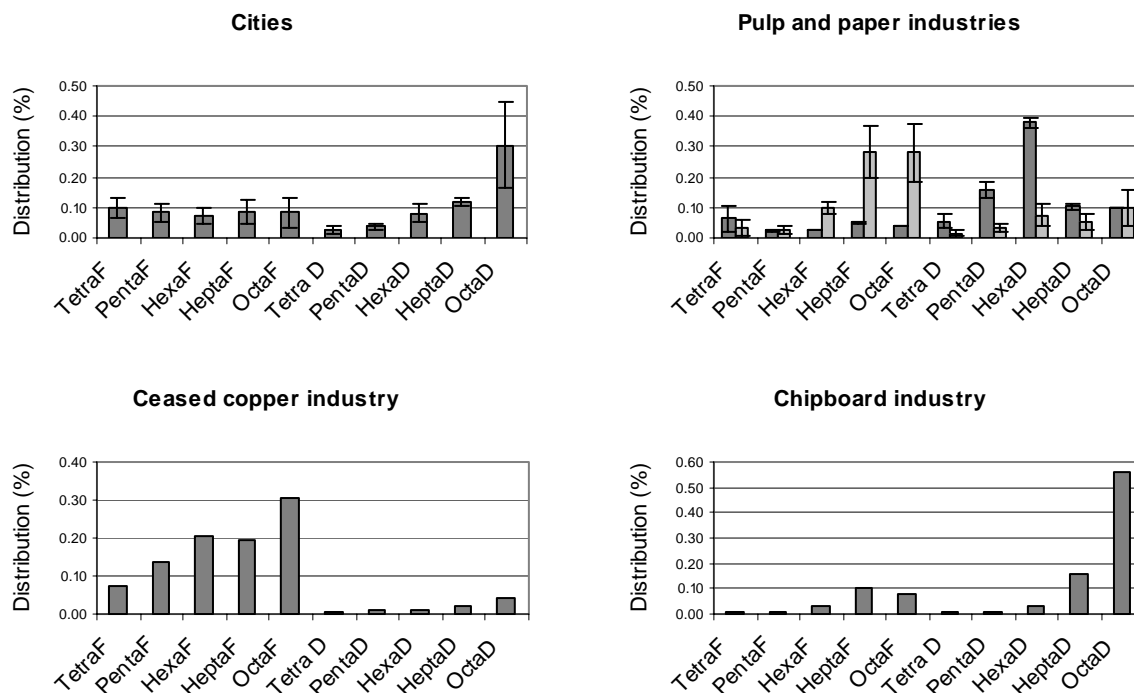
Figure 3. Homolog profiles of PCDD/Fs for the sediment samples taken near large cities (n=5), a ceased copper industry, a chipboard industry and two different profiles seen close to pulp and paper industries (n_1=2, n_2=3). Error bars represent one standard deviation.

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