RECEPTOR MODELING OF PCDD/FS IN SEDIMENT OF THE SUNDSVALL BAY, SWEDEN

Sundqvist KL[1], Tysklind M[1], Andersson R[1], Sjöblom V[1], Cato I[2], Geladi P[3], Hopke PK[4], Wiberg K[1]

[1]Environmental and Biogeochemistry, Department of Chemistry, Umeå University, Umeå, Sweden; [2]Division of Geophysic and Marine Geology, Geological Survey of Sweden, Uppsala, Sweden; [3]Unit of Biomass Technology and Chemistry, Swedish University of Agricultural Sciences, Umeå, Sweden; [4]Department of Chemistry and Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY, USA.

Introduction

In the Sundsvall Bay area, located in the southern Bothnian Sea (a sub-basin of the Baltic Sea), industrial history have included a large variety of activities, from small sawmills to large pulp and paper mills as well as chloralkali production. Previously, several sawmills in the area used chlorophenol formulations for wood preservation, and these were contaminated by PCDD/Fs. Chloralkali production using graphite electrodes and bleaching of pulp using chlorine are manufacturing processes also known to have caused PCDD/Fs emissions. A chemical industry has been active in the area since the 1930s and an aluminum smelter was built in 1942. Aluminum production, like many high temperature processes, is known to produce PCDD/Fs.

The aim of this study was to investigate the possibility of using receptor modeling for identification and apportioning of the major sources of PCDD/Fs in the Sundsvall Bay. The Sundsvall Bay was chosen as the first study area of this modeling technique along the Swedish coast since there are several possible sources of PCDD/Fs in the area and a relatively large number of sediment samples have been analyzed. Current PCDD/F emissions have been investigated by sampling river water, industrial effluent entering the bay and, in addition, soil from two contaminated sawmill sites.

Materials and Methods

The sampling and analysis of the sediment samples were presented previously[1]. In the present study, 20 surface sediment samples were included. Water samples were collected from the major rivers in the Sundsvall area (Indalsälven, Ljungan and Selångersån, Figure 1) and from two effluents from a pulp mill. The sampling was performed with a high volume sampler (sampling volume 800-850 L) using polyurethane foam plugs (PUFs; ∅ 60 mm, length 50 mm) and filters (Millipore, 0.8-8 µm and Whatman GF/F 0.6-0.8 µm). The filter combination captures the particulate fraction and PUFs the dissolved fraction. Soil samples were collected from two contaminated sawmill sites in the area (Figure 1). Soil, PUFs and filters were extracted and analyzed in the same way as sediments.

Traditionally, only the 17 toxic PCDD/F congeners are analyzed, but it has been shown that for source identification and receptor modeling, it is better to use comprehensive congener specific data[5]. In the present study, a total of 63 chromatographic peaks corresponding to individual congeners or groups of congeners were quantified and used in the modeling. Values below the detection limit (DL) were set to DL/2 and missing data to the average concentration of the peak in other samples. Uncertainties of each data point was estimated to be DL+0.1*concentration. The uncertainty of values below the DL and for missing data were set to 5*DL/6 and 4*average concentration, respectively. Prior to modeling, both the concentration matrix and the uncertainty matrix were normalized to the total concentration of each sample. This normalization enables pollution pattern analysis and excludes the concentration variance from the modeling. All source profiles were primarily identified on a congener basis, but for clarity only homologue profiles are presented below.

The principal assumption of receptor modeling is that pollution patterns are conserved from source to receptor (in this case the sediments), and that the source patterns can be reconstructed by analyzing the receptor patterns by multivariate statistical tools. The contribution from each source type can also be quantitatively described. The technique has lately been used successfully for apportioning PCDD/F sources for polluted sediments[e.g. 2,3]. In this study, Positive Matrix Factorization (PMF) was used for modeling. PMF is a receptor model with non-negative constraints resulting in profiles that can be directly interpreted as source patterns[4]. Equation 1 describes the model and equation 2 describes Q, the weighted sum of squares of the difference between the model output and the original data, which is minimized in the calculations to obtain an optimal solution.

(1) $x_{ij} = \sum_{k=1}^{p} \mathrm{f_{ik}} \times \mathrm{g_{kj}} + \mathrm{e_{ij}}$; (2) $Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\frac{E_{ij}}{s_{ij}}\right]^2$

where x_{ij} is the concentration of the *i*th congener in the *j*th sample of the original data set, f_{ik} is the fraction of the *i*th congener in the *k*th factor, g_{kj} is the contribution of the *k*th factor on sample *j*, e_{ij} is the model residual and s_{ij} is the uncertainty of the *i*th congener in the *j*th sample in the original data set containing *m* congeners and *n* samples.

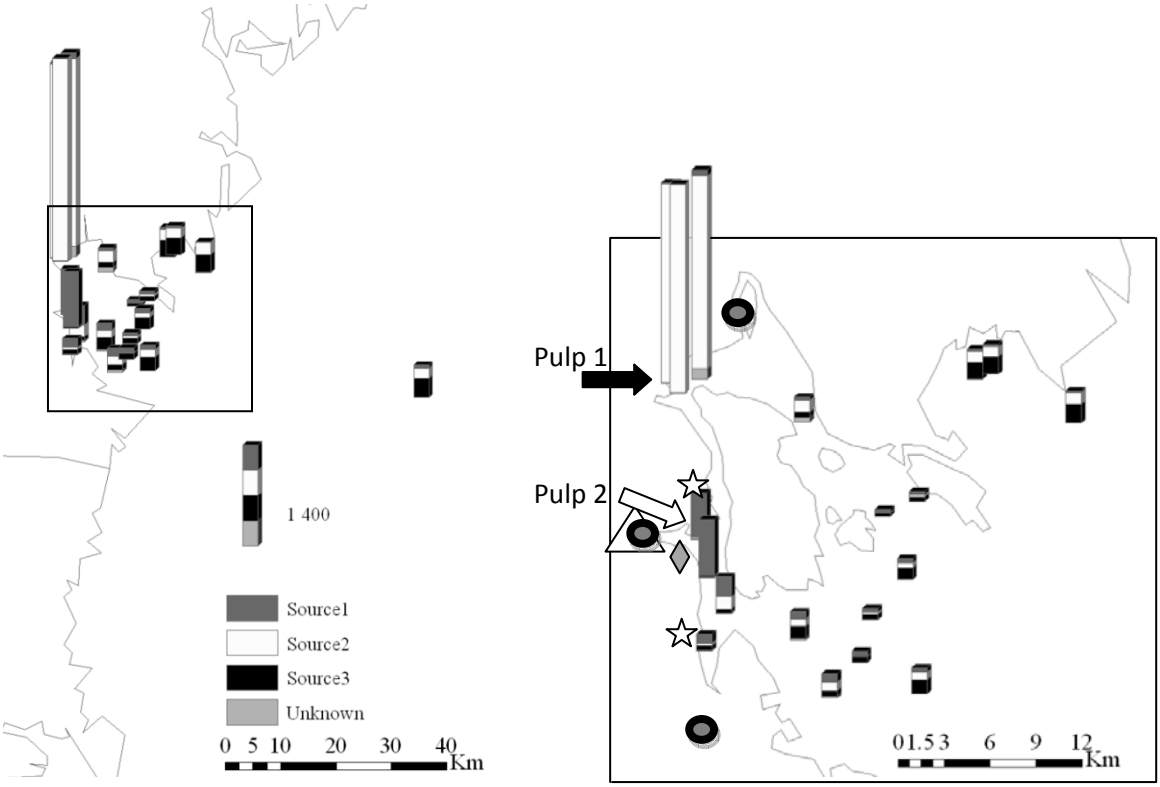

Figure 1. The sampling area and a close up on the Sundsvall Bay showing the modeled contributions of the 3 source types at each site. Water sampling locations are marked with circles, soil sampling locations are marked with stars, the city of Sundsvall with a triangle, the aluminum smelter with a diamond and the two pulp mills are indicated with arrows (filled = effluents sampled). Today, pulp mill 1 produces mostly TCF-bleached pulp and mill 2 produces only TMP (but also uses chemical pulp from pulp mill 1).

Results and Discussion

Elevated concentrations (2 700-2 900 pg/g d.w.) were observed in sediments in the vicinity of pulp mill 1 (Figure 1). Sediment concentrations in the rest of the area were generally below 500 pg/g d.w. The dissolved concentrations in rivers and the industrial effluents were in the same range (180-190 pg/L), but the particulate

associated concentrations (per unit of water) were higher in the industrial effluents (1000 and 1700 pg/L) than in the river water (170-450 pg/L). Presumably, this is due to higher content of particles in the effluents.

The results of the receptor modeling obtained by assuming 3 factors are described in Figure 2. The model showed a normal distribution of scaled residuals but with two positive outliers (boundaries set to 4< e >-4). The calculation was repeated 10 times with different starting points. The results from these calculations were almost identical, which indicates a stable and plausible model. Assumption of 4 factors resulted in no outliers among the residuals, but repeated calculations resulted in different results in the different runs. Therefore, the 3-factor model was chosen as the most realistic model for the current data.

The first source pattern (F1) was similar to the PCDD/F pattern of the particle fraction of the river water from the study area as well as snow contamination pattern from northern Sweden (homologue profiles shown in Figure 2) suggesting an air deposition origin. The second pattern (F2) was identified as the PCDD/F contamination pattern found in tetra-chlorophenol formulations and indicates that this source type is leakage from previously contaminated soil (Figure 2). The final source pattern (F3) showed high similarity to a combustion PCDD/F pattern. However, this is not as apparent on the homologue profile basis shown in Figure 2.

The source type identified as a chlorophenol pattern clearly dominates in sediments from the vicinity of pulp mill 1 indicating leakage from previously contaminated soil rather than ongoing PCDD/F emissions from the pulp and paper plant (Figure 1). The contribution from the source type resembling deposition is most important outside the city, where surface water runoff is likely to be larger than in other areas. The combustion pattern seems to be important only in samples further from the shore were the impact of local sources likely is smaller.

This paper presents the first application of receptor modeling of the PCDD/Fs content of the Baltic sediments. It showed that receptor modeling can be used to apportion PCDD/F source types and detect differences on a high spatial resolution. The results showed that the two major sources in the selected study area are contributing significantly only on a local scale. One of them seems to be leakage from chlorophenol contaminated soil, and could be eliminated or reduced by soil remediation. The third source type is probably related to a diffuse combustion or possibly to air emissions from aluminum production in the area.

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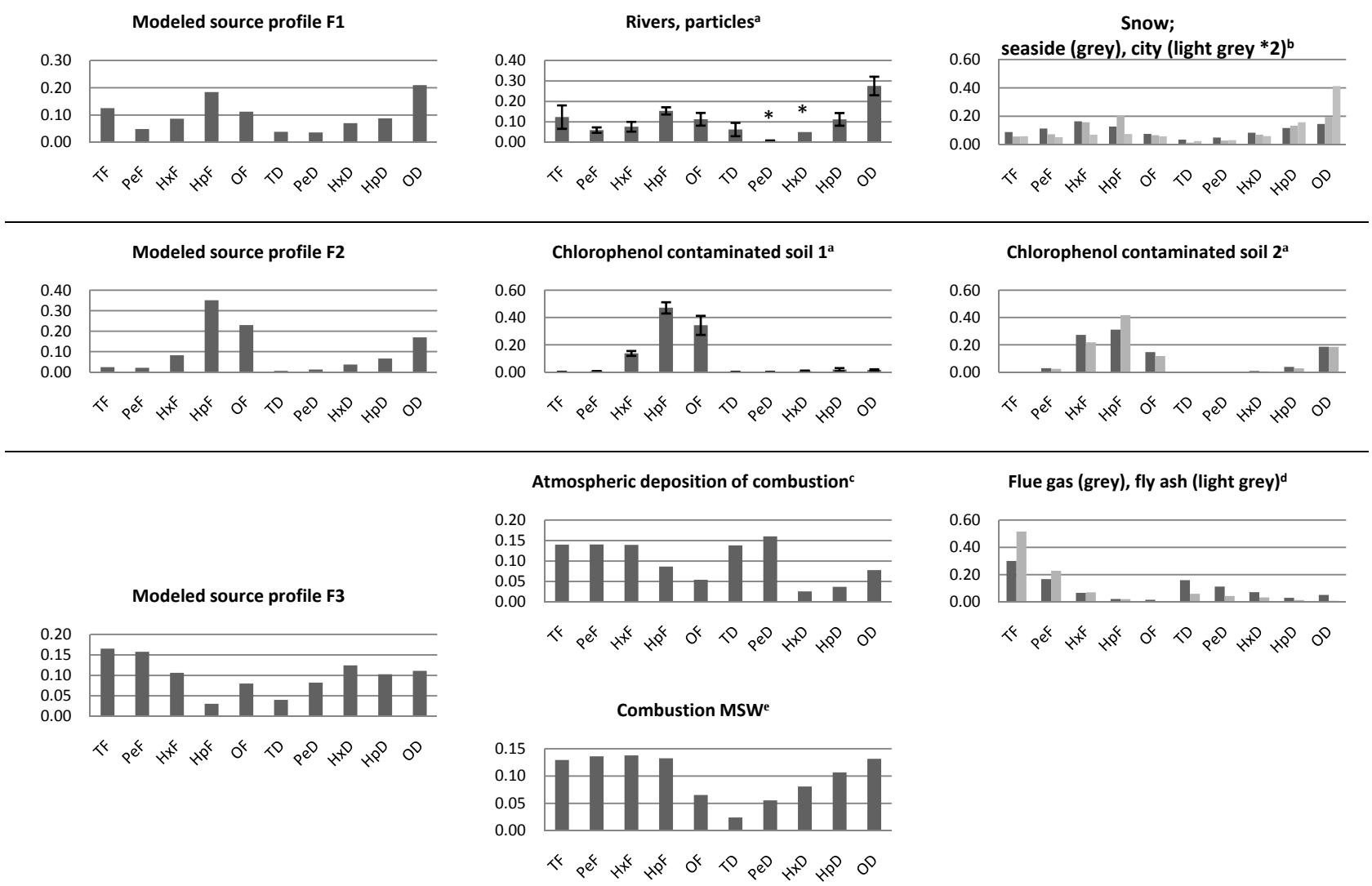

Figure 2. Reconstructed source profiles from receptor modeling (F1-F3) and suggestion of source type candidates for comparison (*the value presented is from a single sample and not an average, [a]this study, [b]Cai (in prep.),[c]ref[6], [d]ref[7], [e]in-house extract).