SOURCES OF DIOXINS TO THE BALTIC SEA – IDENTIFICATION AND APPORTIONMENT USING PATTERN ANALYSIS AND RECEPTOR MODELING

Sundqvist K L[1], Tysklind M[1], Geladi P[2], Hopke P K[3], Wiberg K[1]

[1]Department of Chemistry, Umeå University, SE-90187 Umeå, Sweden; [2]Unit of Biomass Technology and Chemistry, Swedish University of Agricultural Sciences, SE-90183 Umeå, Sweden; [3]Department of Chemical and Biomolecular Engineering and Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY 13699, USA.

Abstract
Multivariate pattern analysis techniques and receptor modeling were used to trace and apportion PCDD/F sources in the Baltic Sea. The data set consisted of all *tetra*- to *octa*-chlorinated PCDD/Fs analyzed in nearly 150 samples of surface sediments. The source tracing analyses suggested that atmospheric deposition, tetrachlorophenol use and other wood related industry are responsible for the pollution. Atmospheric deposition was suggested as the most important source to offshore areas, thus supporting earlier estimates. However, spatial differences indicated a larger fraction of local/regional atmospheric sources, characterized by higher fraction of PCDFs, in the south. This was indicated by the identification of several patterns of atmospheric origin. In coastal areas, the influence of direct emission sources was larger, and among these, chlorophenol used for wood preservation and emissions from pulp/paper production and other wood related industry appeared to be most important. The historic emissions connected to processes involving chemical reactions with chlorine (*e.g.* pulp bleaching) were found to be of less importance.

Introduction
Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) continues to be an environmental problem for the Baltic Sea environment, with levels in fatty fish exceeding the regulatory limits for EU member states.

Detailed analysis of PCDD/F patterns enables identification of source types and calculations as to their relative importance[1]. In this study, a large data set of Baltic surface sediments analyzed for all *tetra*- through *octa*-substituted PCDD/Fs from a previous study was used[2]. The data set included samples from the Swedish east coast and offshore areas of the Baltic Sea.

Materials and Methods
Sediments were sampled along the Swedish coast using gravity corers[2]. 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[1]. For the current data set, *tetra*- through *octa*-substituted PCDD/Fs were analyzed using GC-HRMS. In the presentation of results, individual congeners are abbreviated as follows 2,3,7,8-tetrachlorodibenzofuran = 2378TF, and co-elution with one or more other congeners is indicated with an asterisk in the end of the abbreviation. A total of 63 chromatographic peaks corresponding to individual congeners or groups of congeners were quantified and used in the modeling. Since very few detailed source patterns are given in literature, candidate source samples were also analyzed to obtain full congener patterns for comparison and identification.

Principal component analysis (PCA) was used for investigation of the pattern variation and for interpretation of the fingerprints of individual samples. Indicator congeners were utilized to trace major source types that likely contributed to the pollution of the sediments. Prior to PCA modeling, all samples were normalized to unit concentration (*i.e.* the concentration of each congener was divided by the total concentration of *tetra*- through *octa*-substituted PCDD/Fs) in order to focus on the PCDD/F pattern of the samples and exclude factors such as concentration levels and amount of organic matter. In the PCA software, the data set was log transformed.

In order to apportion PCDD/F sources, the receptor model Positive Matrix Factorization (PMF[3]) was applied. PMF is a multivariate technique that, similarly to PCA, simplifies the data by describing it in a few new variables instead of the large number of original variables. PMF is a receptor model with non-negative constraints resulting in profiles that can be directly interpreted as source patterns[3]. The technique has lately been used successfully for apportioning PCDD/F sources for polluted sediments[4,5]. For PMF, two matrixes are used – one with measured concentrations and one with measured/estimated uncertainties for each data point. 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.

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.

$$(1)\ x_{ij} = \sum_{k=1}^{p} \mathrm{f_{ik}} \times \mathrm{g_{kj}} + \mathrm{e_{ij}}$$

$$(2)\ Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\frac{E_{ij}}{s_{ij}}\right]^2$$

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.

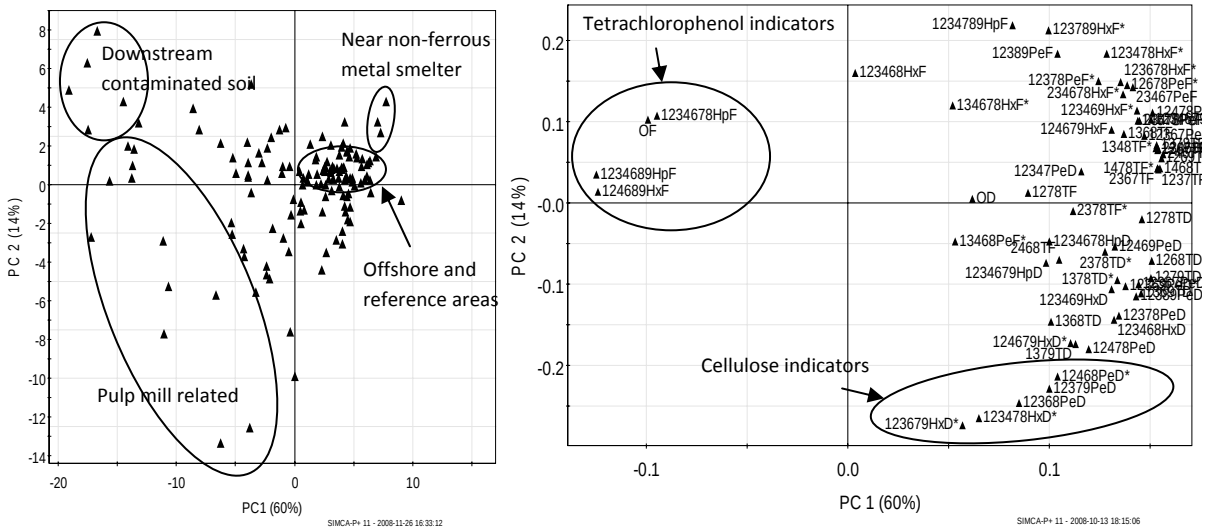

Figure 1. PCA results fro surface sediment samples from the Swedish coastal and offshore areas. PC 1 explained 60% of the variance and PC 14%.

Results and Discussion

The first four principal components (PCs) of the PCA together explained 86% of the pattern variation in the sediments (Fig 1). Tetrachlorophenol indicators (124689HxF, 1234678HpF, 1234689HpF and OF) were identified in the vicinity of an old sawmill site, but also close to pulp and paper mills indicating that contaminated soils from previous wood treatment activities may still be causing important terrestrial PCDD/F-fluxes to the connecting sea (Fig 1; PC 1). Two other groups of marker congeners were found near cellulose industries: 123679HxD together with other HxDs and PeDs (Fig 1; PC 2) and traditional markers for chlorine

bleaching of pulp (1278TF, 2378TF*, 12378PeF* and 2378TD*[6]; PC 4 not shown). The identified HxDs and PeDs were found in pulp and paper products already in the 1990s when changed bleaching procedures lowered the contribution from the traditional "bleaching profile"[7-12]. These high chlorinated PCDDs, including a large fraction of non-2,3,7,8-chlorinated HxDs, were observed in different paper products, recycled paper and inks as well as tall oil and resin. It should be noted that there are no evidence of ongoing point source emissions, and the findings in the sediments could also be due to recycling of old pollution.

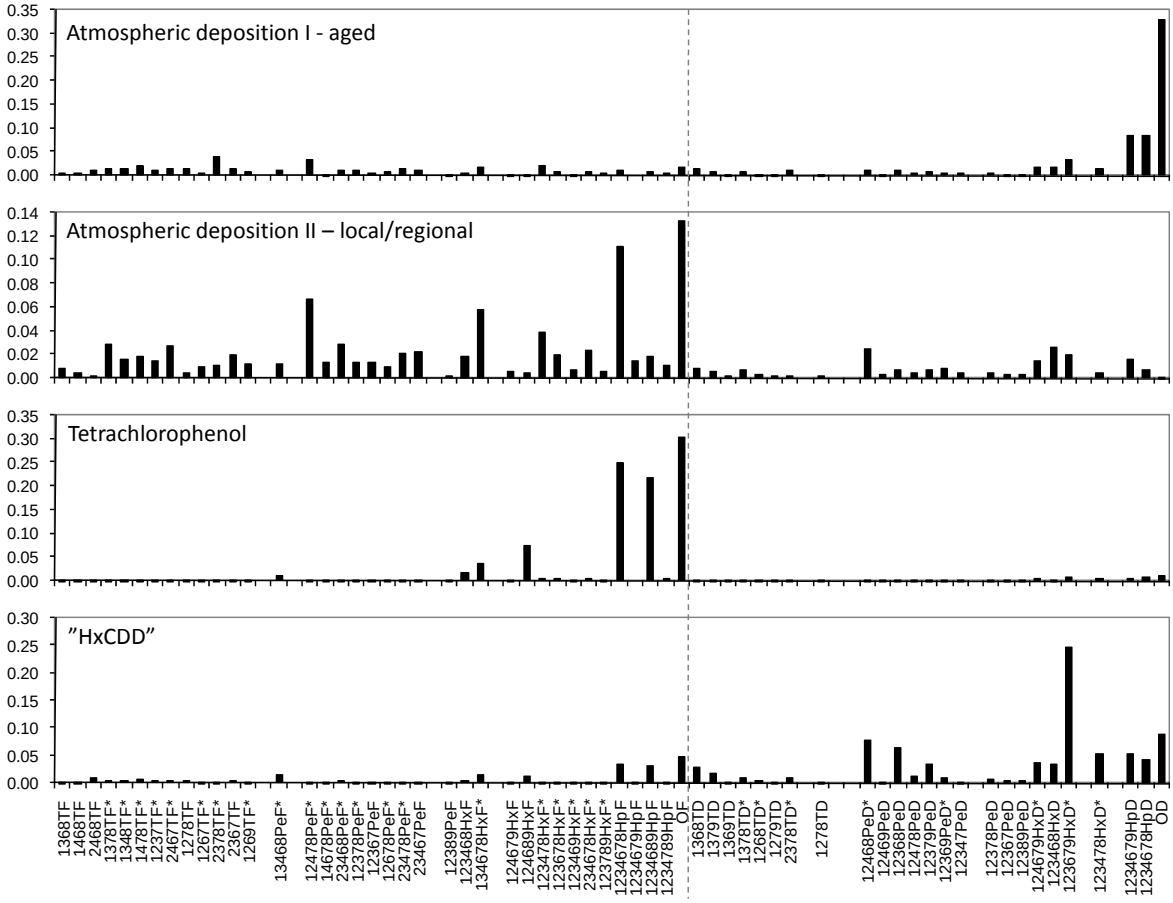

Figure 2. PMF candidate source profiles. Asteriks indicate that the signal originate from more than one congener as a result of co-elution. Blank spaces on the x-axis indicate cromatographic peaks omitted from PMF modeling due to high proportion of values <DL.

The receptor modeling using PMF supported the findings from the PCA analysis. In PMF the number of sources need to be determined by the user and it was found that models with four to six sources best described the sediment data set. The PMF modelling results assuming four candidate sources are presented in Fig 2 and Table 1. The candidate source patterns from the model was interpreted as two patterns which together describe the spatial (and seasonal) variations in atmospheric deposition, a tetrachlorophenol pattern and a pattern dominated by 123679HxD*. The atmospheric source pattern dominated by HpDs and OD possibly represents an air mass that has transported the PCDD/F pollution a long distance, resulting in an "aged" pollution pattern[13]. The second atmospheric pattern was dominated by a range of PCDFs and is suggested to represent more local or regional emissions from combustion and other high temperature processes[13,14]. As seen in Table 1, atmospheric deposition was generally the dominant source. The dominance was especially apparent in offshore areas. The model suggested a slightly higher contribution from the second atmospheric pattern in offshore areas of the Baltic Proper than in the Bothnian Sea, indicating regional differences in the deposition. In certain coastal areas

(both hotspots and less contaminated sites), one or both of the other source patterns dominated. Current and historical activity in coastal regions supported these findings.

Table 1. Range of contributions (25^{th}-75^{th} percentile) of candidate sources to surface sediment along the Swedish coast and in offshore areas of the Baltic Sea.

Candidate source	**25^{th}-75^{th} percentile (%)**
Atmospheric deposition I - aged	27-48
Atmospheric deposition II – local/regional	6.2-27
Tetrachlorophenol	9.1-31
"HxCDD"	3.4-13
Model residual	1.0-16

This study showed the strength of using comprehensive congener patterns when elucidating the sources of PCDD/Fs in the environment. It was shown that most of the variation in PCDD/F patterns of the Baltic sediments analyzed was linked to pulp- and paper industry and other wood industry related activities, and that off-shore samples showed great resemblance to the atmospheric deposition signal.

Acknowledgements
The Swedish Research Council Formas (nr 216-2004-1827) and the Umeå Marine Sciences Centre are acknowledged for financial support. Emeritus Professor Christopher Rappe is thanked for valuable comments concerning historical PCDD/F patterns.

References

1. Masunaga S., Yao Y., Ogura I., Sakurai T., Nakanishi J. *Chemosphere* 2003;53:315.
2. Sundqvist K.L., Tysklind M., Cato I., Bignert A., Wiberg K. *Environ Sci Pollut R* 2009;In Press doi:10.1007/s11356-009-0110-z.
3. Paatero P. *Chemometr Intell Lab* 1997;37:23.
4. Uchimiya M., Masunaga S. *Environ Sci Technol* 2007;41:2703.
5. Uchimiya M., Arai M., Masunaga S. *Environ Sci Technol* 2007;41:3864.
6. Rappe C., Swanson S.E., Glas B., Kringstad K.P., De Sousa F., Johansson L., Abe Z. *Pulp Pap-Canada* 1989;90:8:T273.
7. Rappe C., Glas B., Wiberg K. *Org hal Comp* 1990;3:287.
8. Buckland S.J., Hannah D.J., Taucher J.A., Weston R.J. *Org hal Comp* 1990;3:223.
9. Kitunen V.H., Salkinoja-Salonen M.S. *Org hal Comp* 1990;3:251.
10. Santl H., Gruber L., Stöhrer E. *Chemosphere* 1994;29:1987.
11. Santl H., Gruber L., Stöhrer E. *Chemosphere* 1994;29:1995.
12. Bichlmaier A., Gruber L., Stöhrer E., Tillmann O., Santl H. *Org hal Comp* 1992;9:25.
13. Tysklind M., Fängmark I., Marklund S., Lindskog A., Thaning L., Rappe C. *Environ Sci Technol* 1993;27:2190.
14. Rappe C. *Fresen J Anal Chem* 1994;348:63.