Characterization of the particulate load of PCDD, PCDF and PAH in waters outside various emission sources utilizing multivariate pattern recognition.

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Introduction

The total input of particle-associated hydrophobic organic compounds (HOCs), such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs), to different water areas can be studied with the aid of sediment traps. In the water HOCs settle out primarily in association with large rapidly settling particles[1]. This settling particulate matter (SPM) often consists of aggregates of smaller particles which are formed by biotic processes, such as faecal pellet formation, and by abiotic processes, such as flocculation and agglomeration. Further, the comparatively high organic content of SPM results in a high absorbing capacity for the dissolved PCDD/Fs and PAHs due to the high organic carbon - water partition coefficients displayed by these compounds. SPM collected in sediment traps during a longer period of time therefore reflects an integrated picture of the PCDD/Fs and PAHs found in the water mass due to the efficient scavenging capacity of SPM for both dissolved and suspended particulate forms of these compounds[2]. This is also confirmed in an earlier study from the Baltic[3] in which the PAH and PCDD/F chemical profiles of SPM collected in sediment traps in remote areas were compared with the corresponding profiles of the sum of particulate and dissolved matter in the waters.

In addition to the primary settling material collected in the sediment traps contributions may also be obtained in the form of resuspended material, i.e. previously sedimented material which is whirled up from the bottoms only to settle again. By considering different factors during sampling this resuspension can be minimized but can never be totally avoided when sampling for longer periods of time. The flux measured with sediment traps should therefore preferably be designated 'gross' flux.

The study presented in this abstract discusses results of estimated gross fluxes of PCDD/Fs and PAHs in water areas outside various potential emission sources as well as at remote background locations along the Swedish Baltic coast. Estimates of the total load in the Baltic Sea are also given. To investigate possible similarities and/or differences in the chemical pattern of the various sediment trap samples and to point out emission source characteristic

PCDD/F and PAH compounds a multivariate pattern recognition method called SIMCA (Soft Independent Modelling of Class Analogy) has been used[4].

Materials and Methods

The different emission source areas studied were situated along the Swedish Baltic coast from the mid Baltic proper in the south to the Bothnian Bay in the north. From north to south these emission sources were; one metal smelter (5 traps), one graphite electrode producing industry (5 traps), one aluminum smelter (6 traps), one pulp and paper mill (5 traps), one large non-industrialized city (Stockholm, 11 traps), one petroleum refinery (6 traps) and one steel plant (5 traps). At these different locations there may also be contributions from other emission sources (except the industries here mentioned) that may have an impact on the total PCDD/F and PAH load in the water areas studied. As background areas were chosen one location in the mid Baltic proper and one location in the Bothnian Bay (3 traps at each location).

The sediment traps which were placed in gradients with increasing distance to the potential sources, were of a self-suspended buoyant type with cylindrical collection vessels of glass contained in a gimbal-mounted PVC cylinders. The trap design and anchorage technique used are described in detail elsewhere[5]. To avoid microbial activity during the one year long collection period, chloroform was used as a preservative in the collection vessel as described by Broman et al.[6]. Descriptions of work-up procedures, as well as clean-up procedures and analyses techniques can be found in refs [2,3,6-9]. For the analyses of the PCDD/Fs eight ^{13}C-labeled PCDD/F standards (2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,4,7,8-PnCDF, 1,2,3,7,8-PnCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD) were used and for the PAH analyses four standards were used (2-methylanthracene, picene, D_{12}-perylene, and dibenz(a,i)pyrene). The quantitative analysis of the PCDD/Fs was done by GC/MS using a VG 70E MS and a Hewlett-Packard 5790 GC with a 40 m SP-2331 capillary column. Analyses of the PAHs were done by GC/FID (VARIAN 3300) and a 25 m CP-Sil-8 capillary column (Chrompack). Fifteen PAHs were analyzed (PAH_{15}) (see Appendix).

Results

For all areas studied the direct influence of the emission sources was limited to the inner part of the recipients respectively (approx. 10-50 km[2]) which indicated a fast settling of particulate PCDD/Fs and PAHs.

A pulp and paper mill was identified as a major PCDD/F source generating a gross flux of 68 g/y (1.1 g/y toxic equivalents, TEQ) in the 10 km[2] closest to the source. Corresponding fluxes of the other industrial sources were 19 - 7 g/y (0.22 - 0.05 g/y as toxic equivalents). The flux of PCDD/F to the whole Baltic (375.000 km[2]) was estimated to approx. 300 kg/y (4 kg/y toxic equivalents) from the background sediment trap data.

The flux of PAH_{15} within the 10 km[2] closest to the aluminum smelter was 560 kg/y, which was 56 times the background flux. The other emission sources caused fluxes between 300 and 10 kg/y. The flux of PAH_{15} to the Baltic was estimated to approx. 400 tons/y.

Characterization of the emission source samples

The objective of the multivariate pattern recognition analysis (SIMCA) was to investigate the possibility of pin-pointing the various emission sources and if so which PCDD/F isomers and PAH compounds would be of greatest importance for this possible separation. The SIMCA method combines pattern recognition with principal component analysis and has been successfully used for classification problems in e.g. environmental chemistry[10,11]. With sufficient amount of variables it is possible to investigate similarities between objects (samples) even though a limited number of objects are present in the data set.

The variables in the PCDD/F data set were the concentrations of all 2,3,7,8-substituted isomers plus the sum of these, the 8 congener group concentrations, the total sum of all PCDD/Fs and the total sum of all TEQ concentrations (i.e. 28 variables). The PAH variables were the concentrations of all analyzed compounds (see Appendix) plus the sum of all PAHs (i.e. 16 variables). The two data sets were analyzed separately.

The projections of PC1 (principal component 1) versus PC2 of the PCDD/F and PAH data sets showed that the various objects separated clearly with regard to emission source clustering. For the separation of the pulp and paper mill samples primarily 1,2,3,6,7,8-HxCDD and 2,3,4,8-/2,3,7,8-TCDF were important. A relatively high separation capacity was also displayed by 1,2,3,7,8,9-HxCDD, total HxCDD, 1,2,3,4,7,9-HxCDF and 2,3,7,8-TCDD especially the last two compounds mentioned for the separation of the metal smelter and the aluminum smelter from the others. The PAHs that contributed most to the separation of the objects in PC1 and PC2 were Flu, Pyr, B(a)A, Chr/Tri, Ind and total PAH.

The SIMCA classification analyses of the PAH samples significantly separated all the different emission source samples (except the petroleum refinery samples). In the classification analysis of the PCDD/Fs four emission source class models were made and the first two of these were the aluminum smelter samples and the steel plant samples. In this analysis all test objects (all other samples) differed significantly from the two class models. This was also the case for the classification analysis of the second two emission source class models made of the pulp and paper mill samples and the metal smelter samples. The SIMCA classification analysis of the PAH and PCDD/F data sets showed that it was possible to distinguish the different emission source areas from each other by their 'emission source patterns'.

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APPENDIX

PAH_{15}:

Fluoranthene	Flu	Pyrene	Pyr
2-methylpyrene	2-mePyr	1-methylpyrene	1-mePyr
Benzo(ghi)fluoranthene	B(ghi)F	Benzo(a)anthracene	B(a)A
Chrysene/triphenylene	Chr/Tri	Benzo(k)fluoranthene	B(k)F
Benzo(e)pyrene	B(e)P	Benzo(a)pyrene	B(a)P
Perylene	Per	Indeno(1,2,3-cd)pyrene	Ind
Benzo(ghi)perylene	B(ghi)P	Coronene	Cor