Chemometric source identification of PCDD/Fs and other POPs in sediment cores of North-East Germany

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Introduction

A broad range of persistent organic pollutants (POPs) and selected heavy metals has been analysed in sediment cores of North-East Germany. The pollutants analysed include polychlorinated dioxins and furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), several pesticides (DDT, HCH, CBz) and its metabolites as well as selected heavy metals [1].

The sediment cores were sampled at five locations, reflecting a range of anthropogenic influences and background contamination: Arkona Basin (AK) representing a remote marine site, Lake Bugsin (BS) a background location only with atmospheric deposition, Lake Quenz (QS) close to the industrial city of Brandenburg, Teltowkanal (TK) in the suburban-industrial zone of Berlin and Lake White (WS) in the centre of Berlin. The age of the lower part of the AK, BS and TK cores were dated at 100-150 years.

Results of selected pollutants (PCDD/Fs) have been presented earlier, focussing on the depth profile and the pollutant patterns [2]. Here, a comprehensive overview of the source identification of all pollutants and the related applications of chemometric methods is presented.

Methods and Materials

The sediment cores were sampled using the freeze coring techniques [3], an Eijelkamp sediment sampler and a Rumohr sediment corer. The compounds were analysed following common procedures. Contamination levels in the blanks were usually far below the sediment levels. A detailed description of the sampling and analytical procedures is given elsewhere [4]. Chemometric methods were applied using SPSS 9.0, Statistica 5.1 and Statgraphics 4.0 [1].

Results and Discussion

The pollutant levels vary tremendously between the locations and with depth. The AK and the BS cores usually reveal lower contamination levels, while the QS, TK and WS cores show high to very high contamination levels. The depth profiles usually illustrate low concentrations at greater depths, a subsurface peak and decreasing concentrations at the sediment surface. The range of pollutant levels in the sediment cores is given in the following Table 1.

Table 1: Pollutant levels in the sediment cores of N-E Germany.

	AK	BS	QS	TK	WS
PCDD/F (pg/g d.m.)	220 - 4800	19 - 2400	78 - 4100	160 - 11000	97 - 20000
PCB (ng/g d.m.)	0.6 - 5.7	n.d. - 0.6	n.d. - 410	22 - 660	12 - 1400
PAK (ng/g d.m.)	460 - 3700	490 - 6100	470 - 23000	970 - 18000	1700 - 45000
DDX (ng/g d.m.)	0.002 - 25	n.d. - 270	0.15 - 170	68 - 4200	0.09 - 1600
CB (ng/g d.m.)	0.01 - 0.07	n.d. - 6.8	n.d. - 3.1	0.13 - 15	n.d. - 4.2
HCH (ng/g d.m.)	n.d.	n.d.	n.d. - 150	2.9 - 390	n.d.
Pb (µg/g d.m.)	34 - 130	36 - 1000	1.1 - 1100	36 - 260	120 – 580

Factor analysis was applied with 40 selected PCDD/F congeners, both 2,3,7,8-substituted and non-2,3,7,8-substituted congeners reflecting indicator congeners of known PCDD/F sources [1]. The aim was to investigate to what extent the dominating factors can be associated with underlying PCDD/F sources.

Table 2 shows the component matrix of factors 1-4 and their explained variance. The explained variance of the factors was as follows: Factor 1 31%, factor 2 17%, factor 3 12%, factor 4 8%. Factor values above 0.6 were marked in bold to highlight their importance:

- Factor 1 shows major similarities with the PCDD/F congeners in pentachlorophenol (PCP). 1,2,3,4,6,8,9-HpCDF, 1,2,4,6,7,8-HxCDF, 1,2,4,6,8,9-HxCDF, 1,2,4,6,8-PeCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,6,7,9-HxCDD and 1,2,4,7,9-PeCDD are indicator congeners for PCP. These have a factor value larger than 0.6 for factor 1. Therefore, factor 1 can be explained by a PCP-related contamination.
- Factor 2 has PCDD/F congeners closely related to incineration sources. 1,3,7,9-TeCDD, 1,2,3,6,8-PeCDD, 1,2,3,7,9-PeCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD und 1,2,3,6,8-PeCDF are indicator congeners for incineration. Factor 2 can therefore be linked to an incineration-related contamination.
- Factor 3 has a high factor value for 1,2,7,8-TeCDF, which is a known contaminant of chlorine bleaching and PCB. In these sources, usually additional indicator congeners can be found. Factor 3 can therefore be related to chemical sources.
- Factor 4 has high factor values for 1,3,7,8-TeCDF, 1,3,4,6,8-PeCDF und 1,3,6,7,8-PeCDF. These are indicator congeners for incineration. Factor 4 can therefore be explained by an incineration-related contamination.

Overall, the PCDD/Fs in the investigated sediment cores are mainly emitted by PCP (factor 1) and incineration (factor 2 and factor 4). Other chemical sources (factor 3) are of minor importance here.

Table 2: Component matrix of factor 1-4 for 40 selected PCDD/F congeners.

Factor	1	2	3	4
1,3,6,8-TeCDD	**0.67**	0.20	0.53	0.12
1,3,7,9-TeCDD	0.27	**0.65**	0.12	0.06
1,3,7,8-TeCDD	0.07	0.14	0.01	-0.05
2,3,7,8-TeCDD	-0.01	0.52	-0.42	-0.35
1,2,3,4-/1,2,4,6-/1,2,4,9-/1,2,3,8-TeCDD	-0.01	0.45	0.04	-0.19
1,2,3,6-/1,2,7,9-TeCDD	-0.48	-0.04	-0.32	-0.15
1,2,7,8-/1,4,6,9-TeCDD	-0.38	-0.27	-0.18	-0.11
1,2,4,7,9-/1,2,4,6,8-PeCDD	**0.65**	-0.02	0.38	-0.04
1,2,3,6,8-PeCDD	0.29	**0.61**	0.56	0.00
1,2,4,7,8-PeCDD	0.02	0.42	**-0.73**	-0.21
1,2,3,7,9-PeCDD	-0.17	**0.92**	0.16	-0.02
1,2,3,7,8-PeCDD	-0.14	**0.86**	-0.27	-0.06
1,2,4,6,9-/1,2,3,4,7-PeCDD	-0.09	**-0.83**	-0.24	-0.09
1,2,4,6,7,9-/1,2,4,6,8,9-/1,2,3,4,6,8-HxCDD	-0.42	**-0.77**	0.00	0.10
1,2,3,6,7,9-/1,2,3,6,8,9-HxCDD	**0.72**	0.54	-0.08	-0.04
1,2,3,6,7,8-HxCDD	**0.64**	**0.62**	0.13	-0.04
1,2,3,7,8,9-HxCDD	0.20	**0.83**	0.10	0.04
1,2,3,4,6,7,8-HpCDD	**0.69**	0.51	0.21	-0.16
1,3,7,8-/1,3,7,9-TeCDF	**-0.63**	0.21	-0.19	**0.62**
1,4,6,8-TeCDF	0.45	0.35	**0.61**	0.02
2,4,6,8-/1,2,3,8-/1,4,6,7-/1,2,3,6-TeCDF	0.22	**-0.88**	-0.03	-0.10
1,2,7,8-TeCDF	0.13	0.28	**0.77**	-0.17
1,2,6,7-/1,2,7,9-TeCDF	-0.07	-0.21	0.08	-0.14
2,4,6,7-TeCDF	-0.14	-0.05	0.04	-0.31
1,2,3,9-/2,3,4,7-TeCDF	-0.33	0.22	0.32	0.33
2,3,6,7-TeCDF	0.57	0.07	-0.13	0.08
1,3,4,6,8-PeCDF	-0.07	-0.06	-0.13	**0.91**
1,2,4,6,8-PeCDF	**0.85**	-0.25	-0.10	0.35
1,3,6,7,8-PeCDF	-0.15	0.00	0.28	**0.84**
1,2,3,6,8-/1,3,4,7,8-PeCDF	0.20	**0.61**	-0.36	0.51
1,4,6,7,8-/1,2,3,4,8-PeCDF	-0.11	0.33	0.24	0.44
1,2,3,7,8-/1,2,3,4,8-PeCDF	-0.01	0.55	0.35	0.39
1,2,3,6,9-PeCDF	0.50	0.55	-0.03	-0.18
2,3,4,7,8-PeCDF	-0.50	0.24	-0.34	-0.43
1,3,4,6,7,8-/1,3,4,6,7,9-HxCDF	**-0.77**	-0.03	-0.20	0.20
1,2,4,6,7,8-HxCDF	**0.88**	-0.17	-0.14	-0.02
1,2,3,4,7,8-/1,2,3,4,7,9-HxCDF	0.17	0.27	0.26	0.09
1,2,4,6,8,9-HxCDF	**0.94**	0.08	-0.07	-0.02
1,2,3,4,6,7,8-HpCDF	**-0.82**	-0.15	-0.17	0.21
1,2,3,4,6,8,9-HpCDF	**0.83**	0.13	0.20	-0.16

In addition, correlation analysis was applied to reveal underlying sources. The correlation of PCDD/Fs and PAHs as well as the correlation of PCDD/Fs and PCBs/pesticides was investigated.

The PAHs were grouped into 4 main sources during factor analysis [1]:

- Combustion source 1: Benzo(e)pyrene, indeno(1,2,3-cd)fluoranthene, benzo(k)fluoranthene
- Combustion source 2: Anthanthrene, benzo(b)naphto(21d)thiophene, benzo(a)anthracene
- Oil contamination (source 3): methylated phenanthrenes
- Diagenesis (source 4): Perylene and 7,12-dimethyl(a)anthracene

The overlap of sources between different pollutant groups was assessed by correlation analysis. The significant positive correlation of PAH source groups and PCDD/F congeners is given in Table 3.

Table 3: Significant positive correlation of PAH sources and PCDD/F congeners.

PAH source	Significant positive correlated PCDD/F congeners
Source 1: Traffic, combustion of liquid and gaseous fuels, combustion with low dust emissions, fuel combustion with long-range transport	1,2,6,8-TeCDD, 1,2,4,6,7-PeCDD, 1,2,4,8,9-PeCDD, 1,2,3,4,6,7,9-HpCDD, 1,3,6,8-TeCDF, 1,3,7,8-/1,3,7,9-TeCDF, 1,3,4,7-TeCDF, 1,2,6,7-/1,2,7,9-TeCDF, 2,4,6,7-TeCDF, 1,2,3,9-/2,3,4,7-TeCDF, 1,2,6,7,9-PeCDF, 2,3,4,7,8-PeCDF, 2,3,4,6,7-PeCDF, 1,3,4,6,7,8-/1,3,4,6,7,9-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF
Source 2: Coal combustion, combustion of solid fuels, combustion with high dust emissions, fuel combustion without long-range transport	1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 1,2,3,6,8-PeCDD, 1,6,7,8-/1,2,3,4-TeCDF, 1,2,7,8-TeCDF, 1,4,6,9-TeCDF, 1,2,6,9-TeCDF, 1,2,4,7,8-PeCDF, 1,2,4,6,7,8-HxCDF, 1,2,3,4,6,8,9-HpCDF
Source 3: Oil contamination	1,2,3,4-/1,2,4,6-/1,2,4,9-/1,2,3,8-TeCDD, 1,2,3,6,9-PeCDD, 1,2,3,4,6-PeCDD, 1,3,4,6-/1,2,4,8-TeCDF, 2,3,7,8-TeCDF, 1,2,4,7,8-PeCDF, 1,2,4,6,7-PeCDF, 1,2,3,6,7-PeCDF, 1,2,3,6,9-PeCDF
Source 4: Diagenesis	1,2,3,9-TeCDD, 1,2,4,7-TeCDF, 1,3,6,7,8-PeCDF, 1,2,3,7,9-PeCDF, 1,2,3,8,9-PeCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,6,7,9-HxCDF, 1,2,3,4,6,7,9-HpCDF, 1,2,3,4,7,8,9-HpCDF

The PAH congeners related to incineration sources showed a significant positive correlation to PCDD/F congeners known to be emitted by incineration sources. The PAH combustion source 1 was significantly positive correlated with 1,2,6,7-/1,2,7,9-TeCDF, 2,4,6,7-TeCDF etc. The PAH combustion source 2 had a significant positive correlation with 1,3,6,8-TeCDD, 1,3,7,9-TeCDD etc. These two PCDD/F congener groups show similarity to the 2,3-chlorophenol (source 1) and the 2,6-chlorophenol (source 2) type of combustion [5]. 1,3,6,8-TeCDF, and 1,3,7,8-/1,3,7,9-TeCDF are indicator congeners of the 2,3-chlorophenol type of combustion. 1,3,6,8-TeCDD and 1,3,7,9-TeCDD are indicator congeners of the 2,6-chlorophenol type of combustion.

The PAH congeners linked to oil contamination are significantly positive correlated with PCDD/F congeners known as indicator congeners for chemical contamination: 1,2,3,4-/1,2,4,6-/1,2,4,9-/1,2,3,8-TeCDD in PCP; 2,3,7,8-TeCDF and 1,2,4,7,8-PeCDF in PCB. Therefore, these PAH and PCDD/F congeners are emitted by the same source, caused by oil or chemicals.

The PAH congeners related to diagenesis (source 4) are significantly positive correlated with PCDD/F background congeners. These PCDD/F congeners cannot be related to known PCDD/F sources.

Overall, two types of incineration sources, oil contamination and a background source are responsible for the PCDD/F and PAH contamination of the sediment cores. For the PAHs, the incineration sources are differentiated by fuel type, dust content and photolytic effects. For the PCDD/Fs, it can be distinguished between 2,3- and 2,6-chlorophenol-type of incineration. PCDD/Fs and PAHs are therefore emitted by widely overlapping rather than separate sources.

Similarly, the correlation of PCDD/F congeners to PCB congeners and pesticides were investigated, as shown in Table 4.

Table 4: Significant positive correlation of PCDD/F congeners and PCBs/pesticides.

	Significantly positive correlation with
PCBs	1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 1,2,4,7,9-/1,2,4,6,8-PeCDD, 1,2,3,6,7,9-/1,2,3,6,8,9-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, 1,4,7,8-/1,3,6,9-/1,2,3,7-TeCDF, 1,4,6,9-TeCDF, 2,3,6,8-/1,2,4,9-TeCDF, 1,2,4,6,8-PeCDF, 1,3,4,6,9-PeCDF, 1,2,3,4,6,8-HxCDF, 1,2,4,6,7,8-HxCDF, 1,2,4,6,8,9-HxCDF, 1,2,3,4,6,8,9-HpCDF
Pesticides	1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 1,2,4,7,9-/1,2,4,6,8-PeCDD, 1,3,6,8-TeCDF, 1,3,6,7-TeCDF, 2,4,6,8-/1,2,3,8-/1,4,6,7-/1,2,3,6-TeCDF, 1,3,4,9-TeCDF, 1,4,6,9-TeCDF, 2,3,6,8-/1,2,4,9 TeCDF, 3,4,6,7-TeCDF, 1,2,4,6,8-PeCDF, 1,3,4,7,9-PeCDF, 1,4,6,7,8-/1,2,3,4,7-PeCDF (only HCH), 1,2,3,4,9-PeCDF, 1,2,4,6,7,8-HxCDF, 1,2,4,6,7,9-HxCDF, OCDD

1,2,3,6,7,9-/1,2,3,6,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, 2,3,6,8-/1,2,4,9-TeCDF, 1,2,4,6,7,8-HxCDF and 1,2,3,4,6,8,9-HpCDF are indicator congeners for PCB. Some other PCDD/F congeners significantly correlated with PCBs were known indicator congeners for PCP. This illustrates that the PCB source and the correlated PCDD/F congeners consists of a chemical source with a mixture of compounds rather than pure PCB.

The pesticides HCB, HCH and DDX were considered together because of very similar correlations. 1,2,4,6,8-PeCDF and 1,4,6,7,8-/1,2,3,4,7-PeCDF are known contaminants of HCH. For the other pesticides, no PCDD/F chromatograms were available. Again, also for the pesticide-related sources, a mixture of pesticides and chemical contamination is more likely than the contamination of one single pesticide.

Conclusions

Chemometric methods were successfully applied to evaluate the PCDD/F sources and to find common sources for PCDD/Fs, PAHs, PCBs and pesticides.

In factor analysis, it was possible to relate the extracted factors to known PCDD/F sources. Factor 1 consisted of PCP, factor 2 and 4 were mainly influenced by incineration and factor 3 was explained by a chemical-related contamination.

The correlation analysis of PCDD/F congeners and PAH showed similar source groups. The PAH combustion source 1 was significantly positive correlated with several PCDD/F congeners emitted by 2,3-chlorophenol-type of incineration. The PAH combustion source 2 was significantly positive correlated with some PCDD/F indicator congeners for 2,6-chlorophenol-type of incineration. The PAH congeners for oil contamination were significantly positive correlated with PCDD/F contaminants in PCP and PCB.

The correlation analysis of PCDD/F congeners and PCBs/pesticides showed a link between PCDD/F congeners in contamination of a chemical mixture, but no association to pure compounds.

Overall, chemometric methods are a helpful tool for source identification of PCDD/Fs and other POPs. Factor analysis showed a strong link of the factors to known sources and correlation analysis assisted in finding common source groups for a variety of POPs.

Acknowledgements

We would like to thank Wilhelm Knoth, Winfried Mann, Judith Nebhuth, Wolfgang Mailahn, and Josef Pribyl for dioxin analysis.

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