PCDD/Fs IN SEDIMENT CORES OF NORTH-EAST GERMANY

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Introduction

PCDD/Fs are widespread environmental pollutants. They are characterized by chemical stability and poor water solubility. There is growing evidence that these substances are extremely harmful to freshwater and marine ecosystems. Traces of PCDD/Fs have been detected in ancient samples and at remote sites [1-4]. Sediments have earlier been used to obtain information about the PCDD/F fluxes to the environment in the last decades and centuries at sites close to industrial activity and at remote sites. Not much is yet known about PCDD/Fs in sediments and historical PCDD/F emissions in the eastern part of Germany.In this study, depth profiles of PCDD/Fs were analysed in five sediment cores from North-East Germany. The sampling sites (see Fig. 1) were chosen along a transect from a remote marine area (Arkona Basin AK, water depth 46.60 m, eutrophic), via the Biosphere Reserve Schorfheide (Lake Bugsin BS, water depth 7.10 m, oligo- to dystrophic, influenced only by deposition and no surface water influx), a small lake in the industrialized city Brandenburg (Lake Quenz QS, water depth 2.00 m; eutrophic) to the urban-industrial zone of Berlin with industrial and municipal effluents (Teltow Canal TK, water depth 1.5 m, eutroph-hypertrophic) and an isolated pond (Lake Weissensee WS, water depth 9.00 m, mesotrophic-eutrophic) to match different geochemical conditions and to elucidate the influence of industrial point sources and of background atmospheric deposition.

Materials and Methods

In 1995 - 1997 sediment cores were obtained using two freeze-coring devices, beside conventional box-coring systems. Freeze-coring systems are special devices based on liquid nitrogen, adapted to sample sediments with a water content of more than 90% (core length up to 2.5 m and 30 cm diameter). The system is restricted to water depths of 9-10 m. The other system is a light weight alumina pipe working on dry ice. With a maximum core length of up to 1.5 m (10 cm diameter), the system is tested at a water depth of 70-80 m. The frozen samples were cut with a hot wire into individual segments. In addition, the sedimentological parameters TOC, TIC, dry weight, trace metals and metals were measured. The segments BS 26-32 cm, QS 231-236 cm and TK 95-100 cm were dated to the end of the 19th century.PCDD/Fs analysis was performed on 5 – 20 g of freeze-dried sediment, spiked with a mixture of 11 $^{13}C_{12}$ standards, and extracted in a Soxhlet apparatus for at least 24 h with toluene. Clean-up was performed as previously described [5]. It consisted of a multicolumn clean-up including alumina-, mixed-silica-, Bio Bead™- and micro-alumina-columns. Resolution and quantification of PCDD and PCDF were performed on a HRGC-LRMS (Fisons MD800 and GC8000) and HRGC-HRMS using a VG AutoSpec coupled to a Hewlett-Packard series 5890 II gas chromatograph. A fused silica capillary column SP-2331 (60 m x 0.25 mm i.d. x 0.20 µm film thickness; Supelco) was used. Helium was the carrier gas.

Methods blanks were routinely analyzed, and no contributions were detected. The PCDD/F contents are given on dry weight basis.

The results were evaluated statistically to characterise differences between the sampling locations and the segments. Statgraphics Plus v4.0 and SPSS v8.0 were used for statistical analysis. The congener content was divided by the corresponding homologue content and the homologue content by sum PCDD/F. The data was centred and Box-Cox-transformed. Values below detection limit were replaced by the detection limit to allow the data transformation. In factor analysis, the principal component method and Varimax rotation were applied.

Fig. 1: Sampling locations * of the sediment cores

Results and Discussion

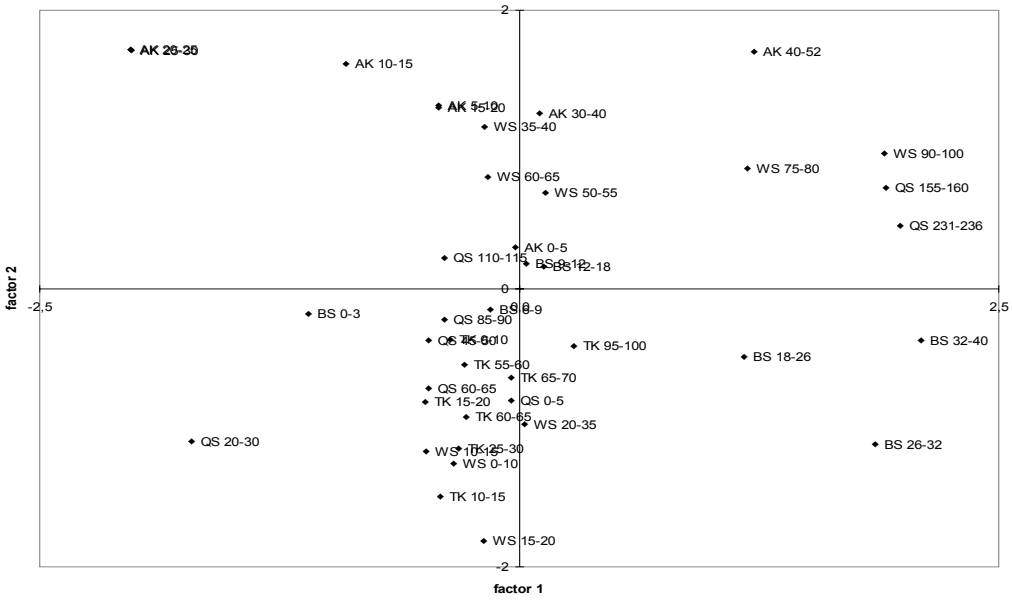
The PCDD/F content in the sediments were between 20 pg/g and 20,000 pg/g and between 0.03 pg I-TEQ/g and 100 pg I-TEQ/g. The PCDD/F content in the recent samples was commonly two orders of magnitude higher than in the oldest samples (see Fig. 2). The levels in the recent TK and WS samples were highest, 7500 – 20,000 pg/g. In the recent AK, BS and QS segments, 2400 – 5000 pg/g were measured. The PCDD/F content of the deepest core samples were 80 – 340 pg/g. The corresponding level for the BS was as low as 20 pg/g.Compared to published data, the lowest concentrations measured ranged at a level of surface sediments at remote sites (<100 pg/g [6]) and in sediment cores dated prior to ~1910 [1,7]. The highest concentrations in the surface sediment samples of WS matched those reported for peak concentrations in Lake Ontario [8] and for hot spots in the Hamburg harbour [1].The depth profiles of the remote sites AK and BS show an exponential decrease with depth. The PCDD/F content of the QS, TK and WS sediments did not decrease substantially near the surface. This indicates mixing processes of the sediments and/or a stagnation or a decrease in the emission to the sediments in recent years or decades. A dramatic decrease with depth was observed for all samples in the deeper part of the cores. This indicates the anthropogenic PCDD/F influx to the sediments have stagnated in the last decades.The homologue profiles of all segments are shown in Figure 2. In many samples, OCDD is the homologue with the highest contribution to sum PCDD/F. The PCDD levels are commonly higher than the PCDF levels. In core segments of medium age, the contribution of PCDF homologues to sum PCDD/F was often higher than in the younger or older samples. This was most prominent at the BS site between 6 and 18 cm depth and at the WS site between 35 and 65 cm. This influence was not as high at the AK and QS site.

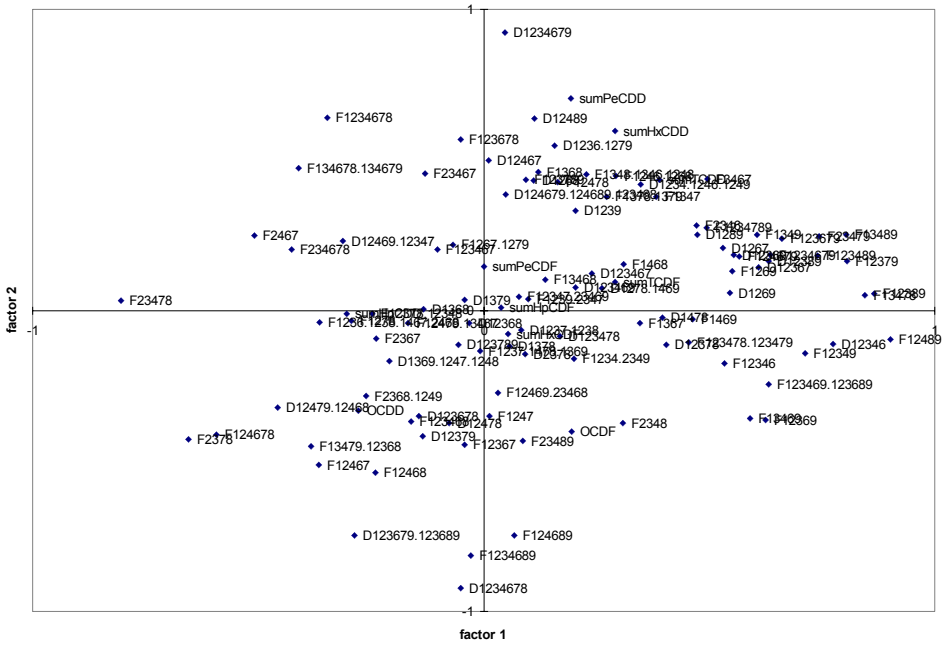
The higher chlorinated PCDDs were dominating at the TK site throughout all segments. In the TK 0-10 cm and QS 231-236 cm sample an unusually high OCDF content was observed. In the oldest sediments, OCDD was often the dominating homologue; the higher chlorinated furans were more abundant than the higher chlorinated dioxins.

The homologue profiles of these sediment samples are similar to those of other sediments and sewage sludges. These often reflect the typical PCP profile. In the BS sediments, the higher proportion of PCDFs reflect the influence only from deposition. The shift of the homologue profile in the lower BS sediments towards higher chlorinated PCDDs illustrates the transformation of PCDFs and lower chlorinated PCDDs. For the elevated relative enrichment PCDF in some WS samples, we suggest a PCB contamination from industrial effluents or thermal sources. The dominance of the PCP profile in all TK samples is likely to reflect contaminated industrial and municipal discharges.

To characterize the underlying processes and sources, factor analysis was applied (see Fig. 3). For the unrotated matrix, 21 factors had an eigenvalue above 1. For the rotated matrix, factor 1 and 2 represent 16% and 12 % of the total variance, respectively. Here, samples with a positive factor 1 are old sediments of the deepest segments investigated. Therefore, this factor may represent transformation processes, but a systematic effect caused by the congeners below detection limit can not be excluded. For negative factor 2, indicator congeners for PCP-related sources are identified: 1,2,3,6,7,9-/1,2,3,6,8,9-HxCDD; 1,2,4,6,8,9-HxCDF; 1,2,3,4,6,8,9-HpCDF. In the corresponding WS and TK samples, PCP-related sources are therefore more relevant than in other samples.

Fig. 3 Score plot (above) and loading plot (below) of factor analysis





Conclusions

The sediment profiles of the five locations in North-East Germany span a broad range from a background sample without any direct human influence to samples heavily affected by industrial and other anthropogenic activities. The PCDD/F concentrations of sediments close to human activity tend to decrease close to the surface while at remote sites the highest concentrations are still observed at the surface sediments. The BS sediment profile without any surface water influx indicates the background levels influenced only from deposition. Factor analysis indicates the importance of PCP-related sources, particularly for some WS and TK samples.

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References

(1) Kjeller, L.-O.: Doctoral Thesis, Umeå University, Sweden 1998.
(2) Alcock, R. *et al.* Environ. Sci. Technol. **1998**, 32, 1580-1587.
(3) Macdonald, R.; Ikonomou, M.; Paton, D. Environmental Sci. Technol. **1998**, 32, 331-337.
(4) Thomas, V.; Spiro, T. Environ. Sci. Technol. **1996**, 30, 82A-85A.
(5) Rotard, W. *et al.* USWF – Z. Umweltchem. Ökotox. **1995**, 7, 3-9.
(6) Bonn, B. Environ. Sci. Technol. **1998**, 32, 729-735.
(7) Schramm, K-W.; Winkler, R.; Casper, P.; Kettrup, A. Wat. Res. **1997**, 31, 1525-1531.
(8) Pearson, R *et al.* Environ. Sci. Technol. **1997**, 31, 2903-2909.

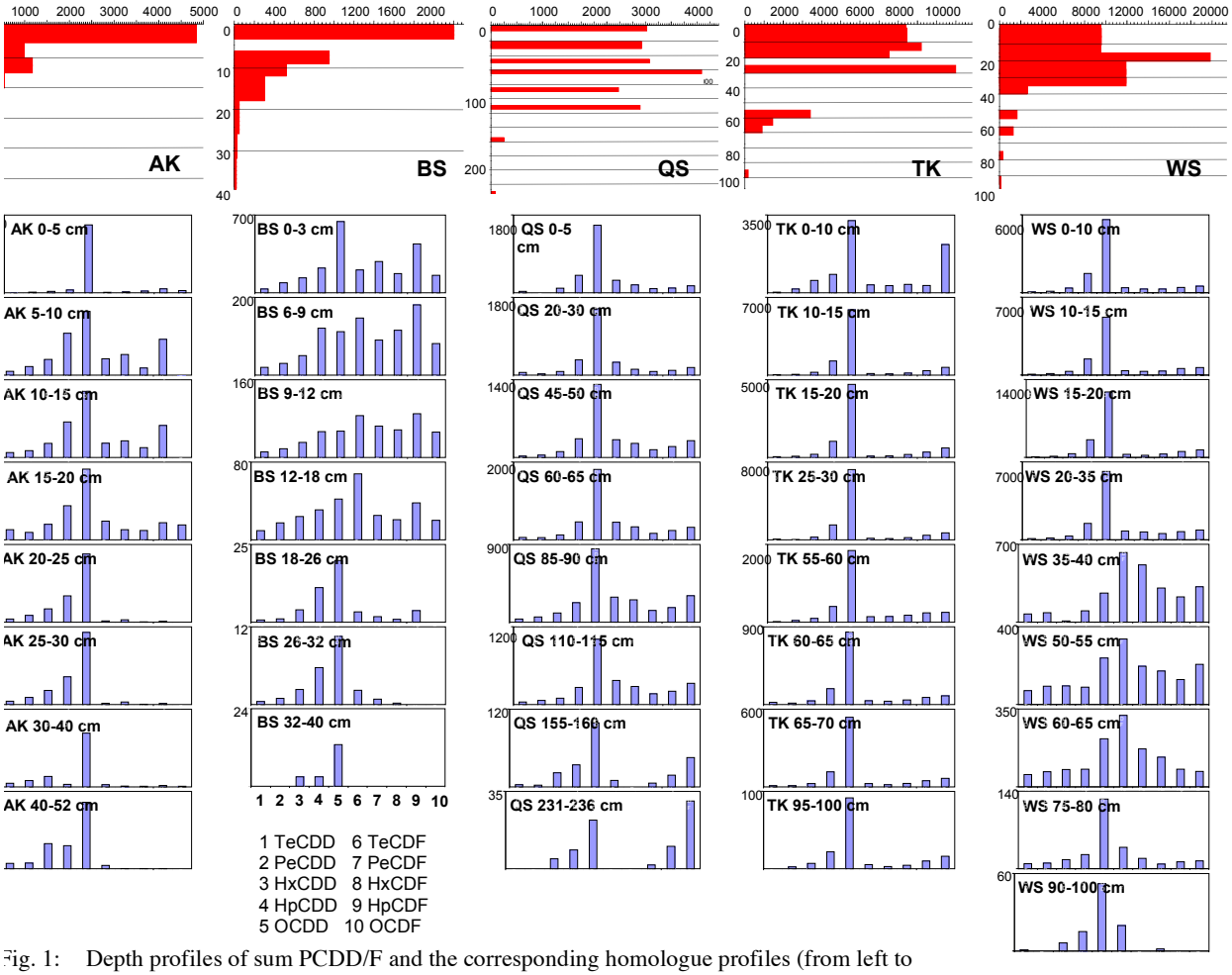
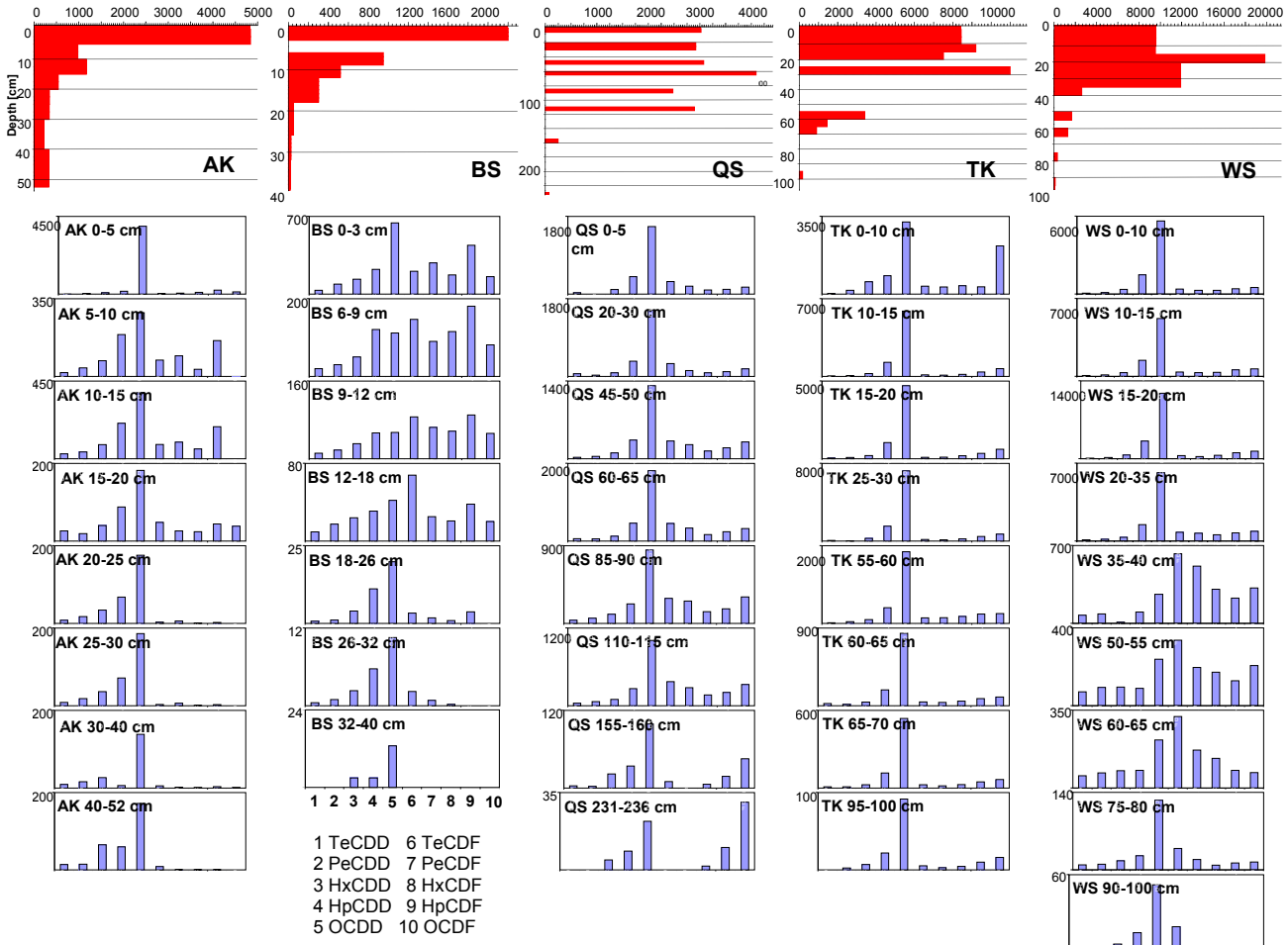


Fig. 1: Depth profiles of sum PCDD/F and the corresponding homologue profiles (from left to right: TeCDD, PeCDD, HxCDD, HpCDD, OCDD, TeCDF, PeCDF, HxCDF, HpCDF and OCDF) in sediment cores of North-East Germany (PCDD/F content in pg/g d.w.)



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