SOURCE IDENTIFICATION OF PCDD/Fs IN SEWER BIOFILM OF INDUSTRIAL AND MUNICIPAL SEWAGE

Matthias Koch [1], Wilhelm Knoth [2], Wolfgang Rotard [1]

1. Technische Universität Berlin, Sekr. KF3, FG Umweltchemie, Strasse des 17. Juni 135, 10623 Berlin, Germany
2. Umweltbundesamt, Aussenstelle Langen, Labor f. Dioxine u. PBT, Paul-Ehrlich-Str. 29, 63225 Langen, Germany

Introduction

PCDD/F levels in municipal sewage sludge have been of concern for many years. Closure of point sources and prohibition of PCP usage have led to reduced levels in sewage sludge. Most sewage treatment plants have reached sludge levels below the limit value for land application of 100 pg I-TEq/g in Germany, but few plants still have sludge levels above this guideline[1]. Because sludge application on agricultural land remains an important secondary PCDD/F source to the environment, further reductions in the PCDD/F levels of municipal and industrial sewage remain a strategic goal.

In this study, we report about the PCDD/F levels and patterns in sewer biofilm of industrial and municipal sewage and their source identification.

Materials and Methods

Twenty-two sewer biofilm samples were taken between March and December 1999 in several German municipalities. Each sample was mainly affected by one of the following industrial and municipal effluents: Metal processing and finishing, textile, leather tanning, printing, pharmaceuticals, solid waste processing and dump site, street run off, airport, swimming pool, harbour, hospital and university.

PCDD/Fs analysis was performed on 8 – 10 g of freeze-dried samples, spiked with a mixture of 17 $^{13}C_{12}$-standards, and extracted in an accelerated solvent extractor™ (Dionex). Clean-up was performed as previously described [2]. It consisted of a multicolumn clean-up including alumina-, mixed-silica-, Bio-Beads™- and micro-alumina-columns. Resolution and quantification of PCDD and PCDF were performed on a HRGC-LRMS (Fisons GC8000 and MD800). 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. Method blanks were routinely analyzed, and no contributions were detected. The peak assignment to individual congeners on SP-2331 is performed according to Ryan[3]. The PCDD/F contents are given on dry weight basis. SPSS v9.0 was used for statistical evaluation.

Results and Discussion

PCDD/F levels

The sum PCDD/F levels in the sewer biofilm samples were 0.07 – 11 ng/g. The corresponding PCDD/F I-TEq concentrations were 0.65 - 86 pg I-TEq/g. Table 1 shows the percentiles of the

sum PCDD/F and I-TEq concentrations. All sewer biofilm samples had concentrations below 100 pg I-TEq/g.

Table 1: Minimum, maximum, median and percentiles of sum PCDD/F and I-TEq concentrations (N=22)

	minimum	10 % percentile	25 % percentile	median	75 % percentile	90 % percentile	maximum
sum PCDD/F (ng/g)	0.07	0.16	0.9	1.4	1.9	4.3	10.8
I-TEq (pg/g)	0.65	1.3	3.2	6.0	9.2	60.6	85.6

High levels were found in the following sewer biofilm samples, near a harbour, an airport and a solid waste dumpsite/composting facility. Their PCDD/F levels were 11 ng/g, 4.4 ng/g and 4.2 ng/g, respectively. The corresponding I-TEq concentrations were 85 pg I-TEq/g, 72 pg I-TEq/g and 13 pg I-TEq/g, respectively. We see this as an indication that the historic burden of the past is responsible for the high levels in the effluents of the dump site and that desinfection activities or contamination of goods may be responsible for the high levels found in sewage of the airport and the harbour.

A working hypothesis that industrial effluents in relation to textile and leather could show high PCDD/F levels was not confirmed. The PCDD/F levels in the sewer biofilm of a tannery and a textile processing company were not elevated: 0.11 ng/g and 1.6 ng/g, respectively. Horstmann and McLachlan[4] and Malisch[5] had reported about high levels in textiles and leather samples, respectively.

Homologue profiles

The homologue profiles were very similar to those earlier reported for sewage, sewer biofilm and sludge [1, 6]. OCDD dominates the homologue profile. A Box-Whisker plot of the profiles is given in Figure 2. The homologue profiles of the sewer biofilm samples are generally very similar to that of PCP [7]. Only few samples showed differences in the typical profile: The airport and a pharmaceutical company also had substantial amounts of lower chlorinated PCDFs (see Figure 3).

Isomeric patterns

The three samples with high PCDD/F levels show characteristic PCDF isomeric patterns:

- The airport sewer biofilm is similar to the pattern of Clophen A60. The dominance of 1,2,4,7,8-PeCDF, 1,2,3,6,8-/1,3,4,7,8-PeCDF and 2,3,4,7,8-PeCDF found in the chromatogram of this sample is well known for the PCB formulation Clophen A60 [7].
- The sewer biofilm sample of the pharmaceutical company has a pattern similar to chlorine bleaching [8, 9]. Their TCDF chromatogram has 2,3,7,8-TCDF and 1,2,7,8-TCDF as largest peaks.
- The harbour sample has a pattern known from PCP [7]. 1,2,4,6,8-PeCDF is the most abundant PeCDF congener.

Figure 4 gives an overview of the PCDF isomeric patterns of the three samples.

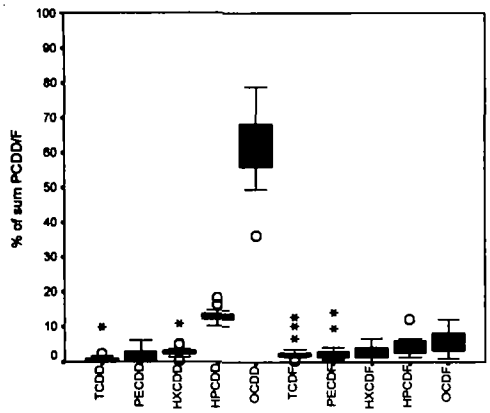

Fig. 2: Box-Whisker plots of the homologue profiles in the sewer biofilm samples (N=22)

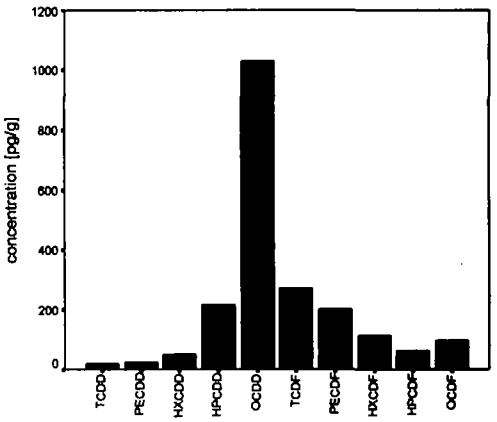

Fig. 3: Homologue profile of the sewer biofilm sample of a pharmaceutical company

Conclusions

Sewer biofilm was sampled near various types of industries in several German municipalities. All sewer biofilm samples had levels below 100 pg I-TEq/g. Three samples had a sum PCDD/F concentration above 4 ng/g. Even though the homologue profile was generally very similar, with a dominant contribution of OCDD, the isomeric pattern showed characteristic differences. Three samples with high PCDD/F levels were affected by the following sources: Theairport sample by PCB (Clophen A60), the effluents of a pharmaceutical company by chlorine bleaching and the harbour sample by PCP. The similarity of the homologue profiles for most sewer biofilm samples indicates that the homologue profile is of little help to identify PCDD/F sources of sewage-related matrices. The homologue profile seems to be unified by physico-chemical transfer processes between the emitting source and the sampling location.

Acknowledgements

We would like to thank Winfried Mann and Judith Nebhuth for dioxin analysis and Martin Gehring for preparing some diagrams. Financial support of the German Federal Ministry for Education and Research under contract no. 02WU9894/2 is gratefully acknowledged.

References

1. Koch, M., W. Knoth, and W. Rotard, *Chemosphere,* accepted.
2. Rotard, W., *et al., UWSF - Z Umweltchem Ökotox,* 7 (1995) 3-9.
3. Ryan, J.J., *et al., J. Chromatography,* 541 (1991) 131-183.
4. Horstmann, M. and M.S. McLachlan, *Environm Sci Poll Res,* 1 (1994) 15-20.
5. Malisch, R., *Organohalogen Compds,* 19 (1994) 73-76.
6. Rappe, C., L.-O. Kjeller, and R. Andersson, *Chemosphere,* 19 (1989) 13-20.
7. Brunner, H., PhD Thesis, Universität Tübingen, 1990.
8. Swanson, S.E., PhD Thesis, Umeå University, 1988.
9. Rotard, W., W. Christmann, and W. Knoth, *Organohalogen Compds,* 4 (1990) 381-386.

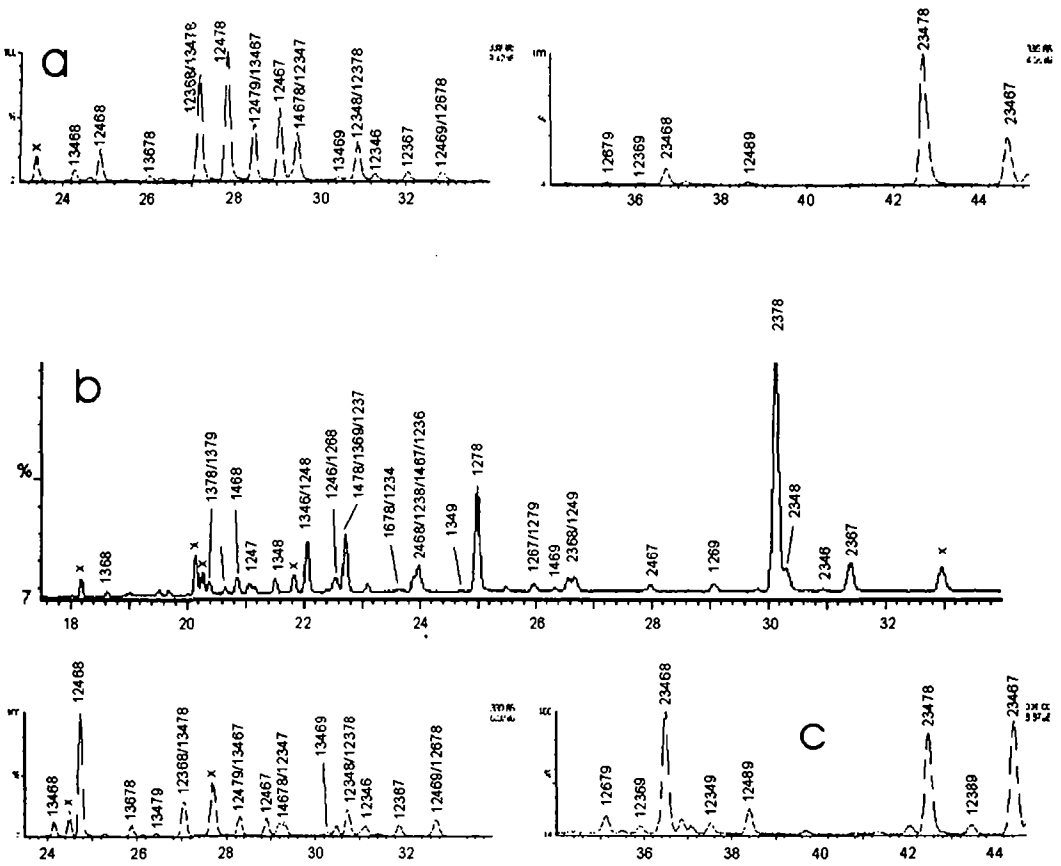

Fig. 4: PCDF chromatograms of the sewer biofilm samples related to an airport (a: PeCDF), a pharmaceutical company (b: TCDF) and an harbour (c: PeCDF); x: no PCDD/F