

SEARCH FOR SOURCES OF CL_xDD / CL_xDF IN SEWAGE SLUDGE OF MIXED
INDUSTRIAL / DOMESTIC ORIGIN

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Abstract:

Polychlorinated dibenzo-dioxins (CL_xDD) and -furans (CL_xDF) are among the most important organic pollutants in municipal sewage sludge. Their origin can be based on various anthropogenic sources. [1]

Our project aims at the localization of CL_xDD/CL_xDF inputs and possible correlations between sources and pathways into the sewage system of Ulm city. Specific sources were detected in two defined sectors of the city. Although the sources are not yet completely identified, the pattern and profile of the CL_xDD/CL_xDF pollution indicates a thermal process as origin.

Introduction:

The profile as well as the pattern of chlorodibenzodioxins (CL_xDD) and -dibenzofurans (CL_xDF), which contaminate the sewage sludge of Ulm city, are unique in certain features and constant over time in comparison to sewage sludges from other cities [1]. A significant pentachlorophenol-correlated input, normally the major source in municipal sewage sludge [2], can be ruled out. Thus a specific source within the city area is likely. The waste water treatment plant of the city of Ulm processes communal, industrial and mixed waste water as well.

Experimental:

In search for possible sources samples of sewer films were investigated. The sewer film found in the sewage system is a material with a high content of fat and therefore is able to trap lipophilic compounds. The existence of sewer films is a result of a dynamic equilibrium between waste water burden and flow speed. The content of compounds accumulated in the films averages over a period of several months or even years at a given location depending on the film's age.

Several samples of sewer films and sewage sludge from Ulm city and its outskirts were collected in order to localize defined input areas. The sampling sites were strategically placed in housing areas, industrial areas and mixed areas.

Polychlorinated paraffins (CP: C_xH_{2x+2-y}Cl_y) are analysed additionally as an indicator for metal-manufacturing industries. Also p,p'-DDE and PCB are included in the investigation. A special clean-up procedure was developed for this purpose, yielding three fractions containing CP, PCB and CL_xDD/CL_xDF. Quantification was done by HRGC on SE 54 and SP 2331/DB Dioxin with ECD and MSD.

Results:

The interpretation of the analytical results is based on the following data sets:

- sum of all chloro homologues Cl_xDD / Cl_xDF ($x = 1-8$) ("profile")
- isomer-specific analysis of Cl_xDD / Cl_xDF ($x = 1-8$) ("pattern")
- toxic equivalent (TE) - values (NATO-system)
- further indicator molecules [3]

Figure 1 shows the total burden of Cl_xDD / Cl_xDF and TE-values in a flow chart. A high level input of Cl_xDD / Cl_xDF was found in a defined sector of the city (F-2) in comparison to other sampling sites of the area (F-3: industrial, F-1: urban and F-4: mixed), where the levels of Cl_xDD / Cl_xDF were neglectable. The presumed source(s) appear to be not diffuse but punctual and the location(s) are restricted within the city centre. The homologue profile (Fig. 3-5) and the isomer patterns indicate a thermal process to be the main source.

More detailed information about the location(s) and type of the possible sources were obtained by a closing-in of the input at the area F-2. Figure 2 illustrates the input levels of the main pathways feeding F-2.

Two major input areas were localized. Area F-7 is a suburb with partly industrial and partly housing areas (TE: 100 ng TE/kg). The highest levels were found at area F-6 (TE: 200 ng TE/kg), a suburb with only some small industry sites. The homologue profile (Fig. 3-5) and the isomer pattern confirm the existence of thermal sources within both areas.

Further indicator molecules:

Other groups of compounds (CP, PCB, *p,p'*-DDE) proved to be significant as indicator molecules. Chloroparaffines (CP) are commonly used as additives in metal-processing industry, which is partly present in Ulm. Polychlorobiphenyls (PCB, as a sum of 7 congeners), can also be considered as an industrial parameter. The *p,p'*-DDE seems to be a good indicator for inputs from housing areas.

In this study the levels of CP and PCB correlate with areas where metal-manufacturing industry is localized. The *p,p'*-DDE levels give a positive correlation with the estimated number of citizens in each input area.

Conclusion:

1. The major input of Cl_xDD/Cl_xDF into Ulm sewage system is caused by two specific sources, located in areas F-6 and F-7.
2. The characters of both sources are similar and hint towards thermal processes generating Cl_xDD/Cl_xDF .
3. The indicator molecules CP and PCB yield additional information about each input area, but do not directly correlate to the Cl_xDD/Cl_xDF input.

References:

- [1] Bacher R., Dissertation Dr. rer. nat., University of Ulm, (1992)
- [2] Hagenmaier H., Brunner H., Haag R., Berchtold A.,
Chemosphere (1986);15: 1421-1428
- [3] Swerev M., Ballschmiter K., *Chemosphere* (1989);18: 609-616

Fig.1: Series 1 (Jan. '91)
total Cl_xDD + Cl_xDF [ng/kg]
TE-values [ng TE/kg]

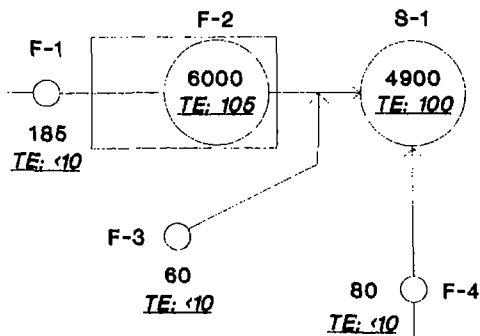


Fig. 1: Flow chart of Cl_xDD/Cl_xDF inputs in the sewer system of the city of Ulm (circles represent sampling location and quantity)

Fig.2: Series 2 (Sep. '91)
total Cl_xDD + Cl_xDF [ng/kg]
TE-values [ng TE/kg]

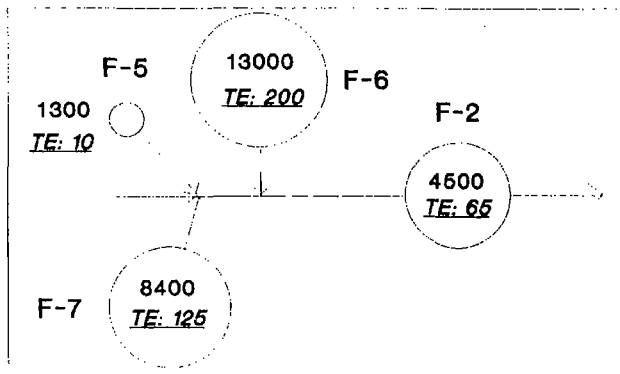
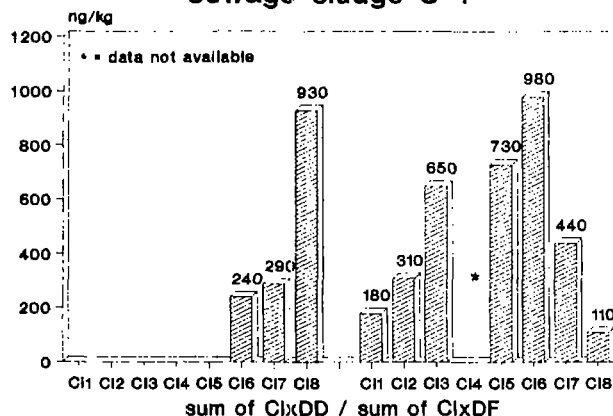


Fig. 2: Flow chart of Cl_xDD/Cl_xDF inputs in area F-2 (Fig.1) of the sewer system of the city of Ulm

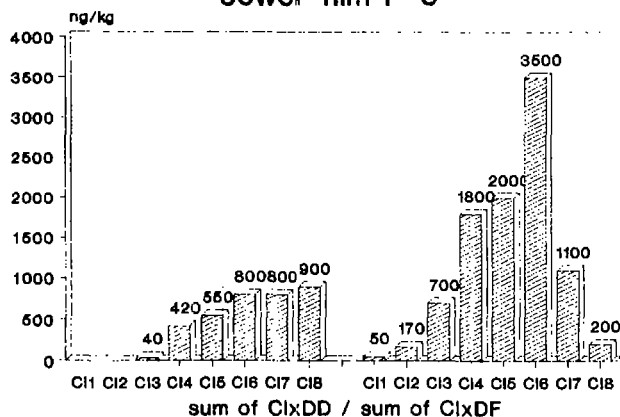
sampling sites:

S-1	sewage sludge (Sewage treatment plant)	F-4	mixed sources
F-1	housing area	F-5	housing area
F-2	mixed sources (city centre)	F-6	mixed sources
F-3	industrial area	F-7	mixed sources

**Fig.3: homologue profile
 sewage sludge S-1**



**Fig.4: homologue profile
 sewer film F-6**



**Fig.5: homologue profile
 sewer film F-7**

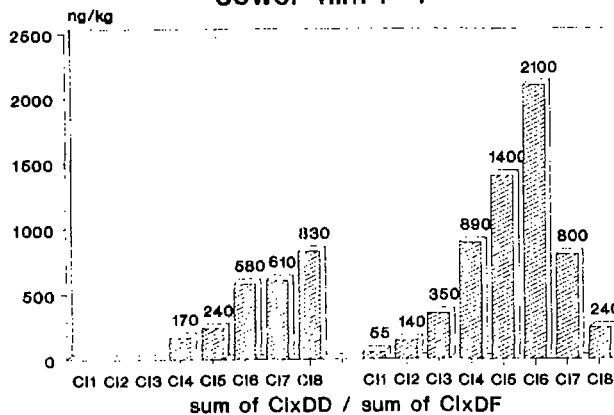


Fig. 3-5: homologue profile of samples S-1, F-6 and F-7.