Contents of PCDD/PCDF in soil, kale and deposition in an area in southern Saxony-Anhalt

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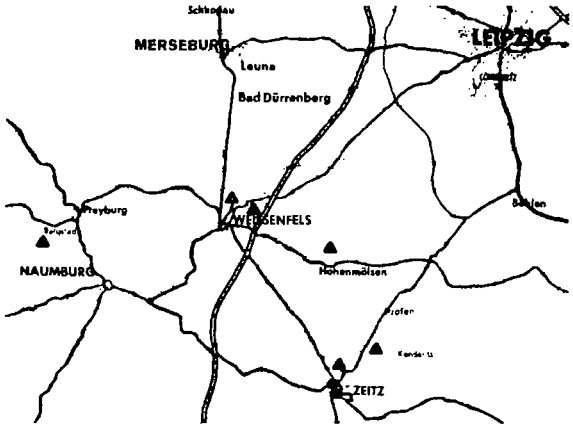
Abstract
Polychlorinated Dibenzodioxins and -furans (PCDD/F) have been detected within three media, bulk-deposition, plant material (curly kale) and soil, in an industrialized area in southern Saxony-Anhalt. An overview of the pollution concerning these compounds is given.
An attempt is made to draw conclusions about the transfer behaviour of PCDD/F from the homologue profiles of the different sample media.

Introduction
The industrialized and relatively densely populated area in southern Saxony-Anhalt is generally seen as heavily environmentally polluted. Typical (exemplary) for this middle German region is the area Zeitz/Naumburg/Weißenfels. But are PCDD/F also part of this environmental pollution? Up to now no sufficient data are available. This paper should make a contribution to gain an overview of the pollution with PCDD/F.
PCDD/F are mainly distributed via atmospheric transport processes. To evaluate the current pollution of an area the deposition has to be determined because this is the pathway of PCDD/F removal from the atmosphere. Two deposition processes are essential: wet and dry deposition. Both contribute significantly to the removal of particle-bound PCDD/F[1]. The residence time of particles deposited on a surface is depended on the size of the particle and increase with decreasing diameters. Häberle et al.[2] reported that residence time amounts to about 4-40 days and thus is smaller then the half-life of particle-bound PCDD/F. Therefore investigations of deposition samples are able to indicate the input level of PCDD/F pollution of the environment. The less chlorinated congeners have higher vapor pressures and significant amounts are found in the vapor phase, thus they are exposed to photodegradation. They can also be transfered as gaseous dry deposition onto surfaces causing the pollution of other media. The gaseous dry deposition is of importance[3] because the gaseous phase uptake from the ambient air of PCDD/F in plants is link to human exposure via the food chain. That and other valuable information about the transfer behavior can be obtained by comparing the homologue profiles of the different sample media. Taking into account both deposition processes, we have investigated bulk deposition samples as well as kale samples. Soil samples were also taken.

Sampling
The samples were taken at six locations. Municipal as well as locations outside municipal areas were selected. Figure 1 shows the location of the field stations. The deposition samples were taken by the use of cylindrical stainless steel containers with a volume of 13000 cm^3 and an effective cross section of about 490 cm^2. Three sampling devices were exposed at a hight of

Fig. 1: Location of the field stations



1,50m for about 6 weeks to the ambient air at each site. The sampling period was carried out for 11 mounths, from May 1993 to March 1994. In order to have enough mass for the later laboratory analysis, the contents of the three sampling containers at each site were combined for one analysis.
The cultivation of the cury kale plants was carried out under standardized conditions in a glasshouse. At each site two plants were exposed at a hight of 1.50 m for 6 weeks in October and November 1993. The kale was grown in flower boxes. Water was provided through glass fibre wicks connecting the soil to a water reservoir.
The sampling areas where the soil samples were taken were used as farm land, grass land and allotment gardens. At each site 10 individual samples to a maximum of 5 cm depth for grass land and to a maximum of 30 cm for plowland were mixed to get a representative sample for analysis.

Experimental

The particulate matter of the bulk deposition was separated from the water by filtration. The filter paper was dried and extracted in a Soxhlet extractor with toluene for 24 hours. The filtrate was extracted three times with 50 ml toluene in a shaking device. After the phase separation the extract was desiccated with anhydrous sodium sulphate.
The kale samples were freeze dried and were minced in a blender and Soxhlet extracted for 48 hours in toluene.
The homogenized soil samples were sieved and the fraction <2 mm was Soxhlet extracted for 24 hours.
All samples were spiked with an isotopically labelled PCDD/F standard prior to the Soxhlet extraction step. The clean up is similar to the procedure described in VDI-Richtlinie 3499. Briefly, this procedure entails a series of liquid chromatographic clean up sequences, which include a celite column, a basic alumina column and a combination silica gel column containing acid modified, base modified and neutral silica gel and silver nitrate/silica-gel. The details of the procedure are desribed elsewhere[4].
The HRGC/HRMS analysis was conducted at a resolution of 10 000 on a Finnigan MAT 95 Masspectrometer.

Results and discussion

The results from the present study are given in Table 1 as average values. The results of bulk-deposition samples showed low levels of PCDD/ PCDF. Samples at all sites have consistently higher levels in the winter than in summer. These seasonal variations in sample concentrations observed within a sampling site are larger than the variations resulting from different sampling locations. This result is confirmed by earlier findings at other regions in Germany[5,6,9]. The concentrations correlate better with reported levels measured away from industrial sources, but not with those reported at urban locations. It is most probable that the variations in deposition

Tab 1: levels of PCDD/PCDF

deposition	average summer	0.33	pg I-TE $m^{-2}d^{-1}$
	average winter	20. Apr	pg I-TE $m^{-2}d^{-2}$
cury kale		1.1 - 3.1	pg I-TE g^{-1} DW
soil	farmland	0.6	pg I-TE g^{-1} DW
	grassland	2.6	pg I-TE g^{-1} DW
	allotment gardens	9.5	pg I-TE g^{-1} DW

samples amoung the different sampling sites are small because there is not a sharp distinction between residential areas and rural areas.

The PCDD/F concentration in curly kale ranged from 1.1pg I-TEg^{-1} DW (dry weight) to 3.1 pg I-TEg^{-1} DW. This result compared with reported values at other locations in Germany show that the investigated area is amoung the least PCDD/F polluted areas. These low concentrations are below the reported ranges of urban sites and are similar to a level typical for a rural environment. Reported field experiments within a large German city showed that the concentrations in soil and green kale are not correlated[7]. We observed this also. In addition there is not a connection between concentrations in curly kale and in depositions.

The concentrations in the soil samples are generally low. The total levels of PCDD/PCDF measured in the farmland samples are found to be between 0.3 and 0.9 pgI-TEg^{-1}DW. As would be expected the levels in grassland are somewhat higher. The value for garden soil was taken from a single measurement; it is shown for a comparison and is not further discussed in this report.

In comparison with other published data our soil values are somewhat lower than the levels at urban regions and lie within the same general range as sampling sites outside industrial and urban regions of Germany[8].

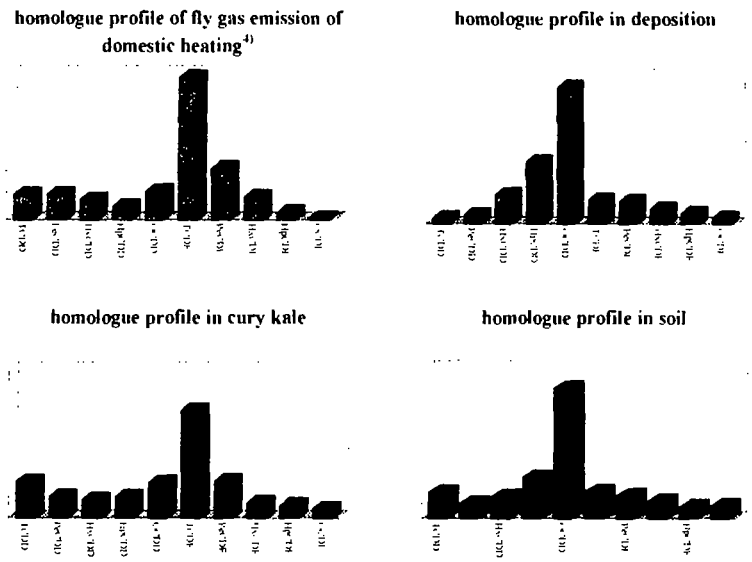
Regarding the quantitative results (given in Table 1) for the different sample media the following statements can be made:

- PCDD/PCDF levels in deposition samples were at the same level as those in German areas located far from potential sources of PCDD/F
- the seasonal variation of the PCDD/PCDF deposition showed a minimum in the summer
- the low concentrations in all sample-media are below the range of industrial sites and are more comparable to levels typical for a rural environment

Figure 2 shows typical homologue profiles measured in this study. For comparison the emission-profile of domestic lignite combustion[4] is added. The homologue patterns of the deposition samples are characterised by low TCDD levels and increasing levels of penta-, hexa-, hepta- and octa-CDD as well as a decrease in PCDF with increasing chlorination. The difference between deposition-profile and emission-profile can be explained by gas-particle distribution of the compounds.

The profile of cury kale displays a characteristic profile with PCDF greatly exceeding PCDD. This profile corresponds better with the emissions-profile than with the deposition-profile, because a part of the PCDD/F in the gas phase is transfered into plants. Reasons for differences in the two profiles include degradation of PCDD/F in the gas phase and the relative long time in takes for equilibrium to be established between the concentration in the gas phase and on the plant surface.

Fig. 2: Comparison of homologue profiles



Independent of the type of soil cultivation, the homologue profils of the soil samples were generally similar. Here the homologue profile display the typical pattern for entry of PCDD/F in the soil from the atmosphere.
In conclusion the results show that there was a low level of PCDD/F entry in the test region. The entry of PCDD/F into the area is characteristic for the atmospheric pathway.

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