Correlation of Environmental Occurance of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans with Possible Sources

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Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) have been demonstrated to occur in nearly all environmental compartments, such as soil, lake and river sediments, and air, in aquatic organisms, plants, and human tissues. The majority of the PCDD/PCDF found in the environment today is of anthropogenic origin. To minimize the risk for human health by these highly toxic compounds it is of great importance to recognize the main sources of PCDD/PCDF and to correlate the environmental occurence of PCDD/PCDF with these sources. Only then it will be possible to minimize the amount of PCDD/PCDF discharged into the environment on an economical basis.
According to our present knowledge major sources are thermal processes in the presence of a chlorine source such as combustion and metallurgic processes, industrial processes based on chlorine chemistry and application of PCDD/PCDF-containing chemicals.
Previous methods applied for source identification are the comparison of the homologue profiles, the comparison of the congener profiles of the 2,3,7,8-substituted PCDD/PCDF, and the comparison of the isomer distribution patterns.
1) Comparison of the homologue profiles
Most frequently the profiles of the ten homologue groups of tetra- to octachlorinated PCDD/PCDF are used for the detection of sources. Characteristic homologue profiles of some sources are shown in Figure 1. The diagrams are based on the mean values of n analytical samples. For the calculation of the arithmetic mean values all analytical data were normalized to the total sum of PCDD and PCDF = 1000.
The homologue profiles of various "thermal" sources show some consistencies and at the same time some variation. PCDD are usually dominated by PCDF, at least in the stack gases. The homologue profiles of ambient air and deposition are different, *for so far unknown reasons. The homologue profiles of some chemicals, e.g.* pentachlorophenol (PCP), polychlorinated biphenyls (PCB), and of electrode sludges

from the chloralkali electrolysis are completely different from those of thermal processes and differ between each other.

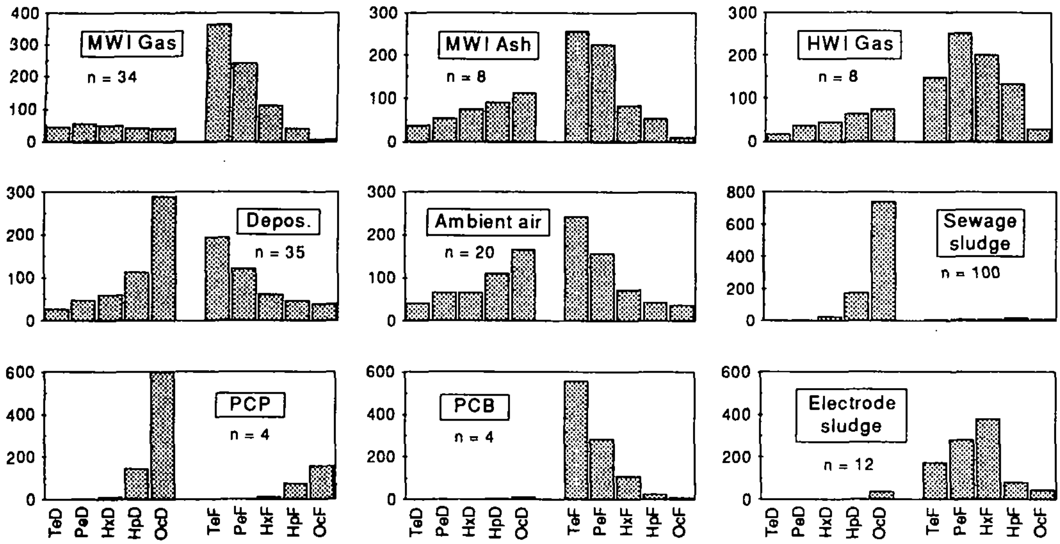

Figure 1 Comparison of some characteristic PCDD/PCDF homologue profiles

However, changes in the homologue profiles can occur temporally and spatially from the source to the sample under consideration resulting in misinterpretation regarding the source. Therefore, the applicability of the comparison of homologue profiles for source identification in environmental samples is limited.

2) Comparison of the congener profiles of the 2,3,7,8-substituted PCDD/PCDF

The congener profiles of different thermal processes (not demonstrated) show also some variation, however, the differences in the congener profiles are smaller than that in the homologue profiles. As with the homologue profiles, the congener profiles of chemicals (PCP, PCB, and chlorine production) are completely different from those of thermal processes. The profile of PCP looks like the profile of sewage sludge. However, in some cases the comparison of congener patterns of sources and environmental samples resulted in discrepancies, e.g. the comparison of ambient air samples and deposition samples of the same site.

3) Comparison of the isomer distribution patterns

The mass fragmentograms, obtained in dioxin analysis by GC/MS, are such patterns. In some cases, the non-2,3,7,8-substituted isomers are of great importance in characterizing the different sources, e.g. 1,2,4,6,8,9-HxCDF and 1,2,3,4,6,8,9-HpCDF to identify PCP as a dioxin source. However, the data of non-2,3,7,8-substituted isomers are not available in many cases, because they are not included in routine dioxin analysis reports.

4) Comparison of the profiles of the relative congener concentrations of the 2,3,7,8-substituted PCDD/PCDF

Because of the limitations of the previous methods in source identification we have developed a new strategy. This strategy is based on the assumption that the concentration changes in the environment of all isomers within one homologue group show the same tendency. Therefore the profiles of relative congener concentrations should be subjected to changes in the environment to a lower degree than the homologue profiles.

We calculated the ratio of the concentration of the 2,3,7,8-substituted congeners to the concentration of the corresponding homologue group. The concentrations of OCDD and OCDF are divided by the concentration of PCDD and PCDF, respectively. The patterns are completed by the PCDD/PCDF ratio in form of the quotient of PCDD concentration and the total concentration of PCDD+PCDF. The profiles of the relative congener concentrations of the same average samples as in Figure 1 are given in Figure 2.

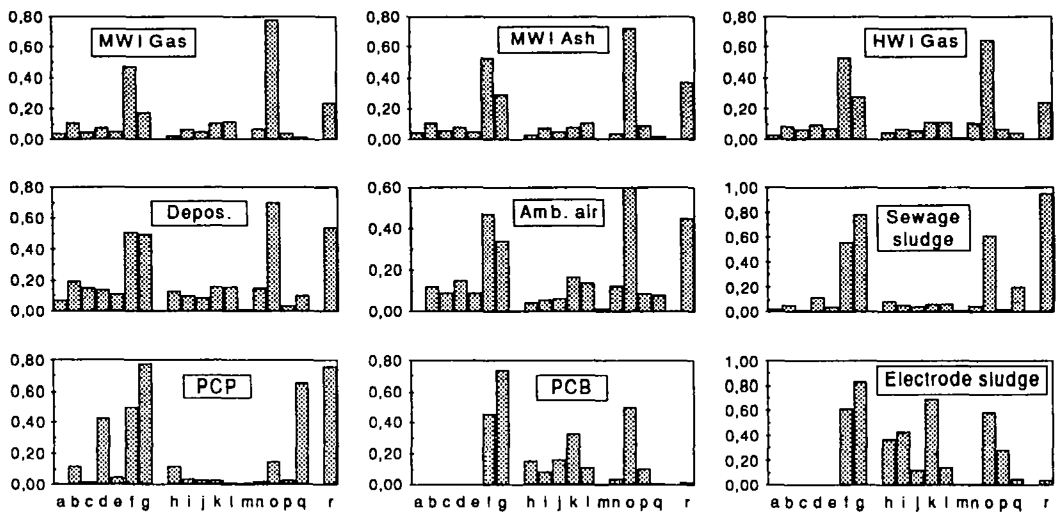

Figure 2 Comparison of patterns of relative PCDD/PCDF congener concentrations
a-f , h-p : ratio of the content of the 2,3,7,8-substituted congener to the content of the corresponding homologue group; g: [OCDD]/[PCDD]; q: [OCDF]/[PCDF]; r: [PCDD]/([PCDD] + [PCDF])

The application of this procedure to the average source analyses results in a close similarity of the relative congener profiles for all thermal processes including automobil exhaust and metallurgic processes (not demonstrated). That implies that the isomer distribution patterns for different thermal processes are quite similar and relatively constant. The isomer patterns of deposition and ambient air are very similar, too. That means that the processes taking place in the air path are homologue-specific but not isomer-specific. Therefore, one should get more information on sources from the relative congener profiles. In contrast to the homologue profiles the relative congener profiles of sewage sludge samples with low PCDD/PCDF concentrations differ significantly from the PCP profile and suggest that the main PCDD/PCDF source of these sludges is of "thermal" origin.

The comparative analysis of the profiles of relative congener concentrations can - besides visual comparison - best be carried out by cluster analysis. Cluster analyses were conducted with a PC using the statistical software SPSS/PC+ (Version 4.0.1) with the algorithm 'Cosine of vectors of variables' as a pattern similarity measure. The results are represented graphically by a dendrogram, in which profiles of samples or groups of greatest similarity are linked together first. The distance between any one sample from each of the others is a measure of the similarity (or dissimilarity) between the sample profiles.

In Figure 3 we compare the dendrograms resulting from the homologue profiles and the profiles of relative congener concentrations of sewage sludge samples, taken from thirty waste water treatment plants in Western Germany, and of some characteristic sources and environmental samples (mean values).

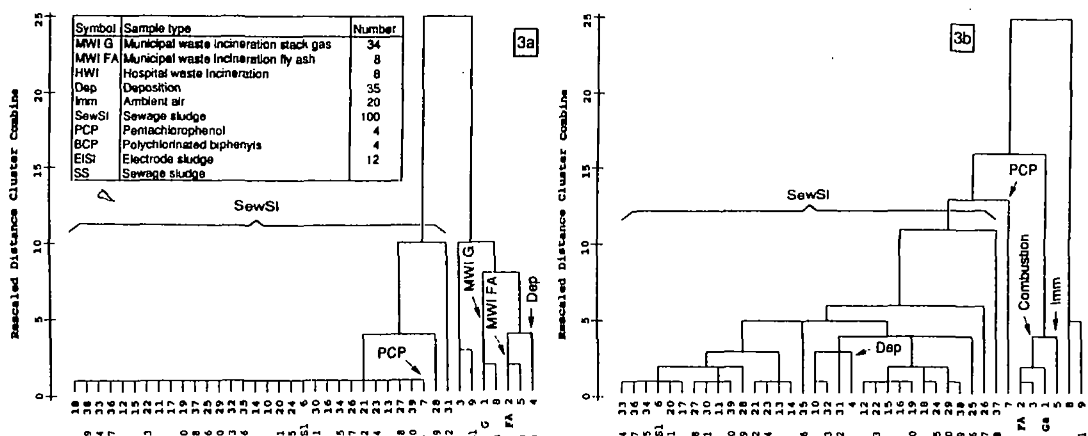

Figure 3 Comparison of the dendrograms of homologue profiles and profiles of relative concentrations of 2,3,7,8-substituted congeners of PCDD/PCDF

In the dendrogram of the homologue profiles (3a) sewage sludge and PCP profiles are linked together first. There is no relation to deposition or thermal processes. Contrary to 3a, in the dendrogram of the relative congener concentrations (3b) the sewage sludge profiles are grouped around the deposition profile and subsequently linked with that of PCP at a higher level. This corresponds to the result obtained, when isomer distribution patterns are compared. Cluster analysis of the relative congener concentrations can produce obviously plausible results.