ISOMER SPECIFIC ANALYSIS OF MONO- TO TRICHLORINATED DIBENZOFURANS AND DIBENZODIOXINS - ANALYSIS OF AMBIENT AIR

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Introduction

Due to the high toxicity of 2378-substituted PCDD/F, much attention was paid on the isomer specific analysis of tetra- to octachlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in the last two decades[1,2].
Since only the congers substituted in all four 2,3,7,8-positions exhibit the dioxin related toxicity, lower chlorinated congeners are not assigned with TEQ values and therefore, not much attention was paid on them.
However, the analysis of low chlorinated isomers seems interesting from several points of view. For the investigation of PCDD/F formation mechanisms, the low chlorinated compounds offer valuable additional information. For on line measurement of PCDD/F in e.g. waste incineration, some research projects recently focus on estimating TEQ values by measurement of low chlorinated PCDD/F[3]. To establish this correlation, it seems important to not only measure the total amount of the low chlorinated homologues but to calculate and correlate specific isomers. Furthermore, the low chlorinated PCDD/F may give valuable information for environmental samples. The analysis of isomer distributions in environmental samples is the key for estimating the origin of dioxins and related compounds. Also in this field, many data are published for T_4CDD/F-OCDD/F. However, no data are available for mono- to tri-chlorinated dioxin/furan.

Ballschmiter presented in his book[4] an uncompleted assignment of MCDD/DF-T_3CDD/DF on the SP-2331 column, including the analysis of a fly ash sample from incineration. Weber et al. reported the analysis of MCDF-T_3CDF on a Sil-88 column for stack gas and fly ash samples from fluidized bed incinerators[5]. In both studies, no complete isomer assignment was made.

The aim of this study was an initial identification of isomer and homologue pattern of dioxins in ambient air samples in Japan including the complete assignment of MCDD/DF-T_3CDD/DF.

Materials and Methods

Standards. All 74 congeners of the MCDD-T_3CDD and MCDF-T_3CDF were synthesized by pyrolysis of the respective chlorophenols or chlorobiphenyls. Additionally, all 23 commercially available isomers were obtained as authentic standard/mixtures for crosschecking the assignment.
Air Sampling. Air samples (1000 m^3) were collected by high volume air sampler with quartz fiber filter (QMF) for particulate and polyurethane foam plug (PUF) for the vapor phase sampling.
GC/MS Analysis. The analysis was carried out using a HP 5890 II gas chromatograph connected to a JMS-700 mass spectrometer (JEOL Ltd. Japan) (operating at a resolution >10 000).

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Temperature program used for isomer specific separation of the MCDD/F-T_3CDD/F on SP-2331 column (60m x 0.25mm x 0.25um): 120°C, 1 min. isothermal; 30°C/min. to 200°C, 2°C/min. to 260°C. Quantification was carried out by isotope dilution mass spectrometry.

Results and discussion

Air samples were taken in 26 different locations in Hyogo prefecture in the western part of Japan. For this study, we chose the data of 8 locations in rural areas to get an initial estimation of only "background levels", trying to avoid the influence of point sources. The TEQ values of all air samples were below 0.1 pg TEQ/m^3.

The chromatograms of MCDF-T_3CDF in a representative ambient air sample are shown in figure 1. The isomer patterns are characterized by a broad distribution of isomers in each homologue group. This is comparable to the pattern we found in some incineration samples and also Ballschmiter[4] in the fly ash from a MWI. Therefore, the origins of the low chlorinated PCDF are combustion sources in accordance with the origin of the major amount of T_4CDF-OCDF in ambient air.

The homologue distributions of the PCDF showed in all locations decreasing concentrations with increasing chlorination degree (Figure 2). In MWI, however, the DCDF and T_3CDF are normally less abundant than the T_4CDF-H_6CDF. The high abundance of MCDF-T_3CDF in the air samples may be explained by the higher volatility of the lower chlorinated isomers, resulting in a shift of homologue pattern due to gas phase - solid phase (soil) distribution. This has to be evaluated in more detail by field studies and the assistance of computer simulations.

Concentrations of MCDD-T_3CDD were detected in around one order of magnitude less than MCDF-T_3CDF in the respective samples. A chromatogram with an "average" isomer pattern is shown in figure 3 and the homologue distribution in figure 4. The isomer distribution also shows similarities with the combustion patterns. A more detailed investigation including PCA seems necessary after evaluating the isomer distribution of other possible sources.

Figure 2: Homologue distribution of PCDF

Figure 4: Homologue distribution of PCDD

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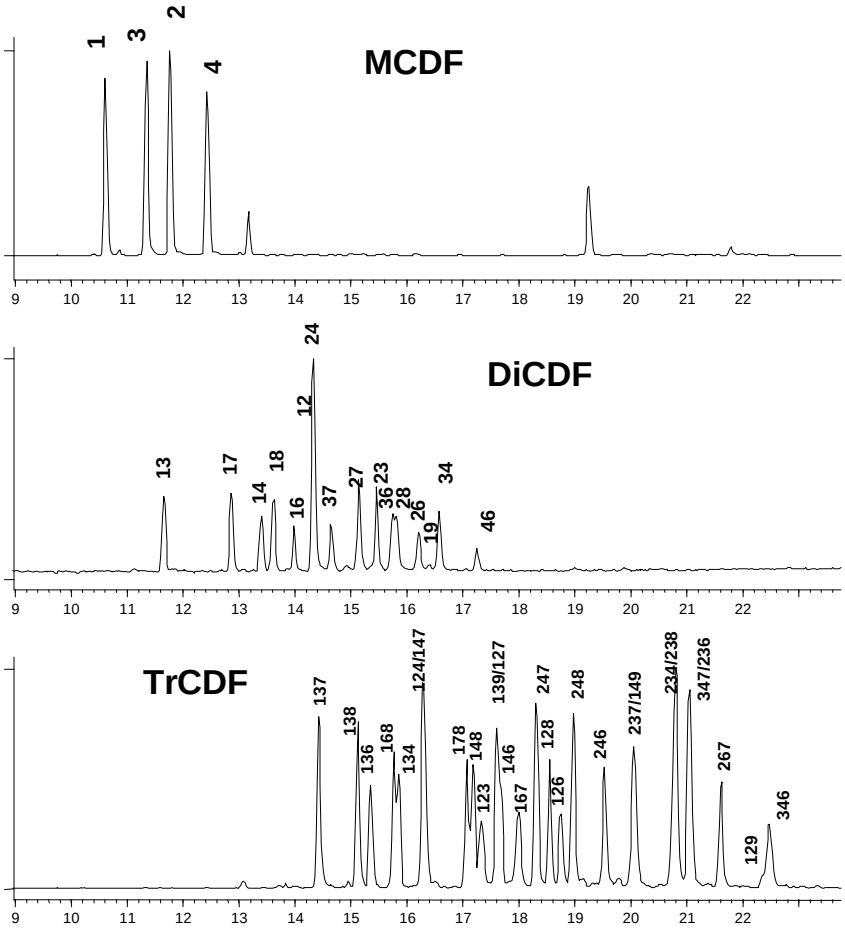

Fig.1 GC/MS-SIMChromatograms MCDF-T3CDF in a representative ambient air

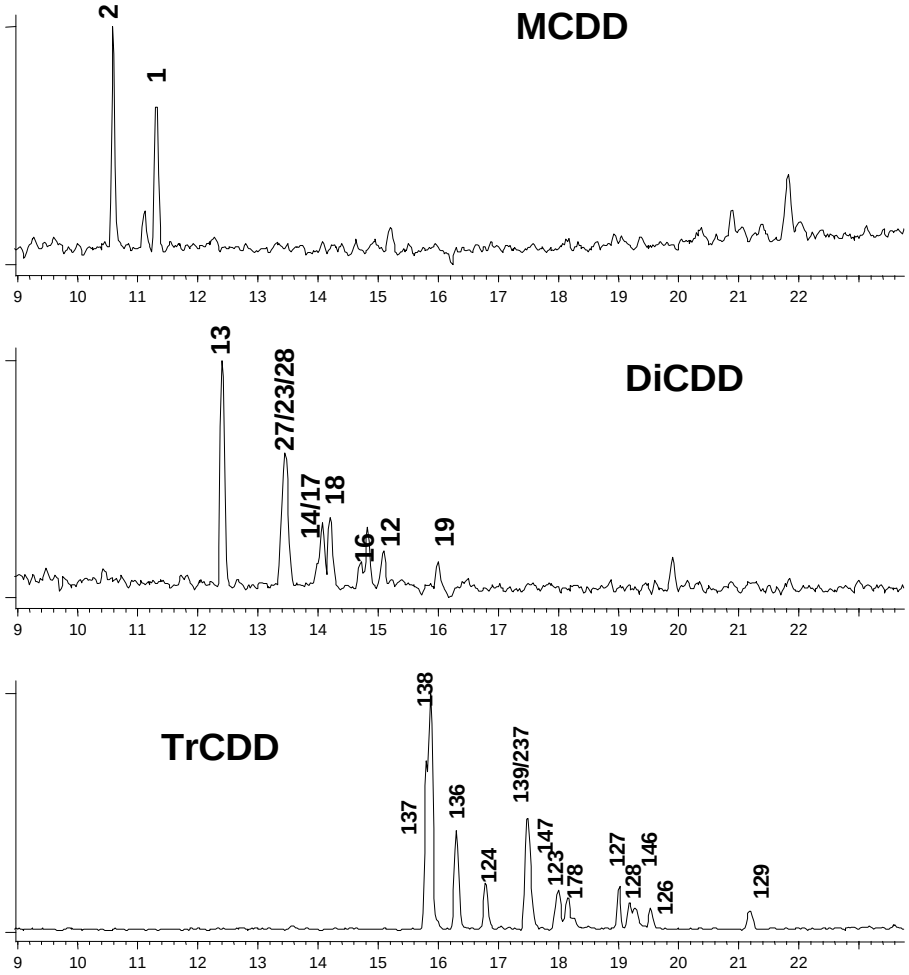

Fig.3 GC/MS-SIM Chromatograms of MCDD-T3CDD in a representative ambient air

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