DIOXIN-LIKE PCB IN THE ENVIRONMENT - IMPACTS OF THE NEW WHO-TEFs ON ASSESSMENT THRESHOLDS.

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Abstract
The re-evaluation of the toxicity equivalents (TE) of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) by the World Health Organisation (WHO) has included the dioxin-like PCBs into the WHO-scheme [1]. Monitoring data of this paper demonstrate how much the dioxin-like PCBs contribute to the total WHO-$TE_{(PCDD/PCDF+PCB)}$ and outline the implications for assessment thresholds and other regulatory purposes. In ambient air, dioxin-like PCB had a contribution of about 15 – 40 % to the total WHO-$TE_{(PCDD/PCDF+PCB)}$, annual averages ranging from 24 – 48 fg WHO-$TE_{(PCDD/PCDF+PCB)}$/m³ in 2002. In the vicinity of strong PCB-sources, such as shredder plants, dioxin-like PCB in ambient air samples can contribute up to 60 – 91 % to the total WHO-$TE_{(PCDD/PCDF+PCB)}$, and up to 85 % in deposition samples. The observed concentration range was 33 – 282 fg WHO-$TE_{(PCDD/PCDF+PCB)}$/m³. In soil samples dioxin-like PCB add about 15 – 40 % to the total WHO-$TE_{(PCDD/PCDF+PCB)}$. Due to its high TEF of 0.1, PCB congener 126 is the most important one, contributing about 40 – 80 % of the WHO-$TE_{(PCB)}$ in ambient air. In deposition samples shares of 10 – 40 % and in soil samples 60 – 80 % were reached, respectively.

Key words
WHO-toxicity-equivalents, PCDD/PCDF, dioxin-like PCB.

Introduction
From the late 1970's to the present, great efforts have been undertaken to reduce PCDD- and PCDF levels in ambient air. Whereas in 1987 up to 330 fg I-TE/m³ were measured in the Rhine-Ruhr-area of North-Rhine-Westphalia (NRW) [4], recent PCDD/PCDF concentrations amount to only 10 % of former levels.
The application of toxic equivalent factors (TEFs) to asses the overall toxicity of a sample was well established. The scheme of TEF-values agreed by NATO (1988) became widely accepted as the standard system. This scheme is often known as the International TEFs and sometimes denoted as I-TEF. Most assessment thresholds of PCDD/PCDF are based on toxic equivalent concentrations (TEQ`s) such as the emission limits of waste incinerators [2], TDI's, and other environmental quality objectives.

The reevaluation of the toxicity of organochlorine compounds by an expert group convened by WHO (1998) created a new scheme of Toxicity Equivalent Factors. They differ from the I-TEF-scheme by an increase for 1,2,3,7,8-PeCDD from 0.5 to 1 and by a decrease from 0.001 to 0.0001 for OCDD and OCDF. In addition to the PCDD/PCDF, the WHO-TEF-scheme now includes 12 dioxin-like PCB (4 non-ortho-, and 8 mono-ortho-PCB congeners) into a total toxicity equivalent (van den Berg et al. 1998) [1]. In addition, the WHO-expert group considered the evidence of human health effects from PCDD/PCDF and dioxin-like PCB and recommended a tolerable daily intake range from 1-4 pg WHO-TE/kg body weight per day (van Leuwen and Younes 1998) [3]. This went beyond the previous TDI of 10 pg TCDD/kg body weight per day by extending the scheme to all 17 2,3,7,8-congeners of PCDD/PCDF and 12 dioxin-like PCB-congeners. The present work shows results from PCDD/PCDF- and dioxin-like PCB monitoring in ambient air samples, deposition samples and soil samples. Congener specific analysis of 17 PCDD/PCDF and 12 dioxin-like PCB allow to estimate the contribution of 12 dioxin-like PCB to dioxin and furan levels expressed as new WHO-TE values.

Experimental

Sampling sites

Ambient air samples and deposition samples were collected at the following fixed monitoring sites in the Rhine-Ruhr-area:

Duisburg-Buchholz	urban
Duisburg-Meiderich	urban
Duisburg-Wanheim	industrial site, vicinity of a metal recycling plant (300 m from plant)
Essen-Vogelheim	urban
Essen-Kray	Urban, industrial influence; vicinity of a shredder plant processing electrical and electronical scrap material (200 m from plant)

Soil samples were collected at different places in North-Rhine-Westfalia classified as rural, urban and urban centre areas. Samples were taken at different depth (0-10 cm and 10-30 cm) in order to get information about the input of pollutants by deposition. In unwrought soil the deposition input obviously is confined to the topsoil.

Ambient air sampling

Ambient air samples were taken by a modified LIB sampler according to the German standard VDI-Guideline 3498 part 1 [5]. The sampler consists of a particle filter (fibre glass filter) followed by an adsorption unit of two polyurethane foam plugs (PUF) to collect the gaseous part of the PCDD/PCDF and PCB. The sampling time was 30 days with fixed periodical sampling cycles per hour. Approximately 1000 m³ of air were sucked through the filter system [4].

Deposition sampling
The samples were collected in Bergerhoff deposition gauges following the German VDI guideline 2090 part 1 [6]. Each sampler is a set of six jars (inner diameter 9.5 cm, height 20 cm). The jars were exposed on 1.5 m high poles for a period of 30+/-3 days.

Soil sampling
Soil samples were mixed samples from 30-40 single perforations. The single samples were mixed thoroughly and air-dried. The mixed sample was passed through a sieve with a mesh size of 2 mm. The sieve fraction < 2 mm was analysed.

Clean up and analysis
Clean up procedure for PCDD/PCDF and PCB follows CEN 1948 part 2, 3 and 4 (in preparation) as well VDI 3498 part 1 [5].

Results and discussion
Since 2000 the complete set of 12 dioxin-like congeners (4 non-ortho- and 8 mono-ortho-PCB) is measured together with the PCDD/PCDF in the framework of the systematic PCDD/PCDF monitoring program in the Rhine-Ruhr-region, which started in 1987.
Figure 1 shows ambient air levels (annual means) at 5 sites for the years 2000 – 2002. As can be taken from the figure, dioxin-like PCBs contribute about 15 – 40 % to the total WHO-TE toxicity equivalents, annual averages in 2002 ranging from 24 – 48 fg WHO-TE$_{(PCDD/PCDF+PCB)}$/m³. For deposition samples, the same ratio was found (compare figure 2).

Figure 1: Annual averages of PCDD/PCDF and dioxin-like PCB in ambient air (fg WHO-TE/m³)

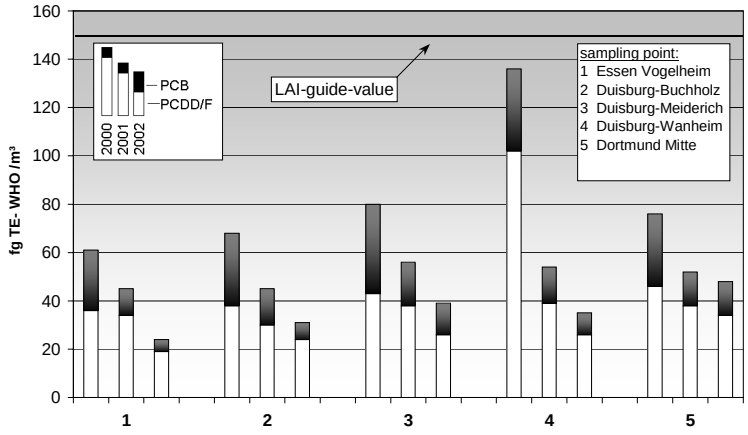


Figure 2: Annual averages of PCDD/PCDF and dioxin-like PCB in deposition

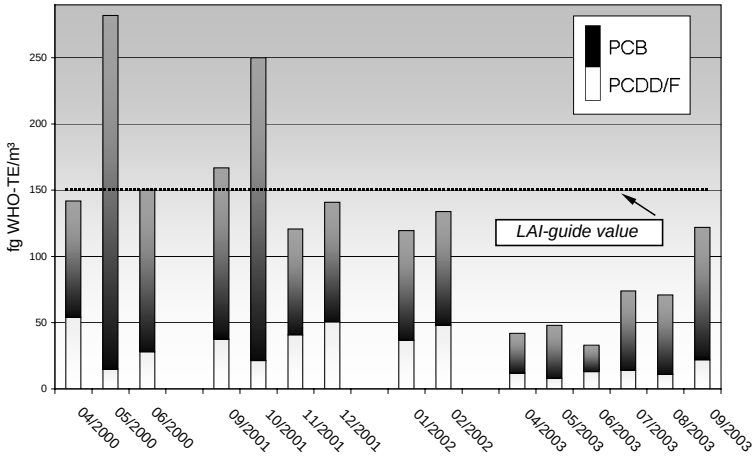
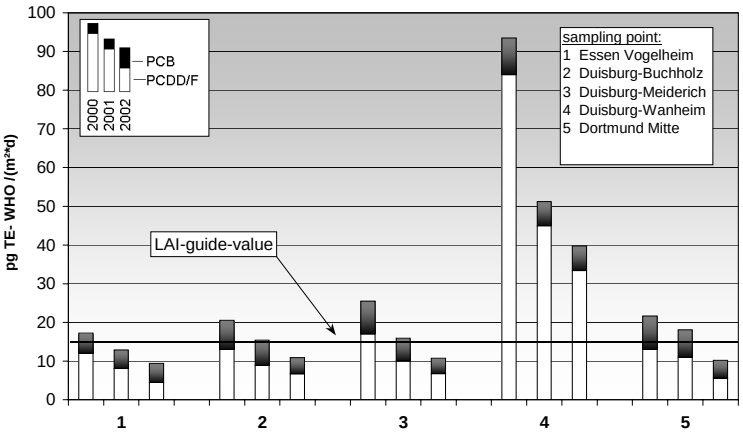


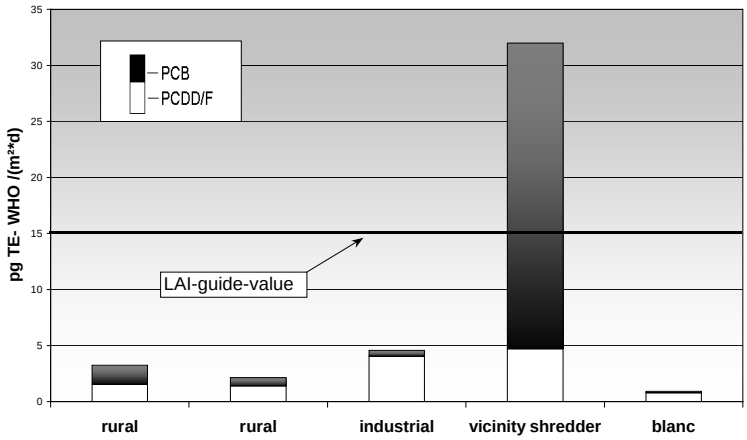
Figure 3: PCDD/PCDF and dioxin-like PCB in ambient air in the vicinity of a shredder plant (Essen-Kray)



In the vicinity of sources with high PCB emissions such as shredder plants processing electronical and electrical scrap material, the contribution of the dioxin-like PCB are distinctively higher with shares from 60 up to 90 % of the total WHO-toxicity-equivalent (figure 3). For comparison, the guide value established by a German expert group (LAI) of 150 fg/m³ I-TE has been added to figures 1 and 3.

Deposition samples exceed the LAI-guide value of 15 pg I-TE/m²*d at sampling locations in the vicinity of certain industrial installations such as metal recycling plants and shredders (Figure 2 and 4). Whereas the share the dioxin-like PCB contribute to the total WHO-$TE_{(PCDD/PCDF+PCB)}$ is not elevated in the case of the metal recycling plant (Duisburg-Wanheim, figure 2), the predominant influence of the dioxin-like PCB on the total WHO-$TE_{(PCDD/PCDF+PCB)}$ is clearly visible from figure 4 in the vicinity of the shredder. In this case, the WHO-toxicity equivalent of the dioxin-like PCB alone exceeds already the LAI-guide-value for the deposition of PCDD/PCDF.

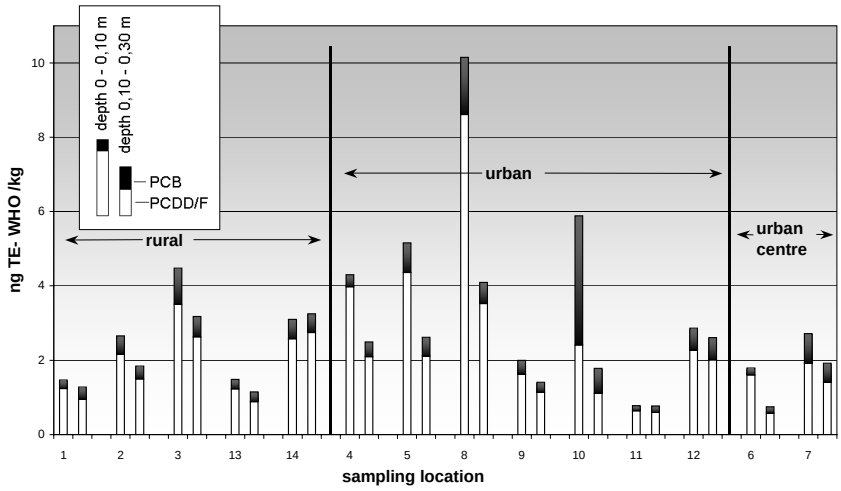
Figure 4: PCDD/PCDF and dioxin-like PCB at rural and industrial sampling sites



Soil samples from areas in the native state show higher PCDD/PCDF- and PCB-concentrations in the upper layer (0-10 cm) than in deeper layers (0-30 cm). This is due to the pollution by atmospheric deposition.

Soil samples show a relation between PCDD/PCDF and dioxin-like PCB which is comparable to ambient air- and deposition samples. Dioxin-like PCB contribute about 15 – 40 % to the overall toxicity equivalent.

Figure 5: PCDD/PCDF and dioxin like PCB in soil samples



PCB congener 126 is the most important one of the 12 dioxin-like PCBs, not by its high concentrations as such but because of its high WHO-TEF of 0,1. In ambient air samples PCB 126 contributes about 40 – 80 % to the WHO-$TE_{(PCB)}$.
In deposition samples this share amounts to 10 – 40 % and in soil samples to 60 – 80 %, respectively.
PCB 126 is one of the major congeners contributing to the total WHO toxicity equivalent. In ambient air samples averaged over one year the most important congeners for the WHO toxicity equivalent are 1,2,3,7,8-PeCDD with shares of 14 %, 2,3,4,7-PeCDF with 23 % and PCB 126 with 24 % respectively. The contribution of every other congener is less than 5 %.

The data presented above can be used for a first assessment what importance dioxin like PCB will have for meeting or exceeding environmental quality objectives such as the German LAI-guide values. It can be stated that the guide value for ambient air (150 fg I-TE/m³ PCDD/PCDF) will generally be met also, if dioxin like PCB are included. This is due to the fact that the PCDD/PCDF burden in ambient air in the Rhine-Ruhr-region fortunately decreased to low levels of 19 – 34 fg WHO-$TE_{(PCDD/PCDF)}$/m³ in the last two decades [4]. Only in the immediate vicinity of strong PCB-sources such as shredder plants the dioxin-like PCB will increase the overall concentration to such an extent that the German guide value (150 fg TE/m³) will be reached or exceeded. The decrease of the PCDD/PCDF burden during the last decades is also observed in deposition samples. At urban sampling sites PCDD/PCDF-depositions are generally below the LAI-guide value of 15 pg I-TE/(m²*d) except at sampling sites in the vicinity of PCDD/PCDF and PCB sources such as metal recycling plants or shredder plants. Near a shredder plant the contribution of the dioxin-like PCB to the WHO-$TE_{(PCDD/PCDF/PCB)}$ can rise up to 85 %.

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