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WHO-TEQ CONCERNING DIOXIN-LIKE PCB AND PCDD/PCDF IN AMBIENT AIR AND PLANT SAMPLES IN SOUTHERN GERMANY

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Introduction

Analytical data established after 1995 in different European countries have revealed that toxicity equivalent concentrations (TEQ) of dioxin-like polychlorinated biphenyls (PCB) in food of animal origin are equal to or even higher than TEQ levels of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF)[1]. Therefore, a considerable part of the European population is still exceeding the tolerable daily intake for dioxin-like contaminants of 1 - 4 pg TEQ/kg b.w. recommended by the World Health Organization (WHO) in 1998. In contrast to food, less data are available on the concentrations of dioxin-like PCB in other environmental matrices. Thus, at present, important questions on sources, transport, fate, and (bio)accumulation of non- and mono-ortho PCB cannot be answered. First data seem to indicate that different transfer factors of PCB than PCDD/PCDF are responsible for PCB enrichment in terrestrial food chains[2]. This work presents data of a monitoring project on dioxin-like PCB in ambient air (immission), deposition and plant samples from Bavaria, southern Germany. These results offer possibilities to evaluate transfer factors of dioxin-like PCB for the transmittance from air to green plants.

Materials and Methods

PCDD/PCDF and dioxin-like PCB have been determined in grass, green kale as well as in ambient air and deposition samples. For immission samples, about 2000 m³ of ambient air were collected in two different areas over sampling intervals of four weeks (from June 2002 until May 2003). A low volume sampler, equipped with particle filter (glass fibre) followed by an adsorption unit of two polyurethane foam plugs, was used for sample collection. Deposition samples were taken every four weeks using the funnel adsorber method (DIN 19739) by trapping PCB and PCDD/PCDF on XAD-2 resin. Samples of standardized grass culture[3] were collected during summer 2001 and 2002 and samples of green kale culture[4] harvested in fall 2001 and 2002 at different sites in Bavaria. These plant samples are intended to reflect the air contamination of persistent organic pollutants (POP) explicitly and are used to monitor long-term trends of POP levels.

After addition of all 17 2,3,7,8-substituted PCDD and PCDF as well as 12 WHO-PCB congeners as $^{13}C_{12}$-labelled standards freeze-dried samples were extracted with 750 ml toluene in a Soxhlet

apparatus for 24 h. After concentration of the extracts, samples were purified by open column chromatography on at least 20 g silica/conc. H_2SO_4 (44%). PCB separation from PCDD/F was performed on 25 g alumina B Super I. PCB including non-ortho substitued congeners were eluted with 60 ml benzene followed by 200 ml *n*-hexane/dichloromethane (DCM) (98:2) combined to one fraction while PCDD/PCDF were eluted in the second fraction with 150 ml *n*-hexane/DCM (1:1). The fraction containing PCDD/PCDF was further purified on 2.5 g alumina B. The PCB fraction was purified on acid silica and finally separated on 2.5 g alumina B: after pre-elution with 15 ml *n*-pentane, ortho-substitued PCB were eluted with 35 ml *n*-hexane/DCM (98:2) and then non-ortho congeners with 25 ml *n*-hexane/DCM (1:1).
PCDD/PCDF were analyzed by high resolution capillary gas chromatography with high resolution mass spectrometry (HRGC/HRMS). Gaschromatographic separation was performed on 60 m SP-2331 capillary column (Tetra- through HexaCDD/F) and on 60 m DB-XLB column (Hepta- and OctaCDD/F, WHO PCB).

Results and Discussion

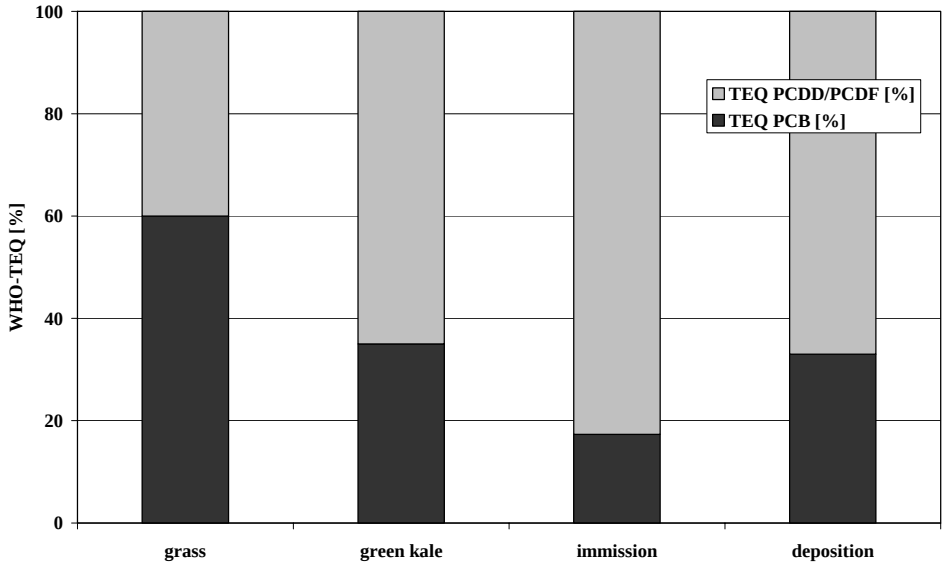
Median concentrations of the four non-ortho and the eight mono-ortho substituted PCB and median PCB TEQ as well as PCDD/PCDF TEQ measured in grass (n=25), green kale (n=18), ambient air (n=21), and deposition samples (n=14), are shown in table 1. Concentrations of mono-ortho PCB are one or two orders of magnitude higher than those of non-ortho PCB. In figure 1, TEQ levels of non- and mono-ortho PCB are compared with WHO-TEQ of PCDD and PCDF.

Table 1: Median concentrations of dioxinlike PCB in ambient air, deposition and plant samples

	grass (n=25) ng/kg	**green kale (n=18) ng/kg**	**immission (n=21) pg/m³**	**deposition (n=14) ng/(m²*d)**
PCB 77	9.1	4.5	0.11	0.047
PCB 81	0.96	0.41	0.011	0.0058
PCB 126	1.5	0.97	0.011	0.0029
PCB 169	0.12	0.085	0.0026	0.0011
Σ non-ortho	**11.5**	**5.9**	**0.13**	**0.053**
PCB 105	60	38	0.58	0.38
PCB 114	2.7	2.6	0.043	0.035
PCB 118	339	157	2.1	2.1
PCB 123	25	14.2	0.13	0.13
PCB 156	73	39	0.30	0.82
PCB 157	6.5	4.2	0.057	0.075
PCB 167	32	19	0.20	0.34
PCB 189	8.2	4.3	0.029	0.11
Σ mono-ortho	**524**	**263**	**3.2**	**3.9**
WHO TEQ PCB	**0.18**	**0.14**	**0.0013**	**0.0010**
WHO TEQ PCDD/F	**0.12**	**0.25**	**0.0062**	**0.0020**

Dioxin-like PCB can be quantified in plant samples as well as in immision and deposition samples. PCB percentage of total TEQ levels in grass samples collected at nine different urban and rural monitoring sites in 2001 was between 19 and 81 %. Similar to grass, PCB TEQ contribution of green kale varied between individual samples from 21 to 80 %. PCB 126 accounted for two-thirds of the PCB TEQ followed by PCB 118 and 156.
In ambient air, median PCDD/PCDF TEQ were 6.2 fg/m³, respectively, and therefore significantly lower than those measured of rural areas in Germany some years ago[5-7]. Median PCB TEQ was lower in immission samples (1.3 fg/m³) resulting in PCB contribution of total TEQ between 5 and 64 %. Within the PCB about two-thirds of the TEQ was attributed to PCB 126, while PCB 118 had the largest contribution among the mono-ortho substituted congeners followed by PCB 156 and PCB 105 from the standpoint WHO-TEF (1998).
Very similar congener patterns were observed at different sampling locations. In nearly all investigated environmental matrices PCB 126, PCB 118, and PCB 105 have the highest contribution to PCB WHO TEQ, an exeption are the investigated deposition samples for which PCB 156 has the highest contribution to PCB WHO TEQ.

Figure 1: comparison of TEQ levels of dioxinlike PCB with PCDD/PCDF TEQ levels (median values)



Contribution of PCB to total WHO TEQ in plant samples show a median value of 60 % for grass and 37 % for green kale. Grass samples are used for monitoring of persistent organic pollutants from June to September, while green kale is used in fall and winter months. Higher PCDD/PCDF

emissions from house heatings may be the reason for lower PCB TEQ contribution in green kale samples rather than grass samples.
Immission and deposition samples were taken during one year. Immission samples show median PCB contribution to WHO TEQ of 17 %, which is lower than for plant samples. Green kale was exposed from August until November, sample collection took place early October and late November. In the second harvest of this plant there is a significantly lower PCB TEQ contribution (e.g. 38 % in comparison to 80 % at the identical sampling place). The same trend is also present in the imission samples of these two periods (5 % versus 20 %).
First data on dioxin-like PCB in plant samples, immission, and deposition samples show that PCB TEQ is as high or sometimes even higher than PCDD/PCDF TEQ. Up to now, samples show no constant rate of PCB TEQ contribution - not even within one matrix, thus investigation of plant samples will be further continued for at least two years. Additionally, PCB concentrations in immission and deposition samples show that a relevant accumulation of dioxin-like PCB in green plants is caused by atmospheric import. Therefore, the transfer from air to plant is an important path for accumulation of POP in terrestrial food chains.

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