Carry-Over Rates of Dioxin-like PCB from Grass to Cows\' Milk

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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.

Recent investigations at different locations in Bavaria, southern Germany, have revealed that 1) dioxin-like PCB substantially contribute to total TEQ (PCDD/F+PCB) in grass and other green plants[2], and 2) the transfer of dioxin-like PCB from ambient air to green plants tends to be more efficient than that of PCDD/PCDF[3]. In contrast to PCDD/PCDF, data on carry-over rates from grass and other fodder to the body fat of cows and other farm animals are not yet available for most dioxin-like PCB congeners. The present study was performed to obtain information on this issue through the determination of the transfer of PCB and PCDD/PCDF from fresh grass to cows' milk at current background levels in southern Germany.

Materials and Methods

The study was performed at a certified organic dairy farm in the region of Augsburg in Bavaria, southern Germany. The cattle there are fed exclusively with grass during summer and with hay and coarse-ground grains in winter. On the morning of July 17 and 21, 2003, about one kg of fresh grass was randomly collected from different sections of the grass distributed in the stable and stored immediately below –20 °C. Simultaneously, 2 L of fresh

milk were collected from the holding tank of the farm, thereby obtaining pool samples from the herd of 26 lactating Guernsey cows with an average age of 6 years (range: 3 - 12 years).

From each milk and grass sample, two aliquots were taken, extracted, purified and analyzed. 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 grass samples were extracted with toluene in a Soxhlet apparatus for 24 hr. The milk fat was separated by centrifugation and then mixed with an excess of sodium sulfate. The mixture was filled in a glass column and the fat extracted by elution with 0.5 L of n-hexane/acetone (2+1, v/v) and the fat mass determined. Clean-up, separation of PCDD/PCDF from PCB and fractionation of PCB was performed for milk and grass samples as described elsewhere[2]. Laboratory blank samples were analyzed in parallel.

PCDD/PCDF and PCB were analyzed by high resolution capillary gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS). Gaschromatographic separation was performed on a 60 m SP-2331 and 60 m DB-XLB capillary column (PCDD/F in grass samples) and on a 60 m DB-XLB column (PCDD/F in milk samples, PCB).

Results and Discussion

The concentrations of the four non-ortho and the eight mono-ortho substituted PCB and PCB TEQ as well as PCDD/PCDF TEQ measured in the grass and milk samples from both sampling dates are shown in table 1.

Table 1: Concentrations of dioxin-like PCB and PCDD/F in pooled grass and milk samples, simultaneously collected at one farm on July 17 and 21, 2003.

	Grass [ng/kg dry matter]				Milk [ng/kg fat]			
Congener /Sample	07-17 A	07-17 B	07-21 A	07-21 B	07-17 A	07-17 B	07-21 A	07-21 B
Non-ortho PCB								
PCB 77	11	14	15	16	3.1	4.5	8.2	8.6
PCB 81	0.31	0.62	0.68	0.74	0.40	0.81	1.3	1.2
PCB 126	1.8	1.7	2.8	2.8	14	15	15	15
PCB 169	0.15	0.14	0.24	0.18	1.6	1.7	1.4	1.2
Mono-ortho PCB								
PCB 105	45	65	63	61	295	357	244	225
PCB 114	1.8	3.7	2.1	3.6	20	29	23	15
PCB 118	211	241	258	279	1461	1745	1223	1209

PCB 123	15	19	17	18	<10	<16	44	38
PCB 156	59	60	71	73	208	207	228	211
PCB 157	5.6	6.1	7.4	7.1	22	22	34	31
PCB 167	28	28	34	36	109	116	126	114
PCB 189	7.6	7.3	8.6	8.8	18	13	25	18
PCB (WHO-TEQ)	0.24	0.24	0.36	0.36	1.75	1.88	1.84	1.75
PCDD/F (WHO-TEQ)	0.045	0.070	0.047	0.040	0.32	0.52	0.46	0.42
% PCB of total TEQ	84	77	88	90	85	78	80	81
PCB 105+118 (TEQ)	0.026	0.031	0.032	0.034	0.18	0.21	0.15	0.14

The levels of dioxin-like PCB in grass were similar to those measured in standardized grass cultures exposed for 4 weeks at 8 different locations in Bavaria in 2001 and 2002 while PCDD/PCDF concentrations were at the lower end of levels found in grass cultures[2,3]. PCDD/PCDF levels in milk were only approximately 1/8 of the current EU limit of 3 pg WHO-TEQ/g fat.

In grass as well as in milk samples, WHO PCB accounted for more than 80 % of total TEQ levels indicating that 1) the most relevant transfer of dioxin-like PCB into terrestrial food chains occurs before the grass is ingested by cattle, and 2) the overall transfer from grass to cows' milk is similar for PCDD/F and dioxin-like PCB.

Thomas et al.[4] analysed various grass and milk samples in 1996 and 1997 and calculated on TEQ basis transfer factors for the sum of PCB 105 and PCB 118 of 13.7 and 11.0 ng WHO-TEQ/kg milk fat per 1 ng WHO-TEQ/kg d.m. plant. In the present study, values of 6.9 (July 17) and 4.4 ng TEQ/kg milk fat per 1 ng TEQ/kg d.m. plant (July 21) were obtained for PCB 118 + PCB 105 (see last line in table 1 for details).

The carry-over rate grass / milk fat of a certain compound is defined as the average daily amount excreted per cow via milk in relation to the average amount taken up daily via grass. For calculation, the following commonly recognized average values were used:

Daily amount of grass consumed per cow:	17.5 kg dry matter (d.m.)
Daily amount of milk fat delivered per cow:	1.0 kg

The resulting carry-over rates grass - cows' milk for both sampling dates and the mean values are shown in table 2. For dioxin-like PCB the highest

carry-over rates were found for #169 > #114 > #126 > #118 > #105 while the lowest transfer rates (values below 0.1) were obtained for the tetrachlorinated congeners 77 and 81, reflecting their comparatively rapid metabolism in mammals[5,6]. No clear correlation of carry-over rates with physico-chemical properties of PCB congeners was observable. While the hexaclorinated congener 169 had the highest carry-over rate of the non-ortho PCB, carry-over rates decreased from penta- to heptachlorinated congeners for the mono-ortho PCB except for PCB 123.

The overall carry-over rates of dioxin-like PCB and PCDD/F, expressed in WHO-TEQ, were almost equal on July 17, but the carry over of PCDD/F was twice as high than that of PCB on July 21.

Slob et al.[7] determined for the the non-ortho PCB congeners 77, 126 and 169 bioavailabilities of 1.2%, 35% and 31% in a field study at two locations in The Netherlands. These values are similar to the carry-over factors found in this study.

The grass / cows' milk carry-over rates obtained for PCDD/PCDF were somewhat higher than those published by several groups and reviewed by Mc Lachlan[8]; e.g. for 2,3,4,7,8-PentaCDF carry-over rates from 0.25 to 0.36 were found in these studies. These differences may be due to the very low levels found in grass in the present study probably resulting in higher gastrointestinal resorption rates.

Table 2: Carry-over factors grass – cows' milk of dioxin-like PCB and PCDD/F calculated from the analytical results shown in table 1.

Congener	07-17-03	07-21-03	Mean Carry-Over
Non-ortho PCB			
PCB 77	0.017	0.031	0.024
PCB 81	0.074	0.099	0.087
PCB 126	0.49	0.31	0.40
PCB 169	0.65	0.35	0.50
Mono-ortho PCB			
PCB 105	0.34	0.22	0.28
PCB 114	0.50	0.39	0.44
PCB 118	0.41	0.26	0.33
PCB 123	0.045	0.13	0.089
PCB 156	0.20	0.17	0.19
PCB 157	0.22	0.26	0.24

PCB 167	0.23	0.20	0.21
PCB 189	0.12	0.14	0.13
PCB (WHO-TEQ)	0.43	0.29	0.36
PCDD/F (WHO-TEQ)	0.42	0.58	0.50

Acknowledgement

The financial support of the Bavarian State Ministry of the Environment, Public Health and Consumer Protection (project no. 7000) and the assistance of A. Kotnig and C. Büker for sample preparation, I. Lachenmair for measurements and S. Rössler for manuscript preparation is gratefully acknowledged.

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