PCDDs, PCDFs AND DIOXIN-LIKE PCBS IN HUMAN MILK AND BLOOD FROM GERMANY

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Introduction

Since the inclusion of 12 "dioxin-like" polychlorinated biphenyls (PCBs) into the assessment of a tolerable daily intake (TDI) for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) by the World Health Organization (WHO)[1] in 1998, the determination of non- and mono-ortho PCBs attracted more and more analytical interest. Within an extensive cohort study 69 individual human milk samples collected from women living in North Rhine-Westphalia/Germany were inter alia analysed congener specific for PCDDs/PCDFs and PCBs in 2001 at the Chemical and Veterinary Control Laboratory (CVUA). As part of their quality control programme, in 2001 the ERGO laboratory prepared a QC pool consisting of 7 litre whole blood. The blood was collected from 13 donors with no known specific dioxin and/or PCB exposure. Aliquots of this QC pool are regularly analysed within batches of blood samples for PCDDs/PCDFs and PCBs. The results of the analyses performed in both laboratories demonstrate that on average PCDDs/PCDFs contribute approximately 50% to the total TEQ values of human milk and blood. However, depending on the matrix, the percentage share of non- and mono-ortho PCBs differs to some extent.

Materials and Methods

Human milk (CVUA)

PCDDs/PCDFs and PCBs are extracted along with milk fat by liquid/liquid partitioning. Aliquots of the fat are fortified with 17 ^{13}C-labelled PCDD/PCDF and 12 ^{13}C-labelled PCB congeners. After removal of fat on a silica gel column loaded with sulphuric acid, PCBs are separated from PCDDs/ PCDFs by means of a Florisil column. The PCDD/PCDF fraction is further cleaned up on a mini column consisting of a mixture of Carbopack C/Celite 545. Separation of coplanar (non-ortho) PCBs from non-planar PCBs is achieved on a Charcoal/Chromosorb WHP column. While analytical measurement of PCDDs/PCDFs and non-ortho PCBs is performed using capillary gas chromatography/ high resolution mass spectrometry (HRGC/HRMS) on a Micromass AutoSpec at a resolution of R=10,000 the mono-ortho PCBs are determined by capillary gas chromatography/ quadrupole mass spectrometry (HRGC/MSD) on a HP 5973 mass selective detector. Quantification of all compounds is based on the internal standards and multiple point calibration curves.

Human blood (ERGO)

Before extraction 17 ^{13}C-labelled PCDDs/PCDFs and 12 ^{13}C-labelled PCBs are added to the samples. After spiking, the samples are extracted with adequate solvents using a solid/liquid extraction for blood. The clean up is done on multicolumn systems involving carbon-on-glass fibre. The measurement is performed by means of high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) on a Micromass AutoSpec operating at a resolution of 10,000 using a DB-5 capillary column. The quantification is carried out by the isotope dilution method. Both

analytical methods applied for blood and milk were successfully tested in various national and international quality control studies and proficiency tests[2].

Results and Discussion

In order to check the comparability of the analytical methods applied for human blood and milk, both laboratories independently analysed a human milk quality control pool several times. The summarized results given in Table 1 demonstrate the good agreement between the two laboratories. Table 2 shows the mean, medium, minimum and maximum levels for PCDDs/PCDFs, non-ortho and mono-ortho PCBs determined in 69 individual human milk samples as well as the mean values of a 6-fold analysis of the human blood pool. A conversion into the respective toxic equiva-lents using the WHO equivalency factors is also included. PCB # 77 and 81 were not quantified in the human milk samples due to elevated reagent blank levels. Although the levels in blood are some-what higher, the PCDD/PCDF pattern in both matrices is pretty much the same. In contrast, the PCB pattern in milk and blood differs to some extent. While in human milk the concentration for PCB # 126 is almost 3-fold higher than for PCB # 169, the latter one slightly exceeds PCB # 126 in the blood pool. With respect to mono-ortho congeners, PCB # 118 predominates in human milk followed by PCB congeners # 156, 167 and 105. Again, the blood pool shows a somewhat different pattern with almost equal concentrations for PCB congeners # 118 and 156 and lower levels for congeners # 167, 189, 157 and 105. The different pattern found in milk and blood also influences the mean contribution of PCDDs/PCDFs, non-ortho and mono-ortho PCBs to total WHO-TEQ in both matrices. While in both cases, PCDDs/PCDFs contribute approx. 48% to total WHO-TEQ, the mean share of non-ortho PCBs is significantly higher and consequently of mono-ortho PCBs remarkably lower to total WHO-TEQ of human milk than their corresponding contributions to blood as can be clearly seen from Figures 1 and 2. Figure 3 shows the percentage contribution of PCDDs/PCDFs and the individual dioxin-like PCB congeners to total WHO-TEQ of milk and blood. The graphs demonstrates the special importance of PCBs # 126 and 156 for human TEQ body burden. Due to the good comparability, as demonstrated by the two laboratories for the analysis of the milk QC pool, the different analytical methods can obviously be excluded as a reason for the different PCB pattern found in milk and blood. The above results demonstrate the importance of dioxin-like PCBs for future assessments of human body burden with dioxins and dioxin-like compounds. It also substantiates the need for more data concerning the correlation between dioxins and dioxin-like PCBs in different matrices, such as human milk and blood from the same donors.

Table 1.

WHO - TEQ in a Human Milk QC Pool
(prepared in 1992; levels in pg /g fat)

Analytes	ERGO (n = 4)	CVUA (n = 3)
WHO - TEQ (PCDDs/PCDFs)	26,8	32,2
WHO - TEQ (non-ortho PCBs)	15,5	15,9
WHO - TEQ (mono-ortho PCBs)	18,9	16,7
Total WHO - TEQ	61,2	64,8

Table 2.

PCDDs/PCDFs and Dioxin-Like PCBs in Human Milk and Blood
(collected in 2001; levels in pg / g fat)

Congener	Human Milk (n = 69)				Blood Pool (n = 13)
	mean	median	min.	max.	mean
2.3.7.8-Tetra-CDD	1,6	1,5	0,27	3,9	2,4
1.2.3.7.8-Penta-CDD	4,1	4,0	0,55	10,3	5,7
1.2.3.4.7.8-Hexa-CDD	2,8	2,4	0,17	10,2	6,5
1.2.3.6.7.8-Hexa-CDD	12,9	11,6	0,68	42,6	28,0
1.2.3.7.8.9-Hexa-CDD	2,4	2,2	0,29	7,5	3,6
1.2.3.4.6.7.8-Hepta-CDD	14,5	12,4	2,0	82,2	31,0
OCDD	86,8	62,9	10,5	538	246
2.3.7.8-Tetra-CDF	0,34	0,30	0,13	0,78	n.d. (1)
1.2.3.7.8-Penta-CDF	0,24	0,22	0,05	1,0	n.d. (1)
2.3.4.7.8-Penta-CDF	11,1	10,0	1,4	26,6	13,0
1.2.3.4.7.8-Hexa-CDF	2,8	2,6	0,58	7,3	6,7
1.2.3.6.7.8-Hexa-CDF	2,4	2,4	0,52	6,6	5,4
1.2.3.7.8.9-Hexa-CDF	0,07	0,06	n.d. (0,5)	0,19	n.d. (1)
2.3.4.6.7.8-Hexa-CDF	1,1	0,9	0,24	3,5	1,5
1.2.3.4.6.7.8-Hepta-CDF	3,7	1,9	0,85	36,2	n.d. (4)
1.2.3.4.7.8.9-Hepta-CDF	0,10	0,08	n.d. (0,5)	0,24	n.d. (3)
OCDF	1,2	0,35	0,12	25,4	n.d. (10)
3,3',4,4'-PCB (77)	n.a.	n.a.	n.a.	n.a.	n.d. (50)
3,4,4',5-PCB (81)	n.a.	n.a.	n.a.	n.a.	n.d. (6)
3,3',4,4',5-PCB (126)	84,1	72,6	9,6	291	71
3,3',4,4',5,5'-PCB (169)	30,5	24,5	1,7	128	90
2,3,3',4,4'-PCB (105)	2147	2000	240	4500	3015
2,3,4,4',5-PCB (114)	857	770	240	2100	936
2,3',4,4',5-PCB (118)	11897	10600	1500	28600	18438
2',3,4,4',5-PCB (123)	360	310	n.d. (120)	910	280
2,3,3',4,4',5-PCB (156)	7075	6300	120	27100	19062
2,3,3',4,4',5'-PCB (157)	990	870	170	3000	3342
2,3',4,4',5,5'-PCB (167)	2434	2300	350	7800	6998
2,3,3',4,4',5,5'-PCB (189)	570	n.d.(500)	n.d.(500)	9800	3769
WHO-TEQ (PCDD/PCDF)	13,9	13,1	1,8	34,7	20,4
WHO-TEQ (non-ortho PCB)	8,7	7,5	1,0	30,4	8,0
WHO-TEQ (mono-ortho PCB)	5,9	5,6	0,2	19,7	14,3
Total WHO-TEQ	28,6	26,7	3,0	78,7	42,7

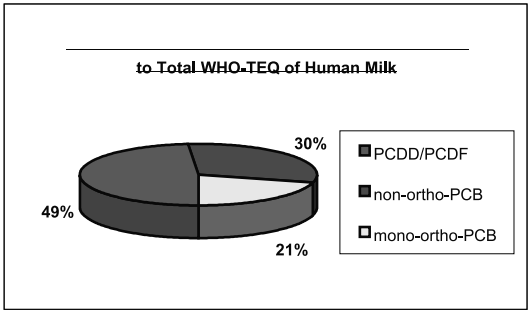

Figure 1.

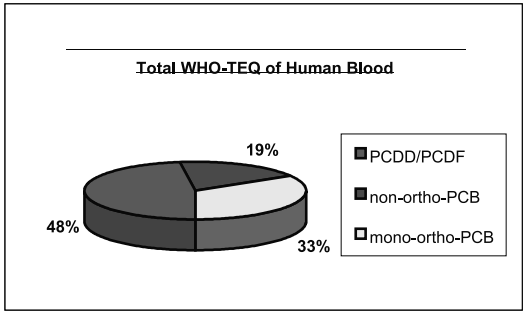

Figure 2.

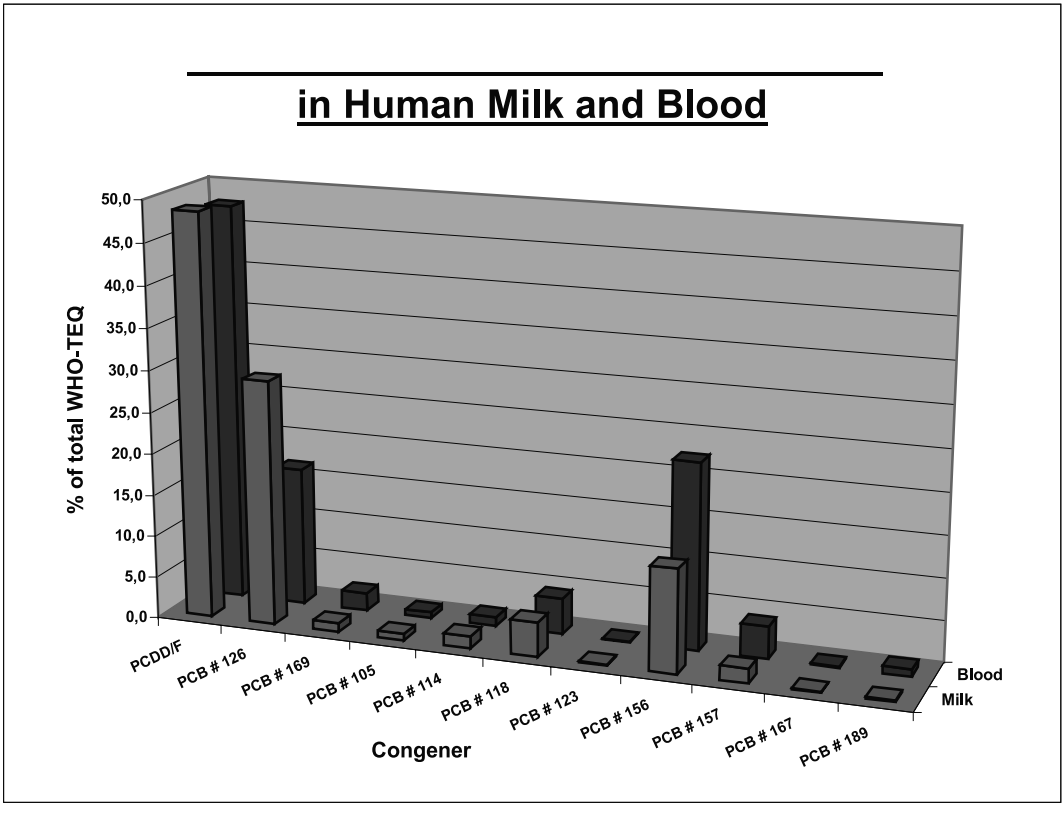

Figure 3.

References

1. WHO (2000) Food Additives and Contaminants. Volume 17, No. 4
2. International Comparison on Dioxins in Food 2001, Final Report 2001:4, Folkehelsa, National Institute of Public Health, Norway, November 2001