Influence of new WHO-TEFs on TEQ-based results of food samples and analytical opportunities

Malisch R[1], Kotz A[1], Adamovic K[1], Gerteisen I[1], Tritschler R[1], Winterhalter H[1]

[1]Community Reference Laboratory (CRL) for Dioxins and PCBs in Feed and Food, State Laboratory for Chemical and Veterinary Analysis (CVUA), Freiburg, Germany

Abstract
1121 food samples were collected between 2002 and 2006 and analysed for their content of dioxins and dioxin-like PCBs. Changes of TEQ-based results as consequence of the application of the new WHO-TEFs should be checked in order to contribute to the evaluation of new maximum and action levels in the European Union. In comparison to use of old TEFs and on basis of medians, levels of WHO-PCDD/F-TEQ, WHO-PCB-TEQ and WHO-PCDD/F-PCB-TEQ are about 14 % lower when calculated with the new TEFs. Depending on the congener pattern of individual samples, there is a range for differences between a decrease of about up to 75 % and an increase of about up to 140 %. An important conclusion is the considerable decrease of the contribution of mono-ortho PCBs to WHO-PCB-TEQ with application of the new TEFs. As consequence, development of fast routine methods based on simultaneous determination of PCDD/F and non-ortho PCB combined in one extract purified for GC/MS determination is a cost-effective alternative to control maximum levels and action levels when the new WHO-TEFs will be established in new regulations.

Introduction
The Community Strategy (1) to reduce the presence of dioxins and PCBs in feed and food comprises legislative measures which consist of three pillars: the establishment of maximum levels at a strict but feasible level in food and feed, the establishment of action levels acting as a tool for “early warning” of higher than desirable levels of dioxin in food or feed and the establishment of target levels, over time, to bring exposure of a large part of the European population within the limits recommended by the SCF. Council Regulation (EC) No. 2375/2001 set first maximum levels for dioxins in food of animal origin and oils and fats (2). The latest amendment of December 2006 sets maximum levels separately for dioxins (calculated as WHO-PCDD/F-TEQ) and the sum TEQ including dioxin-like PCBs (calculated as WHO-PCDD/F-PCB-TEQ) (3). First action levels for dioxins in food were recommended by the Commission in March 2002 (4), whereas in 2006 action levels were set separately for dioxins and dioxin-like PCBs (5). The Commission supports a proactive approach to actively reduce the dioxins and dioxin-like PCBs present in food and feed. Therefore, Commission Regulation 1881/2006 foresees a review of the maximum levels with the objective to set lower levels. Consideration will be given by 31 December 2008 to significantly reducing the maximum levels for the sum of dioxins and dioxin-like PCBs.

The existing maximum and action levels are fixed on basis of WHO-TEFs established in 1997 (6). These TEFs were revised in 2005 (7). These changes will be considered at the review of maximum and action levels. In order to contribute to this discussion, the levels of dioxins and dioxin-like PCBs in 1121 food samples of different matrices collected between 2002 and 2006 were evaluated with both TEF concepts and the results compared.

Materials and Methods
1121 food samples collected between 2002 and 2006 as part of the official food control were analysed for dioxins and dioxin-like PCBs according to validated methods (8, 9, 10, 11, 12).

	WHO-TEQ			WHO-PCDD/F-TEQ			WHO-mono-ortho-PCB-TEQ		WHO-non-ortho-PCB-TEQ		WHO-PCB-TEQ		
	1997	2005	Deviation	1997	2005	Deviation	1997	2005	1997	2005	1997	2005	Deviation
No. of samples	pg/g lw	pg/g lw	%	pg/g lw	pg/g lw	%	pg/g lw	pg/g lw	pg/g lw	pg/g lw	pg/g lw	pg/g lw	%
Meat 120													
Minimum	0,09	0,08	-70	0,02	0,02	-35	0,02	0,003	0,01	0,05	0,06	0,06	-76
Median	0,62	0,58	-12	0,24	0,22	-13	0,07	0,01	0,27	0,36	0,34	0,38	-12
Maximum	53,55	16,16	110	8,1	5,3	18	40,2	5,5	6,5	6,6	45,4	10,8	137
Butter 131													
Minimum	0,27	0,23	-47	0,13	0,10	-24	0,02	0,004	0,11	0,12	0,14	0,13	-53
Median	1,00	0,86	-13	0,30	0,25	-17	0,12	0,02	0,55	0,58	0,67	0,60	-11
Maximum	1,93	1,42	1	0,59	0,47	-12	0,49	0,07	1,41	1,08	1,62	1,11	9
Hen's egg 459													
Minimum	0,13	0,12	-59	0,04	0,04	-29	0,02	0,003	0,05	0,05	0,07	0,06	-68
Median	0,97	0,85	-13	0,39	0,35	-11	0,13	0,02	0,36	0,40	0,46	0,41	-16
Maximum	422,7	410,0	26	22,2	19,4	16	45,6	6,2	392,3	401,1	414,9	404,2	46
Fish 135													
Minimum	0,28	0,25	-56	0,08	0,07	-35	0,04	0,01	0,15	0,17	0,20	0,18	-57
Median	15,35	12,83	-16	3,91	3,32	-18	2,59	0,56	7,66	8,09	10,48	8,68	-16
Maximum	701,8	504,1	55	208,6	199,4	-4	449,7	58,7	340,7	344,7	677,6	372,2	119
Milk 177													
Minimum	0,68	0,54	-34	0,11	0,09	-31	0,07	0,01	0,29	0,30	0,36	0,32	-36
Median	1,17	1,00	-14	0,30	0,25	-16	0,14	0,03	0,69	0,71	0,84	0,73	-12
Maximum	5,32	4,66	-4	0,94	0,77	-3	0,96	0,17	3,63	3,74	4,38	3,88	-2
	pg/kg fw	pg/kg fw	%	pg/kg fw	pg/kg fw	%	pg/kg fw	pg/kg fw	pg/kg fw	pg/kg fw	pg/kg fw	pg/kg fw	%
Vegetables, Fruits, Cereals 99													
Minimum	0,77	0,68	-31	0,23	0,22	-21	0,15	0,03	0,39	0,44	0,54	0,47	-44
Median	22,1	17,9	-13	14,76	12,76	-12	2,46	0,50	6,19	6,43	8,76	7,22	-15
Maximum	3854	3632	1	2342	2092	-1	560,5	86,8	1629	1689	2189	1776	3

Table 1: Results of WHO-PCDD/F-PCB-TEQ (WHO-TEQ), WHO-PCDD/F-TEQ, WHO-mono-ortho-PCB-TEQ, WHO-non-ortho-PCB-TEQ and WHO-PCB-TEQ calculated with WHO-TEFs (1997) and WHO-TEFs (2005) including deviation of 2005 values in comparison to 1997 values

	Percentage of WHO-PCDD/F-TEQ of WHO-TEQ		Percentage of WHO-mono-ortho-PCB-TEQ of WHO-TEQ		Percentage of WHO-non-ortho-PCB-TEQ of WHO-TEQ		Percentage of WHO-mono-ortho-PCB-TEQ of WHO-PCB-TEQ	
	1997	2005	1997	2005	1997	2005	1997	2005
No. of samples	%	%	%	%	%	%	%	%
Meat 120								
Minimum	6,3	6,1	1,3	0,2	2,2	11	10	0,6
Median	29	27	14	3	54	69	21	3,9
Maximum	90	89	77	34	83	92	97	50
Butter 131								
Minimum	16	18	4,7	1,1	36	45	10	1,9
Median	31	29	12	2,7	57	69	17	3,8
Maximum	58	54	28	5,6	73	79	40	8,4
Hen's egg 459								
Minimum	1,8	1,4	1,2	0,2	3	3,2	4,6	0,7
Median	42	44	13	2,5	42	53	23	4,7
Maximum	96	97	68	23	93	98	79	33
Fish 135								
Minimum	2,9	4,6	1,2	0,2	20	26	4	0,5
Median	27	27	16	4,2	53	69	24	6,1
Maximum	77	73	64	20	78	90	67	21
Milk 177								
Minimum	11	12	5,7	1,0	25	31	9,2	1,6
Median	27	26	13	2,8	60	71	18	3,9
Maximum	70	68	41	13	74	85	47	16
Vegetables, Fruits and Cereals 99								
Minimum	16	17	1,1	0,2	17	19	2,9	0,6
Median	53	55	11	2,5	36	42	23	5,5
Maximum	78	80	30	6,4	72	79	55	14

Table 2: Percentage of WHO-PCDD/F-TEQ, WHO-mono-ortho-PCB-TEQ and WHO-non-ortho-PCB-TEQ as proportion to WHO-PCDD/F-PCB-TEQ (WHO-TEQ) respectively to WHO-PCB-TEQ calculated with WHO-TEFs (1997) and WHO-TEFs (2005)

Results and Discussion

Table 1 summarizes the results of WHO-PCDD/F-TEQ, WHO-mono-ortho-PCB-TEQ, WHO-non-ortho-PCB-TEQ, WHO-PCB-TEQ and WHO-PCDD/F-TEQ calculated with WHO-TEFs (1997) and WHO-TEFs (2005). In comparison to use of old TEFs and on basis of medians, levels of WHO-PCDD/F-TEQ, WHO-PCB-TEQ and WHO-PCDD/F-PCB-TEQ are about 14 % lower when calculated with the new TEFs. Depending on the congener pattern of individual samples, there is a range for differences between a decrease of about up to 75 % and an increase of about up to 140 %. The changes of WHO-PCB-TEQ levels are caused by two opposite effects: Whereas for non-ortho PCB-TEQs an increase of about 4 % is observed, mono-ortho PCB-TEQs are reduced by about 80 %.

As a conclusion, the existing maximum and action levels have to be reviewed in the light of changes resulting from the new TEF concepts. Otherwise, a numeric reduction of about 14 % would be observed without real reduction of the dioxin or dioxin-like PCB levels.

Table 2 summarizes the changes of the percental contribution of WHO-PCDD/F-TEQ , WHO-mono-ortho-PCB-TEQ and WHO-non-ortho-PCB-TEQ as proportion to WHO-PCDD/F-PCB-TEQ (WHO-TEQ) respectively to WHO-PCB-TEQ calculated with WHO-TEFs (1997) and WHO-TEFs (2005). As a result, the contribution of WHO-PCDD/F-TEQ and of WHO-PCB-TEQ to WHO-TEQ remains unchanged, whereas the contribution of mono-ortho PCB-TEQ to WHO-TEQ decreases from about 13 % to about 3 % and the contribution of WHO-non-ortho-PCB-TEQ to WHO-TEQ increases from about 50 to about 62 %.

Analytical opportunities

As consequence, development of fast routine methods based on simultaneous determination of PCDD/F and non-ortho PCB combined in one extract purified for GC/MS determination is a cost-effective alternative to control maximum levels and action levels when the new WHO-TEFs will be established in new regulations. The inclusion of mono-ortho PCBs as necessary for control of valid regulations would not be necessary, as the contribution to total WHO-TEQ will decrease to about 3 % on basis of median, with a 90 % percentile of about 8 % and a maximum of 34 %.

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