CONTRIBUTIONS OF PCDDs, PCDFs, *non*-ORTHO PCBs AND *mono*-ORTHO PCBs TO THE TOXIC EQUIVALENCY (TEQ) – RESULTS FROM AN INTERLABORATORY STUDY ON FOOD SAMPLES OF CHICKEN, BUTTER AND FISH

Gunilla Lindström[1], Line Småstuen Haug[2] and Tove Nicolaysen[2]

[1]Man-Technology-Environment Research Centre, Örebro University, SE-701 82 Örebro, Sweden
[2]National Institute of Public Health, Section for Chemical Analysis, P.O. Box 4404 Nydalen, N-0403 Oslo, Norway

Introduction

For regulatory and risk assessment reasons toxic equivalency factors (TEFs) in combination with measured dioxin-like residue data are used for toxic equivalency levels (TEQ-levels) in order to estimate and compare total dioxin toxicity in foods and other biological matrixes. In 1997 a WHO expert meeting launched a new consensus regarding toxic equivalency factors, the [98]WHO-TEF scheme, for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like (non-ortho and mono-ortho) PCBs for human, fish and wildlife risk assessment[1].

The most common praxis so far had been to include the PCDDs, PCDFs and non-ortho PCBs in the TEQ level. Often, in older dioxin data, only the PCDD and PCDF levels are included. The different ways in which TEQ levels have been expressed cause confusion when old and new dioxin data are reviewed and compiled. The most widely used TEF schemes for recent data are either the International TEFs (I-TEFs) for PCDDs and PCDFs in combination with the [94]WHO-ECEH scheme for PCBs, or the [98]WHO-TEF scheme which includes all four groups of dioxin-like compounds. It is usually considered that approximately 10-20% higher TEQ levels are generated by the [98]WHO scheme compared to the I-TEF.

Today, within the European Union, discussions are underway concerning measures for reduction and limit values of dioxins in foods[2]. In this context it is interesting, as well as important, to closer examine the contribution of the different dioxin-like residue groups to the total TEQ. Needles to say the levels should then be expressed in the same 'TEQ-unit'. Also, from a QA/QC point of view, and the application of a single numerical limit value, it is of

importance to know the accuracy and reproducibility in the analytical performances (standard deviations) of the dioxin-like compound groups in order to establish these limits.

Interlaboratory assessment of PCDDs, PCDFs and dioxin-like PCBs

Data are today available from two major international interlaboratory studies concerning assessment of PCDDs, PCDFs and dioxin-like PCBs in foods and biological matrixes. The first study was co-ordinated under the IUPAC Commission VI.5, Food Chemistry Division and completed in 2000. In this study seventeen laboratories reported data PCBs including the mono-ortho PCBs #105, 114, 118, 123, 156, 167 and 189 in human tissue and fish. The interlaboratory analytical performance is summarised in a FCD/IUPAC report. In the human tissue sample in that study the contribution from the mono-ortho PCBs was approximately 3 pg TEQ/g lipid and in the fish (fatty fish) sample 4 pg TEQ/g lipid. Since neither PCDD, PCDF nor non-ortho PCB measurement were done in the IUPAC study the % TEQ contribution by each residue group could only be speculated on. But, qualified estimations gave a potential contribution of 5-10% from mono-ortho PCBs for the human sample. No estimation was done concerning the fish.

To shred some light on the % contributions respectively of the PCDDs, PCDFs, non-ortho PCBs and mono-ortho PCBs in foods, eleven laboratories measured mono-ortho PCBs and PCB #81 in chicken, butter and fish, in the samples included in the Dioxin in Food 2000 study[3]. These results will be discussed here in more detail. Further, in the ongoing Dioxin in Food 2001 study, as many as 60 participating laboratories world-wide determined the analytical performances and contributions of the four dioxin-like residue groups to the total TEQ in samples of beef, human milk and cod liver.

Results of mono-ortho PCB determinations

The eight mono-ortho PCBs with assigned TEFs according to the [98]WHO-TEF scheme were determined in three foods by eleven laboratories world-wide. The results are presented in table 1.

PCDD, PCDF, non-ortho PCB and mono-ortho PCB contributions to the total TEQ

The contributions of the four different groups of dioxin-like compound included in the [98]WHO-TEF scheme were determined for the chicken, butter and fish samples. Table 2 shows the % contributions of the four dioxin-like residue groups.

Table 1 Results on average levels, congener specific TEQs, standard deviations and relative standard deviations in the determinations of mono-ortho PCBs in fish, chicken and butter.

PCB	Average[a] (ng/g)	TEQ[b](pg/g)	SD	RSD %	N consensus[c]	N reported[d]
Fish fresh weight						
105	0.44	0.044	0.070	16	9	10
114	0.024	0.012	0.0039	16	8	10
118	1.3	0.13	0.26	20	9	10
123	0.076	0.0076	0.072	95	7	9
156	0.15	0.074	0.024	16	9	10
157	0.037	0.018	0.0060	16	9	10
167	0.084	0.00084	0.030	36	10	10
189	0.013	0.0013	0.0036	28	8	10
Fish lipid weight						
105	4.3	0.43	1.1	27	9	10
114	0.21	0.11	0.090	42	9	10
118	12	1.2	5.1	43	10	10
123	0.71	0.071	0.62	89	7	9
156	1.3	0.65	0.18	13	8	10
157	0.29	0.15	0.094	32	9	10
167	0.80	0.0080	0.36	45	10	10
189	0.11	0.011	0.031	28	7	10
Chicken fresh weight						
105	0.074	0.0074	0.014	19	10	11
114	0.0049	0.0025	0.0011	22	8	11
118	0.23	0.0226	0.049	22	10	11
123	0.0046	0.00046	0.0043	93	7	10
156	0.032	0.016	0.0057	18	10	11
157	0.0067	0.0033	0.0012	18	10	11
167	0.013	0.00013	0.003	23	10	11
189	0.0026	0.00026	0.00054	21	7	11
Chicken lipid weight						
105	0.48	0.048	0.10	21	10	11
114	0.032	0.016	0.0071	22	8	11
118	1.5	0.15	0.32	22	10	11
123	0.040	0.0040	0.040	99	8	10
156	0.20	0.10	0.039	19	10	11
157	0.043	0.022	0.0087	20	10	11
167	0.085	0.00085	0.020	24	10	11
189	0.017	0.0017	0.0045	26	7	11
Butter fresh weight						
105	0.072	0.0072	0.027	37	10	11
114	0.0071	0.0035	0.0030	42	8	11
118	0.35	0.035	0.15	43	10	11
123	0.012	0.0012	0.016	130	8	10
156	0.038	0.019	0.014	37	9	11
157	0.0093	0.0047	0.0047	51	9	11
167	0.022	0.00022	0.010	46	9	11
189	0.0046	0.00046	0.0034	74	6	11

Butter lipid weight

105	0.087	0.0087	0.032	37	10	11
114	0.0085	0.0042	0.0036	42	8	11
118	0.42	0.042	0.18	43	10	11
123	0.015	0.0015	0.019	131	8	10
156	0.046	0.023	0.017	37	9	11
157	0.011	0.0056	0.0057	51	9	11
167	0.026	0.00026	0.012	46	9	11
189	0.0054	0.00054	0.0041	76	6	11

a) the congener average based on consensus levels
b) TEQ calculated using the ^{98}WHO-TEF scheme
c) the number of laboratories which results qualified for use for consensus calculation (invalid data excluded)
d) the number of laboratories reporting the specific congener

Table 2 The % contributions in chicken, butter and fish samples (fresh and lipid weight) of the PCDD, PCDF and PCB congeners assigned ^{98}WHO-TEFs.

Foods		PCDD	PCDF	PCDD + PCDF	non-ortho PCB	mono-ortho PCB	PCB
Chicken	(*fw*)	18	23	**41**	39	20	**59**
	(*lw*)	18	23	**41**	38	21	**59**
Butter	(*fw*)	25	20	**45**	37	18	**55**
	(*lw*)	25	22	**47**	36	17	**53**
Fish	(*fw*)	12	21	**33**	53	14	**67**
	(*lw*)	12	21	**33**	52	15	**67**

Discussions

The mono-ortho PCBs in these food samples contributed to the total ^{98}WHO-TEQ in chicken with 21%, in butter with 18% and in fish with 14%. These contributions are of the same order as the PCDD and PCDF contributions each. Also, a considerable contribution, 53-67 %, from the PCBs to the total TEQ is seen. For the fish 2/3 of the dioxin-like toxicity stems from the PCBs. The conclusion can be drawn, that when we discuss measures for reduction of levels of dioxin in food we actually should discuss as much the PCBs, in order to achieve a total TEQ reduction.

Important issues on how accurate and comparable reported food data of dioxin-like compounds are have been raised since the 1980's, when food-related dioxin data first appeared in the literature. The current state-of-the-analytical art (for PCDD, PCDF and non-ortho PCB) in food was elucidated in the Dioxin in Food 2000 interlaboratory study[4]. Here the 30 participating laboratories, representing the major dioxin data 'producers', proved their ability to determine dioxin-like compounds in foods, at such low levels as 0.2 pg ^{98}WHO-TEQ/g (on a fresh weight basis). With a 90% confidence, the reported levels are found within ±50% of the 'real' level.

In the assessment of analytical determinations of mono-ortho PCBs it can be seen from table 1 that the SD for determination of PCB #118, which is by far the ^{98}WHO-TEQ $_{\text{mono-ortho PCB}}$ driving congener, is 20-43 %. This is somewhat less than that found for the PCDDs, PCDFs and non-ortho PCBs in the Dioxin in Food 2000 study. Therefore, it can be concluded that the overall SD for TEQ levels are more dependent on the determinations of the PCDDs, PCDFs and non-ortho PCBs than on the mono-ortho PCBs. A margin of up to ~50% uncertainty regarding inter-laboratory dioxin data for food is justified.

Acknowledgements

All the analytical experts and their laboratories are greatly acknowledged for their contributions: Bernhard Henkelmann, GSF-National Research Center, Germany; Takumi Takasuga, Shimadzu Techno-Research Inc., Japan; Roman Grabic/Tomas Ocelka, Chemical Laboratory, District Public Health Department, Frýdek-Místek, Czech Republic; Rainer Malisch, Chemisches und Veterinæruntersuchungsamt Freiburg, Germany; Stefano Raccanelli, Consorzio Interuniversitario Nazionale, 'la Chimica per l'Ambiente', Italy; Hannu Kiviranta, National Public Health Institute (KTL), Finland; Michael G. Ikonomou, Fisheries and Oceans Canada, Institute of Ocean Sciences, Canada; Toshihiko Yanagi, Japan Food Research Laboratories, Japan; Carmen Rodriguez Larena, Institut Quimic de Sarria-PEINUSA, Spain; Chris Wright, Unilever Research, UK; Andy I-Fu Shen, National Institute of Environmental Analysis, Taiwan.

References

1. van den Berg, M., Birnbaum, L., Bosveld A., et al (1998). Toxic equivalency factors for PCBs, PCDDs, PCDFs for humans and wildlife. Environ Health Perspective, 106, 775-792.
2. EU/SCF Opinion on Risk Assessment of Dioxins and Dioxin-like PCBs in Food (22 November 2000) http://europa.eu.int/comm/food/fs/sc/scf/outcome_en.html
3. Lindström, G., Småstuen Haug, L. and Nicolaysen, T. (2000) NIPH (National Institute of Public Health), Intercalibration on Dioxin in Food 2000, Rapport 2000:9, Oslo, 210 pages.
4. Lindström, G, Småstuen Haug, L., Nicolaysen, T. and Dybing, E. Comparability of world-wide analytical data of PCDDs, PCDFs and non-ortho PCBs in samples of chicken, butter and salmon. Chemosphere (submitted 2001).