Contribution and Importance of Non-Ortho (Coplanar) PCBs for the I-TEQ Evaluation in "Dioxins Analysis" of Biological Matrices

Jean-François Focant, Gauthier Eppe, Jean-Sébastien Houziaux, Céline Xhrouet, Jean-Emmanuel André, Dominique Dipede and Edwin De Pauw

Mass Spectrometry Laboratory, University of Liege, B6c Sart-Tilman, B-4000 Liege, Belgium
e-mail : JF.Focant@ulg.ac.be

Introduction

Dioxins (this term covering PCDD/Fs) and Dioxin-like PCBs are a class of organic compounds which have similar physical and biological properties. The substitution pattern of some PCBs allow them to adopt a planar geometry similar to the one of PCDD/Fs. Due to their respective affinity to bind the Aryl hydrocarbon Receptor (AhR) these compounds have been attributed Toxic Equivalency Factors (TEFs) (1,2).
In spite of the great concern of evaluating the presence of these molecules in foodstuffs, only limited sets of data are available. Last year's events that occurred in Belgium have urged authorities to invest in laboratory measurements (3,4,5). Due to the "hot source of PCBs" contamination (used transformer oil, Aroclor 1260), many PCBs (the 7 PCBs [28, 52, 101, 138, 153, 180, 209] used as tracers) analyses have been carried out. It has been brought to the fore that, for this isolated case of contamination, a logarithmic correlation between the amount of PCBs and dioxins existed for eggs, chicken meat and feedstuff (6). For beef, milk and pork, this correlation was far less obvious (7). Even if attention has been mainly focused on PCBs screening, lots of dioxin analyses have also been carried out (8).
Regarding foodstuff containing more than 2% fat, the Belgian government voted a dioxin norm (5 pgTEQ/g fat) at the end of last year (9). This norm includes the monitoring of 7 PCDDs and 10 PCDFs (see Table 2). No cPCBs have been included so far. For the preliminary results presented here, some marine matrices have also been analysed in addition to agricultural foodstuffs concerned by the norm. Sperm whale sample has been included as well due to its possible link to food chain via quartering (10). First results on cPCBs content in human serum are also presented.

Materials and methods

All food samples originated from the Belgium market. Pork meat , beef meat, chicken meat, horse meat, chicken eggs, sperm whale, mackerel fillet and prawns were extracted using ASE; milk powder and cheese were Soxhlet extracted; serums were extracted on SPE cartridges. Lipids were determined by gravimetry. When necessary, lipids were removed on GPC. Subsequent clean-up was performed on Power-Prep® system (FMS Inc., USA) (11). Purified extracts were analysed on a HP 6890 GC coupled to a Finnigan MAT95XL high resolution mass spectrometer. Samples were analysed for the 7 PCDDs, 10 PCDFs and 3 cPCBs (77,126,169). TEQs were calculated using WHO TEFs (1). Reference materials (RM 533, RM 534) (12), blanks and "in-house" quality control samples were included in the analysis scheme.

Results and Discussion

The cPCBs contribution is ranging from 29 to 83% (average of 53%) for the I-TEQ estimation (Table 1). The relative contribution of some congeners to the global toxicity is roughly the same for all matrices.

Table 1: PCDD/Fs and cPCBs contribution to the I-TEQ

	PCDD/Fs			cPCBs			
Matrices	Mean pg TEQ/g fat	Range pg TEQ/g fat	% Total TEQ	Mean pg TEQ/g fat	Range pg TEQ/g fat	% Total TEQ	n
Foodstuffs							
Pork	0,10	[0,1 - 0,2]	*71*	0,04	[0 - 0,1]	*29*	14
Beef	1,8	[0,3- 4,1]	*42*	2,4	[1,3 - 6,0]	*58*	9
Chicken	0,2	[0,1 - 0,6]	*33*	0,4	[0,3 - 0,8]	*67*	8
Eggs	2,6	[1,2 - 7,6]	*66*	1,3	[0,7 -3,8]	*34*	3
Horse	6,1	[3,3 - 10,3]	*35*	11,3	[7,5 - 14,7]	*65*	3
Milk	1,4	[1,4 - 1,5]	*46*	1,7	[1,6 - 1,7]	*54*	4
Dairy fat	0,4	[0,3 - 0,8]	*37*	0,6	[3,5 - 7,7]	*63*	5
Cheese	1,7	[1,6 - 1,7]	*51*	1,6	[1,4 - 1,7]	*49*	3
Marine							
Sperm whale	272,0	-	*44*	344,0	-	*56*	1
Mackerel	51,6	-	*17*	257,3	-	*83*	1
Prawns	44,2	[38,1 - 45,8]	*44*	56,9	[48,6 - 63,2]	*56*	3
Human							
Serum	12,8	[5,4 - 19,7]	*84*	2,4	[1,2 - 4,5]	*16*	3

The toxic congeners 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF are always present in such quantities that they account to about 75% (range [42–100]) of the PCDD/Fs TEQ. 2,3,4,6,7,8-HxCDF and 1,2,3,4,7,8,9-HpCDF are always absent or negligible. The PCB 126 contributes to about 92% (range [85–100]) of the cPCBs TEQ. The congeners contributions to the total toxicity are exposed in Table 2.

First results on human serum of some Belgian residents (men 20-40 years old) indicate that levels as swell as cPCBs contribution are very close to results of other studies (13,14).

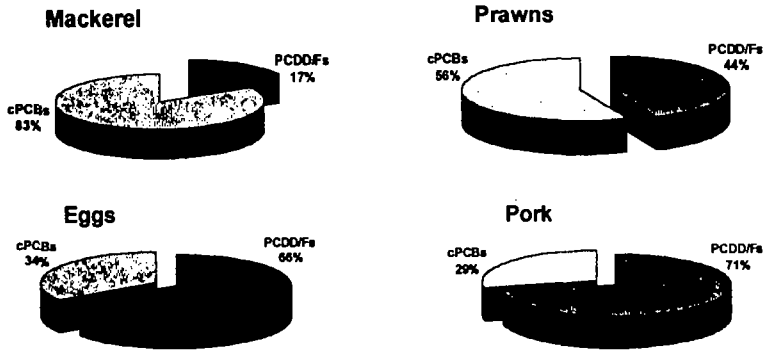

Figure 1 : Distribution of PCDD/Fs and cPCBs in foodstuff

The levels of the sperm whale blubber put back into question the problem of stranded mammals carcasses management.
The marine foodstuffs (sperm whale excluded in this appellation) are 40 times more contaminated than the agricultural foodstuff and the cPCBs contribution is generally greater (70% against 52%). Knowing that agricultural foodstuff containing more than 5 pg I-TEQ/g fat are considered as inappropriate to the human consumption, it seems to be necessary to extend the actual Belgian norm, maybe after slight modifications, to the marine matrices.
The evaluation of the I-TEQ using the TEFs model is the route of risk assessment of dioxin-like compounds. The contribution of cPCBs to the I-TEQ indicates the importance of their analysis to be able to integrate them into the total exposure evaluation. In addition to the cPCBs, 8 mono-ortho PCBs having TEFs should be included as well. According to available data, one can expect a significant increase in the I-TEQ if mono-ortho PCBs are taken into account (15). Considering that, the Tolerable Daily Intake (TDI) recommended by the WHO (1-4 pg/kg bw/day) (16) could sometimes be exceeded.

Acknowledgements

This research was supported by the "Fonds pour la Formation à la Recherche dans l'Industrie et l'Agriculture" (F.R.I.A), the O.S.T.C. (contract n° MN/DD/85) and the "Region Wallonne" (contract n° 981/3901). Sperm whale blubber (winter 94-95, Belgian coast) was kindly provided by the "MARIN" research group, O.S.T.C. project n° MN/DD1/005.

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Table 2: PCDD/Fs and cPCBs congeners contribution (pg I-TEQ/g fat)

	Pork	Beef	Chicken	Eggs	Horse	Milk	Dairy fat	Cheese	Mackerel	Prawns	Sperm Whale	Human Serum
2,3,7,8-TCDD	nd	<LOQ	nd	<LOQ	0,2500	nd	nd	0,1500	4,2894	4,1722	28,8368	1,2100
1,2,3,7,8-PeCDD	nd	0,4255	<LOQ	0,5638	1,4300	0,3500	<LOQ	0,3800	5,0473	2,2941	93,3718	4,2600
1,2,3,4,7,8-HxCDD	nd	0,0258	<LOQ	0,0477	0,1070	0,0250	<LOQ	nd	0,0324	0,0130	5,2037	0,1920
1,2,3,6,7,8-HxCDD	<LOQ	0,1175	0,0240	0,1718	0,3220	0,0870	0,0320	0,0740	0,1182	0,2459	14,1256	0,6650
1,2,3,7,8,9-HxCDD	nd	0,0222	<LOQ	0,0388	0,0580	0,0240	<LOQ	0,0220	<LOQ	0,0541	1,6532	0,2210
1,2,3,4,6,7,8-HpCDD	<LOQ	0,0014	<LOQ	0,0066	0,0332	0,0017	<LOQ	0,0012	0,0010	0,0269	0,0390	0,0575
OCDD	0,0006	<LOQ	<LOQ	0,0063	0,0061	0,0003	<LOQ	nd	<LOQ	0,0151	0,0008	0,0003
2,3,7,8-TCDF	nd	0,0268	0,0220	0,1797	0,0380	0,0430	nd	0,0590	25,4839	12,8311	1,3304	0,2060
1,2,3,7,8-PeCDF	nd	nd	<LOQ	0,0609	0,0240	nd	nd	nd	0,2280	0,8969	0,8617	nd
2,3,4,7,8-PeCDF	0,0950	0,9147	0,1450	1,0910	2,9950	0,7300	0,2800	0,8300	16,3070	22,9258	109,1022	4,8300
1,2,3,4,7,8-HxCDF	<LOQ	0,0933	0,0190	0,1238	0,1220	0,0480	0,0240	0,0630	0,0297	0,3924	8,8471	0,4100
1,2,3,6,7,8-HxCDF	<LOQ	0,0753	<LOQ	0,1234	0,3850	0,0490	0,0240	0,0380	0,0497	0,2466	4,6155	0,5900
1,2,3,7,8,9-HxCDF	nd	0,0709	nd	0,1046	0,2150	0,0380	nd	0,0440	0,0400	nd	3,8035	<LOQ
2,3,4,6,7,8-HxCDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
1,2,3,4,6,7,8-HpCDF	<LOQ	0,0078	0,0022	0,0405	0,0798	0,0088	<LOQ	0,0098	0,0118	0,0922	0,1624	0,1142
1,2,3,4,7,8,9-HpCDF	0,0058	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OCDF	<LOQ	<LOQ	<LOQ	0,0002	0,0001	0,0001	<LOQ	<LOQ	<LOQ	0,0007	nd	<LOQ
TotalPCDD/Fs	**0,10**	**1,78**	**0,21**	**2,56**	**6,07**	**1,40**	**0,36**	**1,67**	**51,64**	**44,21**	**271,95**	**12,76**
3,3,4,4'-TCB (77)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3,6449	0,7953	0,0803	<LOQ
3,3',4,4,5-PeCB (126)	0,0400	2,4235	0,4310	1,3247	11,2930	1,6490	0,6100	1,5860	253,4986	56,0703	343,1683	2,3680
3,3,4,4',5,5'-HxCB (169)	0,0003	0,0051	0,0006	0,0019	0,0147	0,0015	0,0008	0,0016	0,1344	0,0564	0,7682	0,0386
TotalcPCBs	**0,04**	**2,43**	**0,43**	**1,33**	**11,31**	**1,65**	**0,61**	**1,59**	**257,28**	**56,92**	**344,02**	**2,41**
TOTAL I-TEQ	**0,14**	**4,21**	**0,64**	**3,89**	**17,37**	**3,06**	**0,97**	**3,26**	**308,92**	**101,13**	**615,97**	**15,16**

- nd : not detected
- <LOQ : below the limit of quantification, 0.15 pg/g fat except for 1,2,3,4,6,7,8-HpCDD (0.91), OCDD (4.13), 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF (0.62), 1,2,3,4,7,8,9-HpCDF (0.25) and OCDF (1.16)