LEVELS AND TRENDS OF PCDD/FS AND cPCBs IN BELGIAN FOOD-STUFFS ONE YEAR AFTER THE "DIOXIN CRISIS"

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Introduction

Since the so called « Dioxin crisis » that took place in Belgium during spring and summer 1999, increased number of samples have been analyzed in different monitoring programs. Even if after this event, attention has mainly been focused on screening of marker Polychlorinated biphenyls (PCBs, Aroclor 1260), independent analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are regularly carried out. This allows the estimation of the 2,3,7,8-TCDD equivalents (TEQ) content of the samples and the respect of the established norms [1]. In addition to these PCDD/Fs measurements, coplanar PCBs (cPCBs) which are also monitored even if they are not yet included in the regulations. We present here some results obtained during the period of June 2000 to February 2001 for several types of food-stuffs matrices produced in Belgium. These 150 samples can be considered as representative of the Belgian products during this period of time.

Materials and methods

All samples are representative of the food-stuffs available on the Belgian market and potentially candidate to exportation outside the country. Sampling before analysis have been carried out by veterinary officers or under manufacturers control. They were all individually sealed and separately frozen until analysis.

Sample preparation and extraction was dependent of the matrix type. All samples except dairy products were mechanically ground using liquid nitrogen to produce homogenate before freeze drying. They were then ground again in order to produce a fine powder which was extracted using accelerated solvent extraction (ASE™ 200, Dionex, Sunnyvale, CA, USA) in hexane. Dairy fat were prepared by manufacturer and directly processed through the clean-up step. Powder milk samples were Soxhlet extracted using a mixture of pentane:dichloromethane 1/1. Isotopic dilution labelled standards were added to the extracted fat after gravimetric "lipid percent" determination.

Clean-up was carried out using the Power-Prep™ (FMS Inc., Waltham, MA, USA) system with multilayer silica, basic alumina and PX-21 carbon columns [2]. Purified extracts were analyzed on a HP 6890 GC (Hewlett-Packard, Palo Alto, CA, USA) coupled to a Finnigan MAT95XL (Finnigan, Bremen, Germany) high resolution mass spectrometer. The column is a RTX-5SIL-MS (30m x 0.25mm I.D., 0.25μm film thickness) capillary column (Restek, Evry, France); The mass spectrometer operates in the electron impact ionization mode using selected ion monitoring (SIM) at a minimum resolution of 10.000 (10% valley). In addition to daily sensitivity and relative response factor (RRF) checks, the mean RRF are regularly re-evaluated for each congener.

In this validated method, reference materials, blanks (both instrumental and method) and "in-house" quality control samples were included in the analysis scheme to ensure the control of the analysis. Samples were analyzed for the PCDDs, PCDFs and cPCBs. TEQs were calculated using WHO TEFs [3].

Results and Discussion

The different types of meat present different background level depending of many factors such as the age of animals when slaughtered, the way and location where they were grown, the type of feeding-stuffs they were eating, their fat content, etc... For horse meat, according to the longer life-time of animals, higher levels are observed in comparison with pork and beef for example (see Table 1).

Table 1: Relative contributions to the TEQ (values in pg WHO-TEQ/g fat)

		PCDDs		PCDFs		cPCBs	
Matrices	**n**	**Mean**	**% Total**	**Mean**	**% Total**	**Mean**	**% Total**
Horse	12	4,19	***21***	3,84	***20***	11,57	***59***
Lamb	2	1,39	***26***	0,85	***16***	3,11	***58***
Beef	25	0,74	***14***	1,10	***21***	3,48	***65***
Pork	34	0,08	***22***	0,14	***38***	0,15	***41***
Chicken	48	0,16	***15***	0,19	***18***	0,73	***68***
Creme	4	1,15	***53***	0,39	***18***	0,62	***29***
Butter	8	0,35	***20***	0,45	***26***	0,94	***54***
Milk	4	0,02	***2***	0,32	***25***	0,95	***74***
Powder milk	13	0,44	***15***	0,87	***29***	1,68	***56***
Prawn	3	20,81	***17***	46,69	***38***	56,91	***46***
Trout	4	1,85	***8***	4,27	***17***	18,31	***75***

Concerning prawns and trout, the evaluation of the PCDD/Fs content on a lipid basis yield to values above the general norms for food-stuffs containing more than 2% of fat (67.5 and 6.12 pg TEQ/g fat respectively). Following some recommendations, calculations should be carried out on a whole weight basis. In this case, values for analyzed prawns and trout fall down to respectively 0.65 and 0.04 pg TEQ/g whole weight. This illustrates the importance of the choice to express results either on a lipid corrected basis or not for these matrices for which a variation factor of 2 order of magnitude can be observed.

While dairy products background levels are very close from those reported last years in other European countries, in the particular case of pork and chicken, the values are lower than in other EC places (e.g. chicken levels are more than 10 times lower in Belgium) [5,6,7]. One possible reason for this could be the lower relative contribution of the 2,3,7,8-TCDD in the case of dairy products in comparison with meat products for which an even small variation in the 2,3,7,8-TCDD content can have significant effect on the TEQ. In addition, depending on the amount of sample processed, levels can be very close to the limits of quantification (LOQ) of the method and differences can therefore appear. This laboratory dependant factors can be relativized by using the "lower-upper bound" system which allows easier comparison between different country studies.

Although relative contributions of PCDDs, PCDFs and cPCBs to the TEQ are not constant ([2%-53%] for PCDDs, [16%-38%] for PCDFs and [29%-75%] for cPCBs) as previously reported [4], one can see in Table 2 that, in a very reproducible way, most of the PCDD/Fs TEQ is due to of the 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF congeners. Actually, these 2 analytes contribute to a mean of 77% an 68% for dairy products and meat products respectively and is decreased to 49% for "fish-type" food-stuffs in which 2,3,7,8-TCDD and 2,3,7,8-TCDF congeners are presents in more significant amounts.

This statistically constant distribution of the 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF in food-stuffs samples could be used as bio-marker for high number of samples screening on a simplified GC/MS method. This potential screening having the advantages of using physico-chemical tool rather than delicate biological assays and to monitor representative congeners of both dioxins and furans families instead of some selected PCBs.

In conclusion, these results show that the levels in analyzed Belgian food-stuffs are all (excluding horse meat and including "fish-type" samples if expressed on a whole weight basis) below the limit of 5pg TEQ/g of product fat depicted in the norm and sometime lower than background levels observed in other EC countries.

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Table 2: PCDD/Fs and cPCBs levels in some food-stuffs (pg WHO-TEQ/g fat)

		Horse	Lamb	Beef	Pork	Chicken	Creme	Butter	Milk fat	Powder milk	Prawn	Trout
	N	12	2	25	34	48	4	8	4	13	3	4
PCDDs	2,3,7,8-TCDD	0,80	0,42	0,19	0,02	0,03	n.d.	n.d.	n.d.	0,02	10,08	0,78
	1,2,3,7,8-PeCDD	2,48	0,89	0,40	0,04	0,09	0,95	0,30	n.d.	0,33	8,91	1,00
	1,2,3,4,7,8-HxCDD	0,17	0,02	0,02	<LOQ	0,01	n.d.	n.d.	n.d.	0,00	0,26	n.d.
	1,2,3,6,7,8-HxCDD	0,46	0,03	0,08	0,01	0,03	0,15	0,04	0,02	0,07	0,86	0,07
	1,2,3,7,8,9-HxCDD	0,10	0,03	0,02	<LOQ	<LOQ	0,05	n.d.	n.d.	0,01	0,42	n.d.
	1,2,3,4,6,7,8-HpCDD	0,17	<LOQ	0,01	0,01	<LOQ	n.d.	<LOQ	<LOQ	<LOQ	0,27	<LOQ
	OCDD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0,01	0,00
	Total PCDDs	**4,19**	**1,39**	**0,74**	**0,08**	**0,16**	**1,15**	**0,36**	**0,02**	**0,44**	**20,81**	**1,86**
	Range	0,47-9,49	0,05-1,36	<0,01-0,90	<0,01-1,97	<0,01-0,24b	0,01-0,39	0,01-0,46	0,01-0,02	0,06-1,11	13,06-26,81	0,01-2,11
PCDFs	2,3,7,8-TCDF	0,14	0,03	0,02	n.d.	0,03	n.d.	0,01	n.d.	n.d.	14,38	1,67
	1,2,3,7,8-PeCDF	0,07	n.d.	0,01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1,32	0,07
	2,3,4,7,8-PeCDF	2,84	0,70	0,84	0,11	0,15	0,25	0,32	0,25	0,71	27,94	2,50
	1,2,3,4,7,8-HxCDF	0,17	0,05	0,07	0,01	0,01	0,05	0,03	0,02	0,07	0,86	n.d.
	1,2,3,6,7,8-HxCDF	0,28	0,02	0,05	0,01	n.d.	0,05	0,03	0,02	0,05	0,79	0,03
	1,2,3,7,8,9-HxCDF	0,20	0,03	0,04	0,01	n.d.	n.d.	0,02	n.d.	n.d.	0,43	n.d.
	2,3,4,6,7,8-HxCDF	0,07	0,02	0,04	<LOQ	n.d.	0,04	0,02	0,02	0,04	0,83	n.d.
	1,2,3,4,6,7,8-HpCDF	0,04	<LOQ	0,02	<LOQ	<LOQ	n.d.	n.d.	n.d.	n.d.	0,15	<LOQ
	1,2,3,4,7,8,9-HpCDF	0,03	n.d.	0,01	<LOQ	<LOQ	n.d.	n.d.	<LOQ	<LOQ	0,01	<LOQ
	OCDF	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0,00	<LOQ
	Total PCDFs	**3,84**	**0,85**	**1,10**	**0,14**	**0,19**	**0,39**	**0,45**	**0,32**	**0,87**	**46,69**	**4,27**
	Range	0,02-0,44	0,03-1,20	0,1-1,18b	<0,01-0,79	<0,01-0,46b	0,15-0,67	0,01-0,87	0,1-0,51	0,54-1,13	26,04-58,45	3,26-6,21
	PCDDs + PCDFs	**8,03**	**2,24**	**1,84**	**0,22**	**0,35**	**1,54**	**0,79**	**0,34**	**1,31**	**67,50**	**6,12**
cPCBs	3,3',4,4'-TCB (77)	0,01	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0,24	0,06
	3,4,5,4'-TCB (81)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0,01	0,00
	3,3',4,4',5-PeCB (126)	11,43	3,06	3,41	0,15	0,72	0,61	0,93	0,94	1,66	56,07	18,06
	3,3',4,4',5,5'-HxCB (169)	0,12	0,05	0,07	<LOQ	0,01	0,01	0,01	0,01	0,02	0,59	0,19
	Total cPCBs	**11,57**	**3,11**	**3,48**	**0,15**	**0,73**	**0,62**	**0,94**	**0,95**	**1,68**	**56,91**	**18,31**
	Range	0,13-18,9	0,03-3,14	<0,01-5,35a	<0,01-0,65	<0,01-1,35b	0,01-1,22	0,01-1,54	0,01-1,39	0,01-2,07	40,44-73,06	11,64-27,40
	PCDDs + PCDFs + cPCBs	**19,59**	**5,35**	**5,31**	**0,37**	**1,08**	**2,15**	**1,74**	**1,28**	**2,99**	**124,41**	**24,43**

a) extreme values of 7,17 and 38,44
b) extreme values of 5,74 and 1,48 and 2,46

- nd : not detected
- <LOQ : below the limit of quantification