

COMPARISON OF PCDD/FS AND cPCBs LEVELS IN COMMERCIAL PASTEURIZED COW'S MILK IN WALLONIA (BELGIUM)

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Introduction

Among the group of persistent organic pollutants (POPs), polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are of major concern since they represent a potential human health risk via the environment and the food consumption. The lipophilic character of these toxicants allows them to bio-accumulate in the food chain up to human for which consumption of fatty food became the most important way of exposure with milk and dairy products a major concern. Their contribution to the daily intake of TCDD-equivalents had been previously estimated to be close to 30% [1].

Materials and methods

Samples

Cow's milk samples were pasteurized full fat grade (around 3.5 % fat) obtained from designated high delivery rate supermarket in the area of Liege (Wallonia, Belgium) between January and April 2001. Each of the 8 selected brands were sampled several times during this defined period of time in order to obtain a representative estimation for each one. Packaging materials were either TetraBrik[®] or poly-ethylene (PE) type. Portions between 100 and 80 ml were used for this study and producer's lipid content values were used to produce the lipid corrected values. A total of 35 samples were analyzed for PCDDs, PCDFs and cPCBs.

Extraction and Clean-up

Automated extraction and clean-up were performed on the new Power-Prep[™] generation system (Fluid Management Systems, Waltham, MA, USA) using disposable columns (octadecyl bonded (C₁₈), multi-layer silica and PX-21 carbon) after sample pre-treatment using a modified AOAC method [2]. This method has been described in more detail elsewhere [3].

Analysis

Analysis were performed (isotopic dilution method) using a validated method routinely used for dioxin monitoring in foodstuffs. An Autospec Ultima high-resolution mass spectrometer (Micromass, Manchester, UK) operating at a resolution of 10.000 in the selected ion monitoring mode (SIM) was used. Gas chromatography was carried out on an Agilent (Palo Alto, CA, USA) 6890 Series gas chromatograph equipped with a RTX-5 (30m x 0.25mm x 0.25µm) capillary column (Restek, Interscience, Louvain-la-neuve, Belgium). TEQs were calculated using WHO TEFs [4].

Results and Discussion

During this preliminary study, collected long-life drinking milk were either packaged in plastic bottle (54% of samples) or milk bricks (46% of samples) issued from popular commercially available brands. For one of the brand, both PE and brick packaging material were collected without any significant differences between mean concentrations as previously reported in a recent study [5].

Figure 1 presents the average congeners profile for all collected pasteurized cow's milk samples.

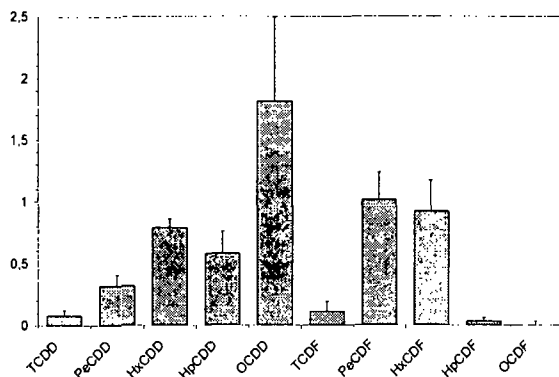


Fig. 1 : PCDD/Fs congeners profile in commercial cow's milk (mean concentrations in pg/g fat).

This congener distribution is very similar to the one previously reported for rural area in other European countries with OCDD exhibiting the highest level [6,7]. In these samples, HpCDFs and OCDF were in low concentration in opposition with results obtained with cow's milk issued from vicinity of potential contaminant sources which usually exhibit higher levels of PCDFs [8,9]. Based on concentration, the dioxin fraction account for 64% (3.58 ± 1.07 pg/g fat) of the mean total PCDD/Fs concentration and the furans for the remaining 36% (2.05 ± 0.46 pg/g fat).

The cPCBs content has also been evaluated and they are present in samples with the average concentration value of 24.23 ± 7.81 pg/g fat.

Table 1 illustrates the levels measured for the different brands in pg TEQ/g of milk fat. The average level for all brands is 1.11 pg TEQ/g of milk fat (PCDD/Fs only) with a fairly high standard deviation value of 0.30 which account for the relatively spread background levels observed between the different brands. This value is somewhat higher than the one observed as average in recent study carried out in Belgian border country but not significant enough to indicate any serious contamination problems [5]. On the other hand, this average value seems to be lower than the one reported by Public Health authorities for 1998 (2.0 pg TEQ/g fat, raw milks sampled in the different provinces of Belgium) [10]. In addition, since global analytical procedures (sampling and analysis) were not the same in all studies, it is always difficult to rigorously compare the results. This value is anyway clearly below the established tolerable value of 5 pg TEQ/g of milk fat. However, efforts have still to be realized in order to decrease this average value under the target value of 1 pg TEQ/g of milk fat recommended by the European Union.

The relative contributions of PCDDs and PCDFs to the TEQ are respectively 44% and 56% (cPCBs excluded). As usually observed in food-stuffs, the main contribution to the PCDD/Fs TEQ is due to 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF congeners [11]. This tendency being the most important for dairy product with, in the present study, a summed contribution of 72%. One can also notes that if cPCBs (which are not concerned by the norm) are included, the average level

goes up to 2.25 ± 0.54 pg TEQ/g of milk fat and account for more than 50% of this value (Fig.2) as previously reported [12]. This value being still under the critical value of 5 pg TEQ/g of fat.

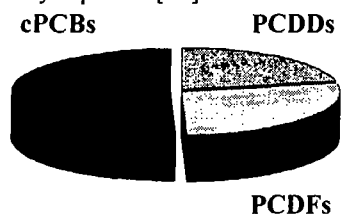


Fig. 1 : Distribution of PCDD/Fs and cPCBs.

On a brand to brand comparison point of view, the range is contained between 0.75 and 1.6 pg TEQ/g on a fat basis, demonstrating that levels can double. This has however to be confirmed in a longer period of time on a larger number of samples to allow possible tracability of potentially more exposed producers.

Finally, it is interesting to note that brand G, which proposes a product issued from biological agriculture (Biogarantie®), presents a background level located in the lower part of the measured range for this study.

Conclusion

These results indicates that levels of PCDDs, PCDFs and cPCBs present in long-life drinking milk (pasteurized cow's milk) generally sold in high delivery rate supermarket in the area of Liege (Wallonia, Belgium) are far below the tolerated value of 5 pg TEQ/g of milk fat.

Acknowledgements

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Table 1: PCDD/Fs and PCBs levels in commercial pasteurized milk in Wallonia (pg WHO-TEQ/g fat)

	Brand A	Brand B	Brand C	Brand D	Brand E	Brand F	Brand G	Brand H	
N	5	5	2	2	5	5	5	6	
PCDDs	2,3,7,8-TCDD	0,054	0,090	0,108	0,000	0,110	0,085	0,088	0,105
	1,2,3,7,8-PeCDD	0,253	0,389	0,350	0,227	0,284	0,323	0,247	0,499
	1,2,3,4,7,8-HxCDD	0,007	0,012	0,000	0,000	0,012	0,020	0,010	0,030
	1,2,3,6,7,8-HxCDD	0,046	0,058	0,061	0,057	0,053	0,058	0,046	0,050
	1,2,3,7,8,9-HxCDD	0,005	0,018	0,016	0,011	0,009	0,021	0,012	0,017
	1,2,3,4,6,7,8-HpCDD	0,005	0,008	0,004	0,006	0,005	0,005	0,005	0,009
	OCDD	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
	Total PCDDs	0,371	0,576	0,539	0,300	0,474	0,512	0,407	0,711
	Range	0,32-0,47	0,38-0,70	0,52-0,56	0,25-0,35	0,42-0,53	0,37-0,64	0,23-0,54	0,53-0,90
	PCDFs	2,3,7,8-TCDF	0,006	0,008	0,016	0,029	0,007	0,007	0,007
1,2,3,7,8-PeCDF		0,001	0,007	0,000	0,000	0,002	0,002	0,002	0,001
2,3,4,7,8-PeCDF		0,322	0,623	0,602	0,017	0,522	0,546	0,381	0,768
1,2,3,4,7,8-HxCDF		0,012	0,020	0,014	0,000	0,023	0,016	0,009	0,021
1,2,3,6,7,8-HxCDF		0,033	0,047	0,059	0,002	0,042	0,044	0,032	0,053
1,2,3,7,8,9-HxCDF		nd.	nd.	nd.	nd.	nd.	nd.	0,000	nd.
2,3,4,6,7,8-HxCDF		0,035	0,044	0,047	0,401	0,039	0,047	0,032	0,050
1,2,3,4,6,7,8-HpCDF		0,000	0,001	0,000	0,000	0,000	0,000	0,000	0,000
1,2,3,4,7,8,9-HpCDF		0,000	0,000	0,000	0,002	0,000	0,000	0,000	0,000
OCDF		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Total PCDFs	0,410	0,750	0,737	0,452	0,635	0,663	0,462	0,901	
Range	0,35-0,49	0,57-0,83	0,61-0,83	0,26-0,55	0,50-0,67	0,60-0,77	0,26-0,74	0,74-0,97	
PCDDs + PCDFs	0,782	1,325	1,277	0,752	1,109	1,175	0,869	1,611	
cPCBs	3,3',4,4'-TCB (77)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	3,4,5,4'-TCB (81)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	3,3',4,4',5-PeCB (126)	0,810	1,241	1,202	0,938	0,973	1,230	0,998	1,596
	3,3',4,4',5,5'-HxCB (169)	0,012	0,017	0,016	0,012	0,013	0,017	0,012	0,022
	Total cPCBs	0,822	1,258	1,218	0,950	0,986	1,247	1,010	1,618
Range	0,63-1,09	1,12-1,46	1,22-1,22	0,65-1,25	0,93-1,08	1,06-1,38	0,55-1,41	1,48-1,75	
PCDDs + PCDFs + cPCBs	1,604	2,583	2,495	1,702	2,095	2,422	1,879	3,229	

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