SPATIOTEMPORAL TRENDS OF PCDD/Fs IN BELGIAN COW'S MILK

Rudy Van Cleuvenbergen [1], Pierre Mannaert [2], Nancy Van Durme [2], Christine Vinkx [3] and Leo Goeyens [4]

[1]Vito, Boeretang 200, B-2400 Mol
[2]Belgian Fed. Agency for the Safety of the Food Chain, Simon Bolivarlaan 30, B-1000 Brussels
[3]Belgian Fed. Agency for the Safety of the Food Chain, Pachecolaan 19 bus 5, B-1010 Brussels
[4]Scientific Institute of Public Health, Juliette Wytsmanstraat 16, B-1050 Brussels

Introduction

The Belgian federal authorities are regularly monitoring dioxins in milk and dairy products. Results and trends are investigated by an informal working group, gathering representatives of the federal food/feed inspection services, the regional environmental inspection services and labora-tories. Initially, emphasis was on PCDD/F analysis; since 1999 non-ortho PCBs are also measured.

The present paper reports on the temporal trend of the average WHO-TEQ (PCDD/F) levels in Belgian milk, seasonal effects, the variability among the Belgian provinces and the congener distribution. It also compares the observed levels with those from other recent studies in Europe.

Materials and methods

Sampling

Cow's milk was sampled one (1994), two (1995-1999) or three (since 2000) times per year, aiming at a representative sample for each Belgian province. The samples were taken at a dairy factory and composed of raw milk from three different trucks, known to collect milk at farms in different parts of one province. Generally two samples were taken for the province of Hainaut, due to practical difficulties in obtaining a representative sample for the province of Brabant-Wallon. For various reasons some other minor deviations occurred in the scheme. Samples were stored in well-cleaned glass bottles and kept cool until analysis.

Chemical analysis

After partly evaporating the milk and mixing with chemical drying agents, the fat fraction was extracted with 2/1 n-hexane/acetone and gravimetrically determined. For clean up ca. 7 g of extracted fat was spiked with 16 ^{13}C-labelled internal standards and subsequently purified by column chromatography on silica/H_2SO_4, HPLC using a carbon column, and column chromatography on basic alumina. The measurements were performed with GC-HRMS. A complete description of the analytical procedure and QA/QC measures applied is given elsewhere[1]. The laboratory has been accredited according to EN 45001 for this analysis since 1998 and participates successfully in international interlaboratory studies.

Dioxin concentrations are given in pg WHO-TEQ (PCDD/F) per g fat, using the TEF values published by Van den Berg[2]. They were calculated as upper bound levels, as proposed in Council Regulation (EC) N° 2375/2001[3]. Lower bound levels were, on the average, 4.2 % lower.

Results

The yearly average dioxin levels in Belgian cows' milk show a clear decreasing trend from 3.1 pg TEQ per g fat (range: 5.1-1.3; n=8) in 1994 to 1.1 pg TEQ per g fat (range: 1.9-0.5; n=29) in 2001

(Figure 1). In 2000 the background dioxin level in cow's milk had reached 48 % of the 1995 level. This procentual decrease is almost equal to the reduction of dioxin emissions in the Flemish part of Belgium during the same period, as calculated from the emission inventory for the various sources[4].. None of the levels in 2001 exceeded a value of 2 pg TEQ per g fat, which is far below the limit value of 5 pg TEQ per g fat imposed by the Belgian legislation[5].

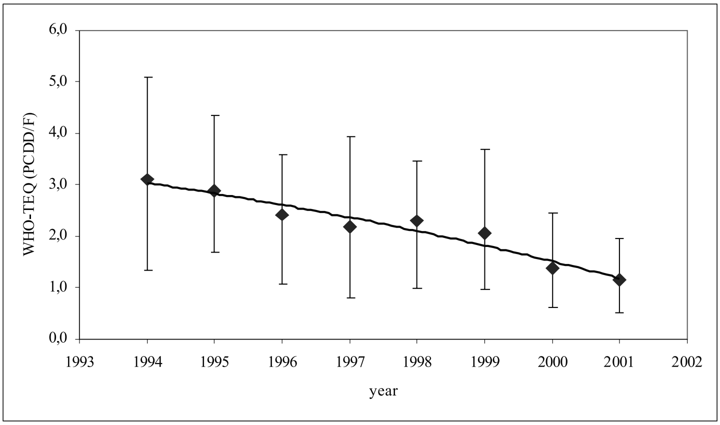

Figure 1. average PCDD/F levels and their range in Belgian cow's milk

Provincial trends confirm the overall decrease of the background levels; the TEQ values measured in 2000 and 2001are consistently and markedly lower than earlier values. Between the highest value and the one observed in 2001, the relative decrease ranges from 49 to 74 % depending on the province.

In order to assess seasonal variabilities, for each of the 16 campaigns in the period 1995-2001 the procentual deviation of the campaign's average from the yearly average TEQ level was calculated and related to the month of sampling. Though all months were not represented equally in the sampling history, the average deviations per month (Figure 2) indicate that winter background levels tend to be higher than spring and summer levels. Similar seasonal effects have been noticed in the dioxin deposition monitoring programme in Flanders, Belgium, as well as in other studies[6].

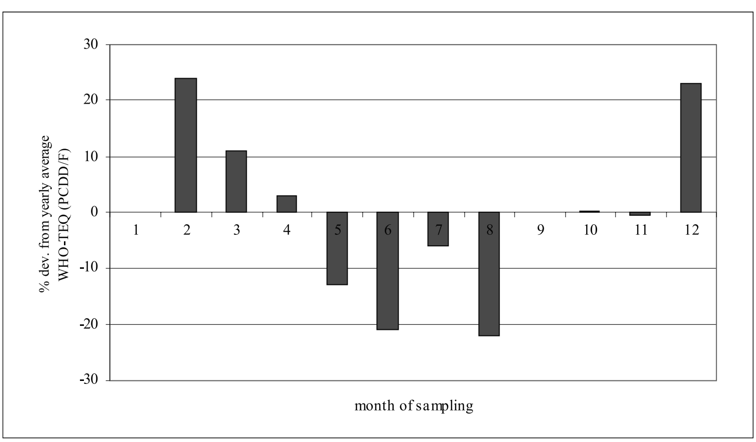

Figure 2. seasonal variability of PCDD/F levels in Belgian cow's milk

Spatial variability was investigated by comparing yearly averages for the different provinces with overall yearly averages. As shown in Figure 3, overall averages are exceeded almost consistently in 4 provinces, being Oost-Vlaanderen, West-Vlaanderen, Hainaut and Vlaams- Brabant. Though in the period 1994-1999 dioxin levels in some provinces were up to ca. 70 % higher than the overall yearly average, this has dropped to ca. 20 % in 2000-2001.

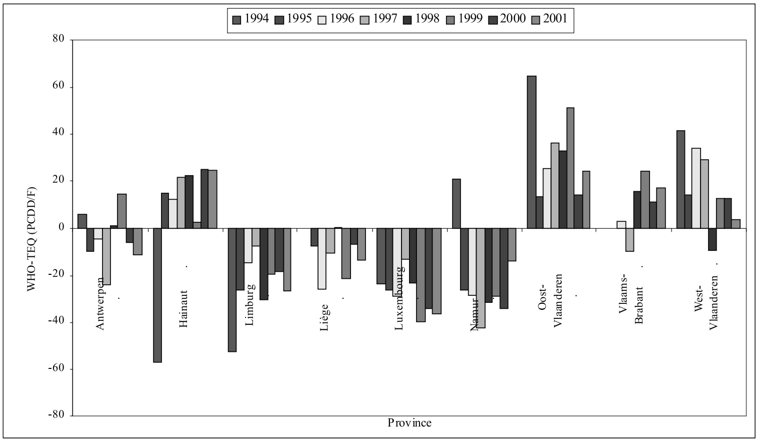

Figure 3. spatial variability of PCDD/F levels in Belgian cow's milk

The contribution of the various PCDD/F congeners to the WHO-TEQ (PCDD/F) was found to be quite stable throughout the years, with 3 congeners (23478-PCDF, 12378-PCDD and 2378-TCDD) representing approx. 80%. Figure 4 presents the contribution of 12 congeners in early and recent years; the remaining congeners contributed less than 1% to the total TEQ. The observed pattern agrees well with literature data for Belgium[7] as well as other European countries[8].

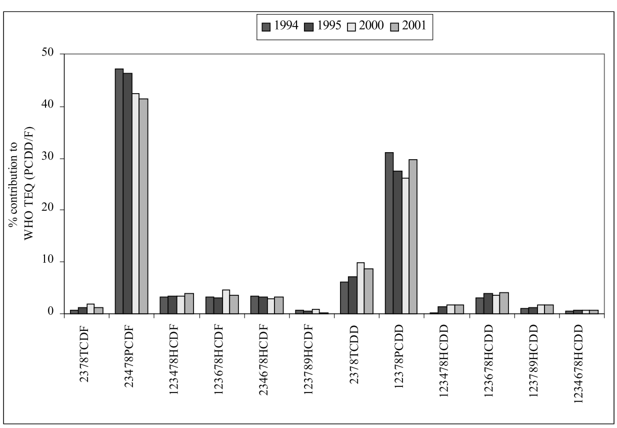

Figure 4. contribution of the various congeners to the total WHO-TEQ (PCDD/F) level in Belgian cow's milk; only congeners with contribution >1 % are shown

Since mid 2000, also non-ortho PCBs (PCB 77, 81, 126, 169) have been measured. The average WHO-TEQ for non-ortho PCBs in 2000 and 2001 amounts to 1.9 and 1.7 pg TEQ per g fat, and is made up almost entirely by PCB 126. The limited number of data obtained so far does not indicate seasonal variability of the non-ortho PCB TEQ level. The contribution of the non-ortho PCB TEQ to the sum of PCDD/F and non-ortho PCB TEQs ranges from 53 to 65 %.

Discussion

In general, the background dioxin levels in Belgian milk in 2001 still would appear slightly higher than recent values reported for other European countries (Table 1). However, taking into account the inherent spread on average values, possible effects of sampling strategy and treatment of non-quantifiable congeners, apparent differences might not be significant. More data on dioxins (in pg NATO-TEQ per g fat) and dioxin-like PCBs in European foodstuffs up to 1999 have been compiled in a SCOOP report[12].

Table 1. recent background levels (pg WHO-TEQ per g fat) for European dairy products

		PCDD/Fs	non-ortho PCBs
Belgium	raw milk, 2001 (n=29) (present study)	1.15	1.65
	pasteurized milk, 2001 (n=35) [7]	1.11*	1.14*
	cheese, 2000-2001 (n=15) [9]	0.93	1.16
The Netherlands	milk-butter-cheese, 1999 (n=6 **) [8]	0.64 *	0.69 *
	raw milk, 1998-1999 (n=12) [8]	0.64 *	0.87 *
Germany	milk-dairy products, 1998 (n=26) [10]	0.77 *	1.55 *
Various European	butter, 1998 (n=8 **) [11]	0.72 *	0.94 *
countries	cheese, 2000-2001 (n=15) [9]	0.65	0.85

* lower bound value (<LOQ = 0); ** composite samples

Acknowledgement

The authors gratefully acknowledge participation in the working group by K. Aksajef, P. Beirens, M. Blondeel, E. Daeseleire, J. Delfosse, M. Desmedt, F. François, J. Gosselé, S. Goux, E. Hoc, M. Delanghe, W. Smedts, S. Srebrnik, D. Standaert, M. Ulens, R. Van Havere, I. Vanpoucke, R. Van Renterghem, X. Veithen and other previous members.

References

1. Goyvaerts M.-P., Ooms D., Van Cleuvenbergen R., Schoeters G. (2002) Chemosphere, subm.
2. Van den Berg M. et al. (1998) Environ. Health Perspect. 106, 775
3. Council Regulation (EC) N° 2375/2001 of 29.11.2001, OJ L 321, 6.12.2001, 1
4. Wevers M., De Fré R., Schoeters G. (2001) in: MIRA-T 2001, VMM (Ed.), ISBN 90-441-1195-7 (in Dutch)
5. Royal decree of 19.05.2000, Belgisch Staatsblad 31.05.2000 Ed. 2, 18791 (in Dutch/French)
6. Van Lieshout L., Desmedt M., Roekens E., De Fré R., Van Cleuvenbergen R., Wevers M. (2001) Atmos. Environ. S83
7. Focant J.-F., Pirard C., André J.E., Massart A.C., De Pauw E. (2001) Organohal. Comp. 51, 340
8. Freijer J.I., Hoogerbrugge R., van Klaveren J.D., Traag W.A., Hoogenboom L.A.P., Liem A.K.D. (2001) RIVM report 639102 022
9. Food Inspection Services (Brussels), unpublished monitoring data
10. Fürst P. (2001) Organohal. Comp. 51, 279
11. Santillo D., Fernandes A., Stringer R., Johnston P., Rose M., White S. (2001) Organohal. Comp. 51, 275
12. SCOOP Task 3.2.5 - Final report, 04.05.2000, EC-DG SANCO (Ed.)