PCDD/F and PCB levels in Austrian Cow's Milk

Gerhard Thanner[1], Wolfgang Moche[1]

[1]Umweltbundesamt Wien

Introduction

In 2003 the Federal Environment Agency carried out a first Austrian wide milk monitoring study with the objective to get an overview of average PCDD/F levels in cow's milk, additionally dioxin-like PCBs, according to WHO, and indicator PCBs, as listed by national regulations, were analysed.

Methods and Materials

Samples

Raw cow's milk was collected in collaboration with the Austrian Federal Institute for diary farming in Wolfpassing, a subsidiary of the Austrian Agency for Health and Food Safety. Pooled raw milk samples have been collected from 25 dairy factories in Austria. Additionally 7 samples have been collected from 7 alpine dairies located in Vorarlberg and Tyrol. Sample collection has been carried out from February to April 2003 (21 samples) and in September 2003 (9 samples). Samples were collected in polypropylene bottles and stored at –20°C until analysis.

Analytical methods

Procedures used for fat extraction and clean-up are based on methods published earlier[1]. A short description is given in the following.

Cream was separated by centrifugation of 500 ml raw milk. After freeze drying of the cream layer the residue was soxhlet extracted by toluene/ethanol 2:1. After determination of fat content 5g of milk fat were redisolved in n-hexene and spiked with 17 ^{13}C-labeled PCDD/F congeners, 12 ^{13}C-labeled dioxin-like PCBs and 6 ^{13}C-labeled indicator PCBs. The fat removal occurred by treatment of the sample with concentrated sulfuric acid adsorbed on celite. Further clean-up comprised a multilayer silica column and alox column.

High resolution GC/MS was carried out on a Finnigan MAT 95 coupled to a HP 6890 gaschromatograph equipped with a cool injection system by Gerstel. PCDD/F have been analysed using a J&W DB5 and a DBDIOXIN, PCBs using a DB5ms. The mass spectrometer was operated in single ion mode at a mass resolution of 10000.

Detection limits for PCDD/F were in the range of 0,2 to 0,5 pg/g fat, for dioxin like PCB in the range of 0.5 to 1.5 pg/g fat and for indicator PCB in the range of 5 to 10 pg/g fat.

The calculation of toxic equivalents for PCDD/F was carried out according I-TEF and WHO schemes as well. The PCB levels are expressed as TEQ according to WHO and as sum of six indicator PCBs, comprising congener 28, 52, 101,138,153 and 180 (numbers according IUPAC).

Results and Discussion

The results of the current study are summarised in Table 1 and 2 giving the levels of PCDD/F and PCB in cow's milk from dairy factories and alpine dairies.

The PCDD/F levels originating from dairy factories are in the range of N.D. to 0.33 pg I-TEQ/g fat with an average of 0.14 pg I-TEQ/g fat. This PCDD/F levels compare very well with recent results of a Swiss study[2] which found levels of 0.51 ± 0.19 pg I-TEQ/g fat based on samples from 2001. The PCB concentrations in Austrian dairy factory samples were in the range of 0.36 to 1.11 pg WHO-TEQ/g fat with an average value of 0.83 pg WHO-TEQ/g fat. The concentrations of the indicator PCB were in the range of 2.6 to 10.1 ng Σ-PCB/g fat. This concentrations are in the same range as reported by former studies carried out in Austria[3,4] showing PCB levels of 8.4 ± 4.8 ng Σ-PCB/g fat based on samples originating from 1999.

Due to economic concentration processes since 1995, when Austria joined the EC, the number of dairy factories in Austria decreased significantly. As a result for most of the dairy factories no precise milk-collection area can be defined. Therefore the results, as given in Table 1 are sorted by federal state which provides a rough allocation of the sample origin.

The results of the samples originating from selected alpine dairies showed nearly the same levels of PCDD/F an dioxin like PCBs compared to dairy factory samples With respect to the indicator PCBs a significant lower level could be observed, showing concentrations in the range from 0.2 to 6.6 ng Σ-PCB/g fat with an average value of 1.78 ng Σ-PCB/g fat.

The results showed that Austrian milk samples are clearly below the current EC limit value of 3 pg WHO-TEQ/g fat. No significant differences, with respect to PCDD/F and dioxin-like PCB, could be found between milk samples originating from diary factories and alpine diaries with an regional limited collection area. The differences in the levels of indicator PCBs in cow's milk are a clear indication for still continuing industrial influence showing significant lower levels for milk samples from remote alpine regions.

Table 1 PCDD/F and PCB levels in raw cow's milk form dairy factories in Austria

Sampling month	Federal State	PCDD/F		PCB	
		TEQ (ITEF) pg/g	TEQ (WHO) pg/g	TEQ pg/g	Σ I-PCB ng/g
Apr 03	Carinthia	0.04	0.03	0.95	7.3
Sep 03	Carinthia	0.08	0.08	0.69	7.6
Apr 03	Carinthia	0.23	0.23	0.75	7.3
Sep 03	Carinthia	0.33	0.37	0.72	7.0
Apr 03	Lower Austria	N.D.	N.D.	0.79	5.8
Apr 03	Lower Austria	N.D.	N.D.	0.43	3.5
Sep 03	Lower Austria	0.14	0.14	0.71	6.0
Sep 03	Lower Austria	0.17	0.17	0.78	5.9
Apr 03	Lower Austria	0.20	0.20	0.64	5.4
Apr 03	Upper Austria	N.D.	N.D.	0.57	6.2
Sep 03	Upper Austria	0.05	0.05	0.87	6.3
Sep 03	Upper Austria	0.08	0.16	0.76	6.5
Apr 03	Upper Austria	0.16	0.16	0.83	8.4
Apr 03	Upper Austria	0.20	0.20	0.64	7.9
Sep 03	Upper Austria	0.21	0.20	0.85	5.9
Apr 03	Upper Austria	0.25	0.25	0.92	6.7
Apr 03	Upper Austria	0.29	0.35	0.66	6.6
Sep 03	Salzburg	N.D.	N.D.	0.85	5.2
Apr 03	Salzburg	0.03	0.02	0.96	6.1
Apr 03	Salzburg	0.29	0.29	1.11	8.3
Sep 03	Styria	0.01	0.01	0.36	3.9
Apr 03	Styria	0.15	0.14	1.00	8.6
Apr 03	Tirol	0.21	0.20	0.84	10.1
Apr 03	Tirol	0.21	0.20	1.05	8.6
Feb 03	Vorarlberg	0.17	0.17	0.88	2.6

Table 2 PCDD/F and PCB levels in raw cow's milk from alpine dairies in Austria

Sampling month	Federal State	PCDD/F		PCB	
		TEQ (ITEF) pg/g	TEQ (WHO) pg/g	TEQ pg/g	Σ I-PCB ng/g
Apr 03	Tirol	N.D.	N.D.	0.72	6.6
Feb 03	Tirol	0.24	0.24	0.79	1.5
Feb 03	Vorarlberg	0.01	0.01	0.83	1.3
Feb 03	Vorarlberg	0.14	0.14	0.92	0.3
Feb 03	Vorarlberg	0.15	0.15	0.77	1.0
Feb 03	Vorarlberg	0.26	0.26	0.88	0.2
Feb 03	Vorarlberg	0.29	0.29	0.92	1.6

References

1 Malisch R. (1994) Organohalogen Compounds 20, 209.
2 Schmid P., Gujer E., Zenegg M. and Studer C.(2003) Chemosphere 53, 129.
3 ÖMIG (1999), Deutsche Milchwirtschaft 16, 729.
4 Puchwein G., Brodacz W., Stelzer R., Eibelbauer A., Pilsbacher L., Zeller R. and Fuchs K. (1997) Die Bodenkultur 48(2), 105.