

LEVELS OF PCDD/DFs IN RETAIL COWS' MILK IN TAIWAN

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Introduction

The levels of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) in retail cows' milk in Taiwan is not available yet. Analytical data are needed to help evaluating the contribution of PCDD/DFs dietary intake from cows' milk. Milk and dairy products are becoming prevalent food for the Taiwanese. Dietary intake of cows' milk might become one of the major exposure routes of PCDD/DFs for the Taiwanese. The preliminary survey of PCDD/DFs levels in retail cows' milk in Taiwan is, therefore, carried out for the first time.

Materials and Methods

The survey of PCDD/DFs levels in 9 different brands of retail cows' milk was carried out on April 2000. Milk samples were purchased from the supermarkets in Taipei city. All samples were collected in the same day and stored at 4°C refrigerator. Aliquots of the sample were fortified with fifteen ¹³C₁₂ labeled PCDD/DFs congeners as internal standards and ³⁷Cl₄-TeCDD as the clean-up standard. Milk samples were extracted by using a modified AOAC extraction procedure¹ (sodium oxalate, acetone and 50:50 v/v dichloromethane/n-hexane). The fat contents were measured by gravimetric weighting. An activated carbon column was used for fat removal. The fat-free extract was cleaned-up with a sulfuric acid-impregnated silica gel column, followed with another acidic alumina column. ¹³C₁₂-1,2,3,4-TeCDD and ¹³C₁₂-1,2,3,7,8,9-HxCDD were spiked into the cleaned extract as recovery standards. Samples were analyzed for the seventeen 2,3,7,8-substituted PCDD/DFs. The spiked concentrates were analyzed using a HP-5890GC/Fisson Autospec Ultima HRMS equipped with a J&W DB-5ms fused-silica capillary column (60 m × 0.25 mm i.d. × 0.25 μm film). A minimum mass resolution of 10000 (10% valley definition) was maintained. The recoveries of the internal standards are all within the quality control limits. The toxic equivalents (TEQ) were calculated using the WHO-TEF(1998)² and I-TEF(1988)³ system. The concentrations of the not detected congeners are calculated with zero, half the limit of detection (LOD) and the LOD, respectively.

Results and Discussion

The dioxin contents from the seventeen 2,3,7,8-substituted PCDD/DFs in cows' milk are listed in Table 1, together with the fat contents information. Dioxin levels in milk samples range from 0.33 to 1.83 pg WHO-TEQ/g fat. The average value is 0.94 pg WHO-TEQ/g fat (median of 0.80 pg WHO-TEQ/g fat). To facilitate the comparison to literature data, different unit systems are used to express the dioxin levels in milk. The average value is 0.59 pg/g wet weight (median of 0.52 pg/g wet weight), 19 pg/g fat (median of 16 pg/g fat), 0.032 pg WHO-TEQ/g wet weight (median of 0.022 pg WHO-TEQ/g wet weight) and 0.89 pg I-TEQ/g fat (median of 0.82 pg I-TEQ/g fat), respectively. In this survey, congeners 2,3,7,8-TeCDD, 2,3,7,8-TeCDF and 1,2,3,7,8-PeCDD were

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11. Vieth, B., Heinrich-Hirsch, B. and Mathar, W. (2000) *Organohalogen Compounds*, 47, 300-303.
12. Fiedler, H., Cooper, K. R., Bergek, S., Hjelt, M. and Rappe, C. (1997) *Chemosphere*, 34, 1411-1419.
13. Vindel, E. E. et al. (1999) *Organohalogen Compounds*, 43, 437-440.
14. Liem, A. K. D. and Theelen, R. M. C. (1997) *Dioxins: Chemical Analysis, Exposure and Risk Assessment*, Thesis, Univ. of Utrecht, NL.

Table 1. PCDD/DFs levels in milk samples (expressed in different unit systems, the concentrations of the not detected congeners are calculated with zero)

Sample	A	B	C	D	E	F	G	H	I	Avg.
pg/g wet wt.	0.46	0.47	0.41	0.38	0.66	0.90	0.60	0.52	0.88	0.59
pg/g fat	14	14	11	12	21	40	16	19	20	19
pg WHO-TEQ /g wet wt.	0.036	0.018	0.012	0.049	0.031	0.017	0.022	0.022	0.081	0.032
pg WHO-TEQ /g fat	1.1	0.53	0.33	1.5	0.97	0.74	0.61	0.80	1.8	0.94
pg I-TEQ /g fat	1.1	0.54	0.33	1.3	0.98	0.76	0.62	0.82	1.5	0.89
Fat content%	3.2%	3.4%	3.6%	3.3%	3.2%	2.2%	3.7%	2.8%	4.5%	3.3%

Table 2. The upper-bound levels of PCDD/DFs in cows' milk when the concentrations of the not detected congeners are calculated with zero, half the limit of detection (LOD) and the LOD

Sample	A	B	C	D	E	F	G	H	I	Avg.
pg-TEQ/g fat as ND=0	1.1 ^a (1.1) ^b	0.53 (0.54)	0.33 (0.33)	1.5 (1.3)	0.97 (0.98)	0.74 (0.76)	0.61 (0.62)	0.80 (0.82)	1.8 (1.5)	0.94 (0.89)
pg-TEQ/g fat as ND=0.5LOD	1.7 (1.6)	1.2 (1.1)	0.88 (0.78)	1.6 (1.4)	1.3 (1.3)	1.5 (1.4)	0.98 (0.91)	1.4 (1.3)	2.1 (1.7)	1.4 (1.3)
pg-TEQ/g fat as ND=LOD	2.3 (2.0)	1.9 (1.7)	1.4 (1.2)	1.6 (1.4)	1.7 (1.6)	2.4 (2.1)	1.4 (1.2)	1.9 (1.7)	2.3 (2.0)	1.9 (1.7)

^a Calculation with WHO-TEF

^b Calculation with I-TEF

Table 3. The PCDD/DFs levels in cows' milk from different origin (pg I-TEQ/g fat)

Origin (Year of)	Product	Mean	Range	Reference
Finland	Cows' milk	0.83	<0.5-1.8	5
Brazil (1999)	Cows' milk	0.07	--	6
Poland (1999)	Cows' milk	--	0.1-4.0	7
Spain (1999)	Cows' milk	--	0.09-0.90	8
Ireland (1995)	Cows' milk	0.21	0.14-0.5	9
Germany (1989-1993)	Cows' milk	0.87	0.69-1.12	10
Germany (1995-99)	Milk and milk products	0.58	--	11
USA (1994)	Dairy products	0.77	0.42-1.10	12
France (1998)	Cows' milk	0.65	0.29-1.75	13
Netherlands (1992-93)	Cows' milk	1.3	0.9-2.0	14