

## 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 <sup>13</sup>C<sub>12</sub> labeled PCDD/DFs congeners as internal standards and <sup>37</sup>Cl<sub>4</sub>-TeCDD as the clean-up standard. Milk samples were extracted by using a modified AOAC extraction procedure<sup>1</sup> (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. <sup>13</sup>C<sub>12</sub>-1,2,3,4-TeCDD and <sup>13</sup>C<sub>12</sub>-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)<sup>2</sup> and I-TEF(1988)<sup>3</sup> 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 not detected in most samples. Because of the larger TEF value for these congeners, the concept of upperbound levels was used. Three estimates of PCDD/DFs TEQ concentrations were calculated using zero, half LOD and LOD value for the non-detects. The upper-bound levels of TEQs for each milk sample are summarized in Table 2. Detection limit is approximately 0.1 pg/g fat for each individual congener. The determination limit is *ca.* 0.3 pg WHO-TEQ/g fat for the summation of all 17 2,3,7,8-substituted PCDD/DFs. Higher average TEQ levels are obtained when using WHO-TEF. This TEQ increase is attributed to the increasing TEF value of 1,2,3,7,8-PeCDD, namely from 0.5 (I-TEF) to 1 (WHO-TEF). The TEQ increase is 5% (ND=0) and 11% (ND=LOD), respectively. Even though the upper-bound levels are used to represent the PCDD/DFs contents for Taiwanese cows' milk, the levels are far below to the guideline value of 5 pg I-TEQ/g fat for the dairy products set by the Government during the "Belgian dioxin crisis". The levels are also below the guideline value of 3 pg WHO-TEQ/g fat in the EC Regulation<sup>4</sup>.

The WHO agreed on a tolerable daily intake (TDI) of PCDD/DFs and dioxin-like PCBs in the range of 1-4 pg WHO-TEQ/kg bw/day in 1998 when assessing the risk for human health. The mean annual consumption amount of cows' milk is *ca.* 10 kg per Taiwanese. Using the TEQ data in Table 1, the daily intake of PCDD/DFs from cows' milk is about 0.85 pg WHO-TEQ/day, which contributes little to the WHO TDI criteria.

Based on the limited amount of data in Table 3, a slightly higher levels of PCDD/DFs in Taiwanese cows' milk is observed, when comparing to the recent results from other countries. Because of the limited resources of land, the Taiwanese dairy farm usually grew cows in pens and fed the cow with imported feed. Most cows could not easily graze the farm soil. The dioxin exposure from grazing soil was, therefore, a minor route. In stead, the dioxin exposure from feed was the main route. The local practice of feeding cows mainly with imported feed precluded the establishment of a relationship between dioxin levels in cows' milk and farm's environment in Taiwan. Currently, the Taiwan Government has no regulations or any guideline value about the dioxin level in animal feed. The understanding of the influence of dioxin levels in cows' feed upon the dioxin levels in cows' milk is critical. Future investigation of dioxin content in cows' feed is suggested.

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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 <sup>a</sup> (1.1) <sup>b</sup>	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)

<sup>a</sup> Calculation with WHO-TEF

<sup>b</sup> 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