Increase of PCDD/F-Contamination of Milk and Butter in Germany by Use of Contaminated Citrus Pulps as Component in Feed

Malisch, Rainer
Chemische Landesuntersuchungsanstalt Freiburg
Bissierstr. 5, D-79114 Freiburg, Germany

1 Introduction

In Germany, since 1989 numerous measures were taken to reduce the exposure of man and the environment to dioxins (1). Recent surveys proved a decrease of the dioxin burden in food and breast milk in the last years (2 - 5). The Chemische Landesuntersuchungsanstalt Freiburg runs for the state of Baden-Württemberg a comprehensive programme to monitor the PCDD/F contamination of food. Thus, it was alarming to find a reverse of the decreasing trend in milk and butter samples beginning gradually in September 1997. Intense efforts were taken to find out the source.

2 Materials and Methods

Milk and butter samples were collected as part of the official food inspection randomly from the market. In addition, milk from selected farms or tankers (collecting milk from farms on tours to the dairy) was analysed. Feed samples including the individual components of the feedstuffs were collected at farms or production sites. They were analysed according to the successfully tested method for determination of PCDD/PCDF in eggs (6), milk (7) or kale (8) with optimisation of the extraction for each sort of food. Generally, samples were spiked with all 2,3,7,8-substituted $^{13}C_{12}$-labelled PCDD/PCDF. As recovery standard, $^{13}C_{12}$-labelled 1,2,3,4-TCDD was used. GC/MS-detection was performed on a VG Autospec at 10,000 resolution using a 60 m DB-5MS-, DB-Dioxin- or SP2331-column. The AS 200 autosampler injected 5 μl into the Multinjector of a Carlo Erba Mega GC. With every acquisition sequence, a 5 point-calibration curve was acquired in duplicate.

3 Results and Discussion

The Federal Health Office (FHO, former Bundesgesundheitsamt, BGA) calculated for milk and dairy products a contamination with PCDD/F in the period 1986 to 1991 as follows: milk 1.8 pg I-TEQ/g fat, cheese 2.2 pg I-TEQ/g fat, butter 1.1 pg I-TEQ/g fat (9). From 1993 to

1995, we have analysed 708 samples of milk and dairy products. The average contamination was 0.71 pg I-TEQ/g fat for milk, 0.64 pg I-TEQ/g fat for butter and 0.66 pg I-TEQ/g fat for cheese. Table 1 shows the temporal development for butter samples (5).

Table 1: Temporal development of PCDD/PCDF-content of butter samples (in pg I-TEQ/g fat)

Year	No. of samples	mean	minimum	maximum
1993	27	0.83	0.19	1.52
1994	37	0.68	0.46	1.38
1995	92	0.64	0.27	2.00
1996	66	0.55	0.19	0.87

These results have to be compared with guidelines and actions for the PCDD/PCDF-contamination of milk products which were recommended in 1993 by the Federal Health Office (former Bundesgesundheitsamt) and Federal Office for the Environment (Umweltbundesamt) (10) (see table 2). These orientation values should guarantee a harmonised valuation of all dioxin results for these products in Germany.

Table 2: Proposed guidelines for PCDD/PCDF in milk fat and recommended actions

PCDD/PCDF-contamination in pg I-TEQ/g milk fat	recommended action
< 0.9	Target value to be met. Only to be achieved by long-term reduction of PCDD/PCDF release into the environment.
> 3.0	Investigate sources and start measures to minimise release. If no short term measures to reduce emissions are possible, it is recommended to the farm to change pattern of land use. Recommendation not to distribute milk and dairy products directly to the consumer.
> 5.0	Milk and dairy products no longer marketable

Our data from 1993 to 1996 show that the contamination of food in the south-western part of Germany was considerably lower than previously calculated for Germany in general. Thus, obviously the measures to reduce the dioxin release have been successful. By summer 1997, the contamination in milk and dairy products was generally in the range of about 0.6 pg I-TEQ/g fat.

Against this background, a gradually increase of the PCDD/F contamination of milk was surprising. A rigid validation programme confirmed the results: Whereas 76 milk samples collected between January and August 1997 had 0.62 pg I-TEQ/g fat on average (minimum 0.36, maximum 1.02), 36 samples collected between September 1997 and December 1997 had 0.89 pg I-TEQ/g fat on average (minimum 0.35, maximum 1.92) and 43 samples collected in January and February 1998 had 1.38 pg I-TEQ/g fat (minimum 0.46, maximum 4.83).

Also butter samples collected randomly in January and February 1998 showed about twice the PCDD/F contamination of the content by August 1997. Samples from northern Germany had even a higher PCDD/F contamination than samples from south-west Germany. It was obvious that an important new source had an effect at least on the national level. As a key step in the whole procedure, an „emergency collaborative study" was conducted with four other laboratories of the official food control in Germany to confirm these results (7). This contribution summarises the results of two butter samples from northern Germany, two butter samples from south-western Germany and a milk from a farm with a highly contaminated milk in detail. These low number of samples are not representative for the whole market, but were an indication, that other regions were involved, as well, on the national and international level.

It must be emphasized that all samples with an increased I-TEQ-value were obviously contaminated by the same source: In the pattern of PCDD/F congeners, always increased levels of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were dominant.

In March 1998, an alarming 7.4 pg I-TEQ/g fat was found in a milk from a tanker (collecting milk from 70 farms on tours to the dairy). With this high dioxin content, the milk could not longer be considered marketable. Immediately, milk of the 12 biggest farms was investigated. Here, the highest PCDD/F content was found to be about 4.8 pg I-TEQ/g fat which was confirmed in the „emergency collaborative study", as well (7). This high dioxin content was very astonishing because the milk of this farm with 4.8 pg I-TEQ/g fat in a sample from March 1998 used to have a dioxin contamination between 0.5 and 1 pg I-TEQ/g fat in the past four years (determined in a extensive reference testing programme of our institute for the state of Baden-Württemberg).

Immediately, a comprehensive search for the PCDD/F source was conducted on the farm. All kind of possibilities were considered (disinfectants, detergents, pesticides [insecticides, herbicides and others], drugs used in veterinary medicine, paintings for the silos and all kinds of feed. Altogether 11 samples (preparations for udder treatment, detergents and feed) were analysed. As a result, only a compound feed for milk production proved to have considerably higher PCDD/F contamination than other feeds or vegetable food: Whereas the background contamination of feeds or vegetable food is in the range of about 0.1 to 0.3 ng I-TEQ/kg dry weight, this particular compound feed had about 1.8 ng I-TEQ/kg.

Instantly, all six single components of this compound feed were analysed. Whereas five of these single components had the normal background contamination, citrus pulp had about 5.6 ng I-TEQ/kg. An immediate taken second sample of citrus pulp had 7.1 ng I-TEQ/kg.

As an important piece of circumstantial evidence, milk and feed from 9 farms were checked. These farms were among the 12 biggest farms of the tanker tour which had attracted attention because of its high dioxin contamination of initially 7.4 pg I-TEQ/g fat. The highest dioxin contamination of milk was found on a farm were up to 8 kg per cow and day was fed from a certain compound feed containing 25 % contaminated citrus pulp. Four farms had a dioxin contamination in the range between 1.5 and 2.8 pg I-TEQ/g fat. These farms had fed up 4 to 5 kg of a compound feed containing contaminated citrus pulp. Four farms had a dioxin contamination in the milk below 0.9 pg I-TEQ/g fat. Two of these farms didn't feed any compound feed at all; two farms fed a compound feed without contaminated citrus pulp.

Thus, the evidence was striking to have found the source for the dioxin contamination of the milk. Immediately, the feed containing contaminated citrus pulp was removed from the market in Baden-Württemberg. Other states of Germany and the European Community were informed. It turned out that an important market was concerned: Citrus pulps are said to be produced at about 1.5 million tons/year worth about 200 to 300 million US-$. At times, the market in some countries of the European Community collapsed.

Table 3 summarises the detailed results for milk, compound feed and citrus pulp. Assuming that the contribution of the other single components of the compound feed to the dioxin contamination is negligible, a content of about 25 % citrus pulp in the compound feed can be calculated.

Table 3: Dioxin contamination in milk (pg/g fat) of a farm, in the compound feed used on this farm and in citrus pulp used in the compound feed. Additionally: factors for transfer from feed to milk fat.

		milk pg/g fat	compound feed pg/kg	citrus pulp pg/kg	transfer factor feed - milk fat
I-TEQ	(NATO, 1988)	4.68	1745	7154	0.134
2,3,7,8-	TCDD	2.30	549	2324	0.210
1,2,3,7,8-	PeCDD	1.69	450	1975	0.188
1,2,3,4,7,8-	HxCDD	0.43	151	622	0.142
1,2,3,6,7,8-	HxCDD	0.48	86	306	0.281
1,2,3,7,8,9-	HxCDD	0.29	122	513	0.121
1,2,3,4,6,7,8-	HpCDD	0.93	808	2315	0.058
	OCDD	1.00	6292	11726	0.008
2,3,7,8-	TCDF	0.18	632	2562	0.014
1,2,3,7,8-	PeCDF	0.11	325	1155	0.017
2,3,4,7,8-	PeCDF	1.61	434	1675	0.185
1,2,3,4,7,8-	PeCDF	2.13	1134	4609	0.094
1,2,3,6,7,8-	HxCDF	1.11	526	2168	0.106
2,3,4,6,7,8-	HxCDF	2.09	1808	8355	0.058
1,2,3,7,8,9-	HxCDF	< 0.08	56	148	0.000
1,2,3,4,6,7,8-	HpCDF	2.37	11693	45802	0.010
1,2,3,4,7,8,9-	HpCDF	0.36	1552	6072	0.012
	OCDF	3.41	133880	446310	0.001

For calculation of the transfer factors from compound feed to milk fat, the following basic facts can be used: The farm with the highest dioxin contamination in milk fed about 8 kg compound feed per cow for increase of the milk production by about 10 l with 4 % fat (resulting in a production rate of 0.05, as assumed previously by Schuler [12]). Table 3 summarises the resulting transfer factors which were calculated as

$$\text{„transfer rate}_{feed/milk} = (c_{milk}/c_{feed})^* \text{ production rate“}$$

These are in line with findings already reported in the literature (12 - 15). This was another important clue in the whole complex matter.

Finally, after withdrawal of the compound feed with contaminated citrus pulp, the dioxin contamination dropped.

The reason for the contamination of the citrus pulp from Brazil is unknown, so far. The particular PCDD/PCDF pattern is unknown in Europe. An expert committee of the European Community will visit Brazil in May 1998 to find out the source.

Production of citrus pulp is a seasonal business. From September to February, citrus pulp on the world market is dominated by Brazil. Then, US products follow (which had background contamination, so far, according to a limited number of samples). Thus, many countries were involved as producers or customers.

As a result, feed can contribute considerably to the contamination of food. Regarding the huge volumes of the global market of feeds, it is important to pay attention to the dioxin contamination of food and feed by continuous control. Only by analyses of high numbers of samples shifts in trends can be seen early. Seasonal trends require repeated analysis through the year. After all efforts on the national level, the international market must be controlled as well.

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