

**PCDD/PCDF LEVELS IN DAIRY PRODUCTS FROM  
NORTH RHINE-WESTPHALIA 1990 - 1998**

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**Introduction**

In 1998 a total of 111 cow's milk samples and dairy products were collected from all dairies in North Rhine-Westphalia and analysed for polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). The objective of this study was to investigate whether the PCDD/F decline in dairy products observed between 1990 and 1994 (1) further continued in the past four years. Moreover, it should be checked, whether cattle feeding with citrus pelluts possibly containing PCDD/F (2) has led to a significant additional contamination of dairy products in North Rhine-Westphalia.

**Materials and Methods**

Each dairy was sampled four times between spring and fall 1998. Sampling was performed at the same times as in 1994 and 1990 when comparable surveys were conducted. Samples were collected in the morning directly before bottling in order to avoid contamination by the packaging material. In cases where dairies did not produce consumer's milk, other dairy products such as butter, cheese or cream were taken.

Analytical determination was performed using validated procedures which had been successfully tested in a number of national and international quality control studies. Analyses comprise spiking with <sup>13</sup>C-labeled PCDD/F, different clean up steps, including a carbon column, separation by capillary gas chromatography and determination by high resolution mass spectrometry (HRMS) at a resolution of R=10.000 in the selected ion recording mode (SIR). The longterm stability of the methodology is assured by analyzing three different quality control pools since several years.

**Results and Discussion**

All samples contained PCDD/F patterns that are characteristic for specimens originating from mammals. PCDD/F congeners with 2,3,7,8 chlorine substitution are dominating. Other congeners which do not belong to this toxic group could only be determined at levels near the detection limit. Because no significant differences in the pattern and levels were observed between the various matrices (milk, butter, cheese, cream), all results can be combined. The following table shows a summary of the results in comparison to the respective data from the 1990 and 1994 surveys.

## Environmental Levels in Sediment, Sewage, Sludge and Food P313

<b>PCDD/F Levels in Dairy Products from North Rhine-Westphalia 1990 - 1998</b> (ng I-TEq/kg milk fat)			
<b>Parameter</b>	<b>1998 dairies: 29 samples: 111</b>	<b>1994 dairies: 30 samples: 120</b>	<b>1990 dairies: 43 samples: 168</b>
Mean	0,78	1,02	1,35
Median	0,70	1,02	1,27
Minimum	0,47	0,61	0,76
90 percentile	1,12	1,29	1,83
95 percentile	1,29	1,45	2,04
Maximum	1,78	1,75	2,62
N < Target value*	76%	31%	5%

\* N < Target value indicates the number of samples with PCDD/F levels below the target value of 0,9 ng I-TEq/kg milk fat released by the German Ministry of Environment

All levels are expressed as nanogram toxic equivalents (NATO/CCMS) per kilogram milk fat (ng I-TEq/kg fat). The table indicates that the PCDD/F levels of all samples collected in 1998 range between 0,47 and 1,78 ng I-TEq/kg fat.

It was striking that almost 60% of the specimens collected during the first sampling period (March/April 1998) showed a deviant ratio of 2,3,7,8-T<sub>4</sub>CDD to I-TEq levels compared with milk samples analysed earlier. While this ratio is normally between 0,1 and 0,2, the respective samples revealed a ratio up to 0,4 due to elevated 2,3,7,8-T<sub>4</sub>CDD levels. Moreover, these samples contained somewhat higher levels of 1,2,3,7,8-P<sub>5</sub>CDD and OCDF. Because of the typical pattern, it is most likely that these elevations were caused by feeding of PCDD/F contaminated citrus pellets. After citrus pellets were identified as a potential additional PCDD/F source and its feeding to cattle was prevented, an influence on the levels of the specimens collected during the last three sampling periods in 1998 was no longer observable.

Although a number of samples were significantly influenced by contaminated citrus pellets at the beginning of 1998, a comparison of the surveys conducted in 1990, 1994 and 1998 demonstrates

# Environmental Levels in Sediment, Sewage, Sludge and Food

## P313

the further decline of PCDD/F levels in dairy products from North Rhine-Westphalia. While in 1990 a median of 1,27 ng I-TEq/kg milk fat was measured, the corresponding levels amounted only to 1,02 in 1994 and 0,70 in 1998. From this, it can be concluded, that the average PCDD/F contamination of dairy products from North Rhine-Westphalia decreased by approximately 45% since 1990. In Germany, there are no maximum residue limits in force for PCDD/F in food stuffs. There only exist recommendations released by the Ministry of Environment for taking measures in case of PCDD/F contaminated milk and milk products (3). None of the samples analysed in 1998 reached the intervention level of 5 ng I-TEq/kg milk fat, nor the check level of 3 ng I-TEq/kg milk fat. Below the target level of 0,9 ng I-TEq/kg milk fat, which according to the Ministry of the Environment can only be achieved in the longer term by a substantial reduction of dioxin emissions, lay already 76% compared to 31% in 1994 and 5% in 1990. The frequency histogram (Fig. 1) shows the tendency to lower levels of the specimens collected and analysed in 1998 compared to the samples of the 1990 and 1994 surveys. In fact, the samples with the highest levels in 1998 are in the same range as the 1994 specimens, however, this contamination was not caused by industrial emissions but by feeding dioxin contaminated citrus pellets.

The results of this survey clearly indicate that measures to reduce dioxin emissions taken in the past few years have positive effects on the contamination of the environment and subsequently on the PCDD/F levels in food. On the other hand, the problem of contaminated citrus pellets demonstrates the necessity to routinely analyse food samples also in the future for PCDD/F in order to identify and close down new sources as early as possible.

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### References

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**PCDD/F in dairy products**  
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