PCDD/PCDF AND PCB IN DAIRY PRODUCTS FROM NORTH RHINE-WESTPHALIA 2006 AS COMPARED TO LEVELS SINCE 1990

Peter Fuerst

Chemical and Veterinary Control Laboratory, Joseph-Koenig-Strasse 40, D-48147 Muenster, Germany

Abstract
Comprehensive monitoring programmes on the contamination of dairy products with polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and biphenyls (PCB) are conducted from all dairies in North Rhine-Westphalia/Germany every 4 years since 1990. Meanwhile, more than 530 dairy products have been analysed. The occurrence data from 2006 revealed median levels ("upperbound") of 0.51, 0.92 and 1.44 pg WHO_{1997}-TEQ/g milk fat for PCDD/PCDF, dioxin-like (dl)-PCB and the sum of PCDD/PCDF and dl-PCB, respectively. Thus, all levels are considerably below the respective maximum levels laid down in Commission Regulation (EC) No. 1881/2006. The contribution of dl-PCB to total WHO_{1997}-TEQ ranged between 49 and 78% with a mean value of 63%. This indicates the significance of dl-PCB when assessing the contamination of dairy products with toxic equivalents. On a concentration base, a good correlation was also found for dl-PCB and indicator-PCB. Unlike the earlier sampling periods, the samples analysed in 2006 did not show a clear seasonal trend. Since 1990 the PCDD/PCDF levels have decreased by more than 65%. A comparable trend was found for the levels of indicator PCB which were 70% lower in 2006 compared to 1990. The 12 dl-PCB which were attributed toxic equivalent factors (TEF) by WHO in 1997 were first measured in the monitoring programme 1998. Since then, a decrease of 50% could be determined for these contaminants.

Introduction
In 1990 the North Rhine-Westphalian (NRW) Government conducted the first extensive dioxin survey that comprised i.a. analyses of dairy products from all 43 dairies in NRW. The objectives were to assess the distribution of dioxin and PCB contamination in dairy products as one of the major routes of human exposure to these contaminants. Moreover, it was intended to investigate whether seasonal trends exist. Therefore, each dairy was sampled 4 times per year in March, May, July and September[1]. Since 1990 this programme is repeated every 4 years following the same sampling and analytical strategy. In 1998, the 12 dioxin-like PCB that were attributed a toxic equivalent factor by WHO in 1997 were included as a further group of contaminants into the analysis. The programmes performed since 1990 are intended for surveillance of the progressive effects caused by the numerous measures to reduce the emissions of dioxins and PCB into the environment.

Materials and Methods
PCDD/PCDF, PCB and other lipophilic compounds are extracted along with milk fat by liquid/ liquid partitioning. Aliquots of the fat are fortified with 17 ^{13}C-labelled PCDD/PCDF, 12 ^{13}C-labelled dioxin-like PCB and 6 ^{13}C-labelled indicator PCB congeners. After removal of fat on a silica gel column loaded with sulphuric acid, PCB are separated from PCDD/PCDF by means of a Florisil column. The PCDD/PCDF fraction is further cleaned up on a mini column containing a mixture of Carbopack C/Celite 545. Separation of dioxin-like from non dioxin-like PCB is achieved on a Charcoal/Chromosorb WHP column. All analytical measurements of PCDD/PCDF, dioxin-like and indicator PCB are performed using capillary gas chromatography/high resolution mass spectrometry (HRGC/HRMS) on a Thermo Finnigan DFS system at a resolution of R=10,000. Quantification of all analytes is based on the isotope labelled standards and multiple point calibration curves. The method applied was successfully tested in various national and international quality control studies and proficiency tests.

Results and Discussion
Table 1 shows the condensed results of the monitoring programme conducted in 2006. The mean, median, minimum and maximum levels for PCDD/PCDF, dl-PCB and the sum of PCDD/PCDF and dl-PCB as well as their 90th and 95th percentiles are each expressed as pg WHO_{1997}-TEQ/g milk fat. As required by EU legislation, all values represent "upperbound" levels. This means that in case of non-quantified congeners the limit of quanti-

fication is used for the calculation of the TEQ values. Recently, the European Commission laid down maximum levels for dairy products of 3 pg WHO_{1997}-TEQ/g fat for PCDD/PCDF and 6 pg WHO_{1997}-TEQ/g fat for the sum of PCDD/PCDF and dl-PCB. Food samples have to comply with both maximum levels. As can be seen, the levels of all 68 samples analysed are considerably below the legal limits. Table 1 also shows the concentrations for the 3 predominant PCB congeners 138, 153 and 180 which make up more than 60% of total PCB. Harmonized European maximum levels for these contaminants are currently under discussion. Therefore, the levels are compared to the German national legislation. Even the highest levels measured in 2006 are approximately a factor of 20 below the respective legal limits. Figure 1 shows the relationship between dl-PCB and the sum of PCDD/PCDF and dl-PCB, expressed as TEQ values. The contribution of dl-PCB to total-PCDD/PCDF-TEQ ranged between 49 and 78% with a mean value of 63%. Consequently, the TEQ contamination of dairy products is more than doubled by inclusion of dl-PCB compared to contribution of PCDD/PCDF alone. On a concentration basis, a fairly good correlation could be found between dioxin-like and non dioxin-like PCB (Figure 2). However, it has to be considered that all samples were collected in a relatively discrete area with a more or less uniform environmental pollution. The above correlations might be weaker if samples from other regions or countries would be included[2]. Figure 3 shows the distribution of all 530 samples analysed since 1990 in relation to the year of the monitoring programme. For a better comparison, in this graph all values are expressed as I-TEQ (NATO/CCMS) levels because the WHO-TEF were only proposed in 1997 for the first time. The histogram clearly indicates the considerable downward trend of the contamination of dairy products since 1990. Compared to 1990, the median levels determined in the samples from 2006 were 65% lower. Moreover, the contamination range became much narrower in the recent investigations. Figure 4 depicts the decrease of non-ortho and mono-ortho PCB in dairy products since their first inclusion into the monitoring programme in 1998 in comparison to the decline of the PCDD/PCDF levels in the same samples, each expressed as pg WHO_{1997}-TEQ/g milk fat. The data from the past three investigations performed in 1998, 2002 and 2006 show that the contamination of dairy products with dl-PCB has decreased by 50% within the last 8 years.

In summary, it can be stated that the measures taken during the past 30 years have had beneficial effects on the reduced contamination of dairy products with dioxins and PCB and thus on human exposure as dairy products constitute an important part of nutrition, especially for young children.

References

1. Fürst P, Fürst Chr, Wilmers K. *Chemosphere* 1992; 1039:1048
2. EFSA (2005) The EFSA Journal 284, 1-137

Table 1:

PCDD/PCDF and PCB in Dairy Products from North Rhine-Westphalia 2006 (n=68)						
Parameter	**PCDD/PCDF**	**dl-PCB**	**Σ PCDD/PCDF+dl PCB**	**PCB# 138**	**PCB# 153**	**PCB# 180**
	pg WHO-TEQ/g milk fat			**ng/g milk fat**		
Minimum	**0.31**	**0.34**	**0.65**	**0.54**	**0.78**	**0.32**
Maximum	**0.97**	**1.42**	**2.13**	**2.20**	**2.90**	**1.50**
Mean	**0.52**	**0.92**	**1.44**	**1.40**	**1.89**	**0.85**
Median	**0.51**	**0.89**	**1.42**	**1.40**	**1.90**	**0.84**
90^{th} Perc.	**0.66**	**1.21**	**1.79**	**1.90**	**2.50**	**1.10**
95^{th} Perc.	**0.71**	**1.31**	**1.83**	**2.00**	**2.80**	**1.27**
ML	**3.0***	**--**	**6.0***	**50****	**50****	**40****

* ML = Maximum level laid in down in Commission Regulation (EC) No. 1881/2006

** ML = Maximum level laid down in German National Legislation (Schadstoffhöchstmengen-Verordnung)

Figure1:

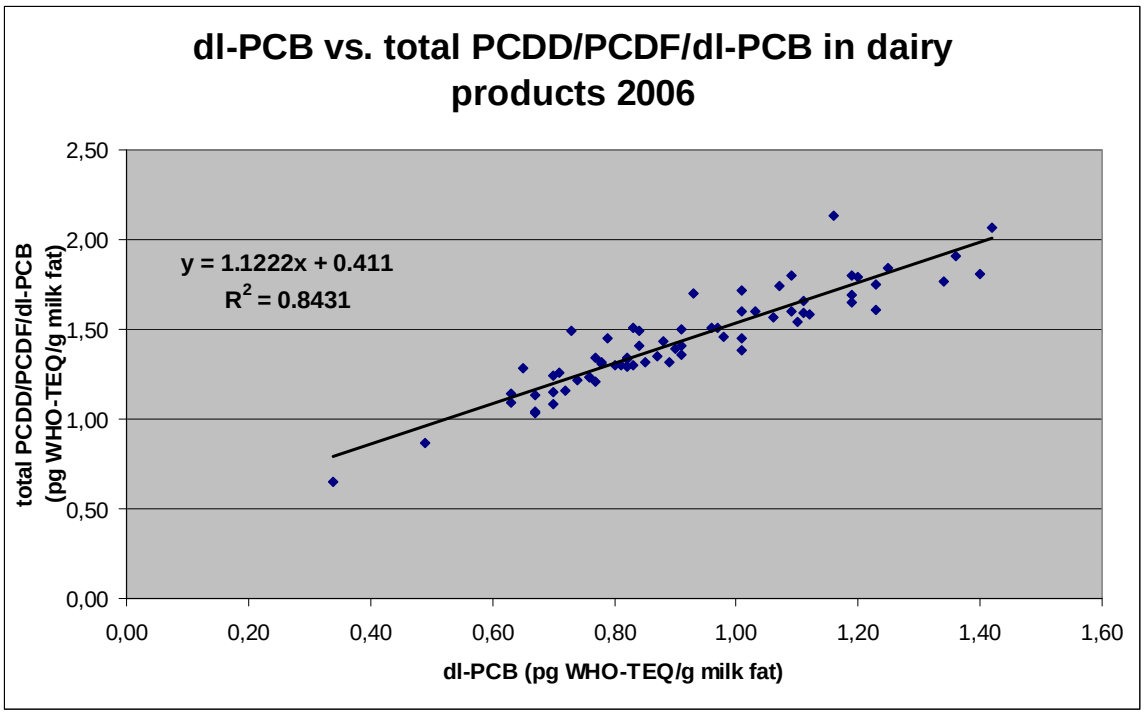
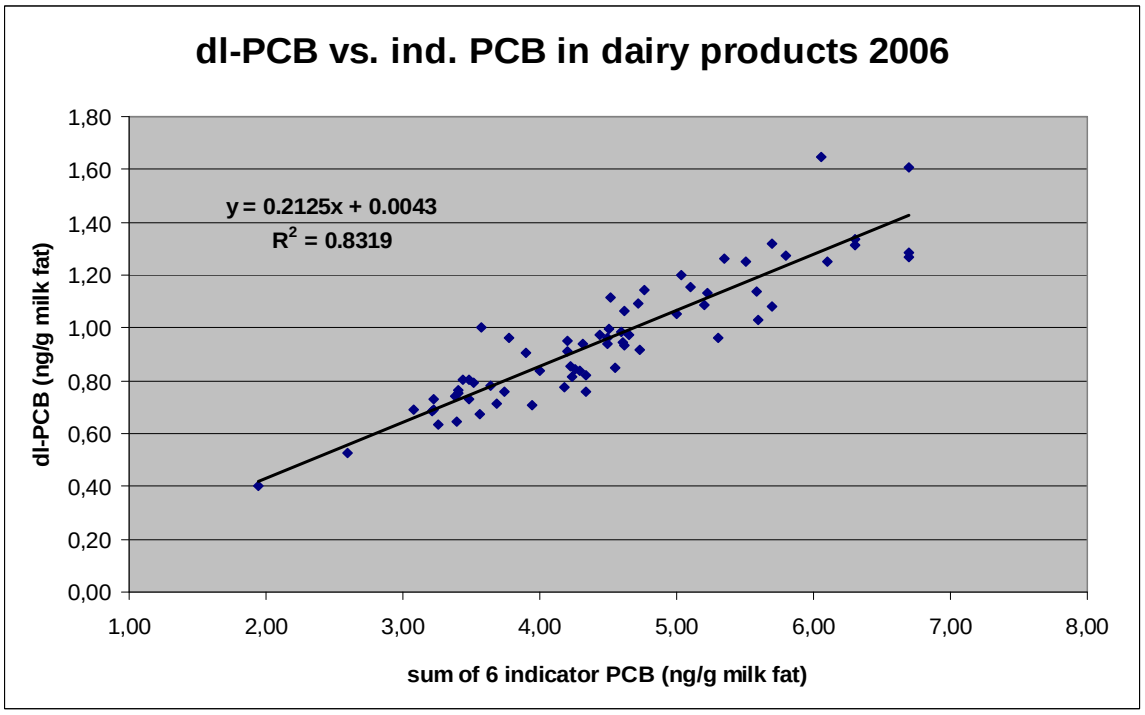


Figure 2:



Sum of 6 indicator PCB = (sum of PCB 28 + 52 + 101 + 138 + 153 + 180)

Figure 3:

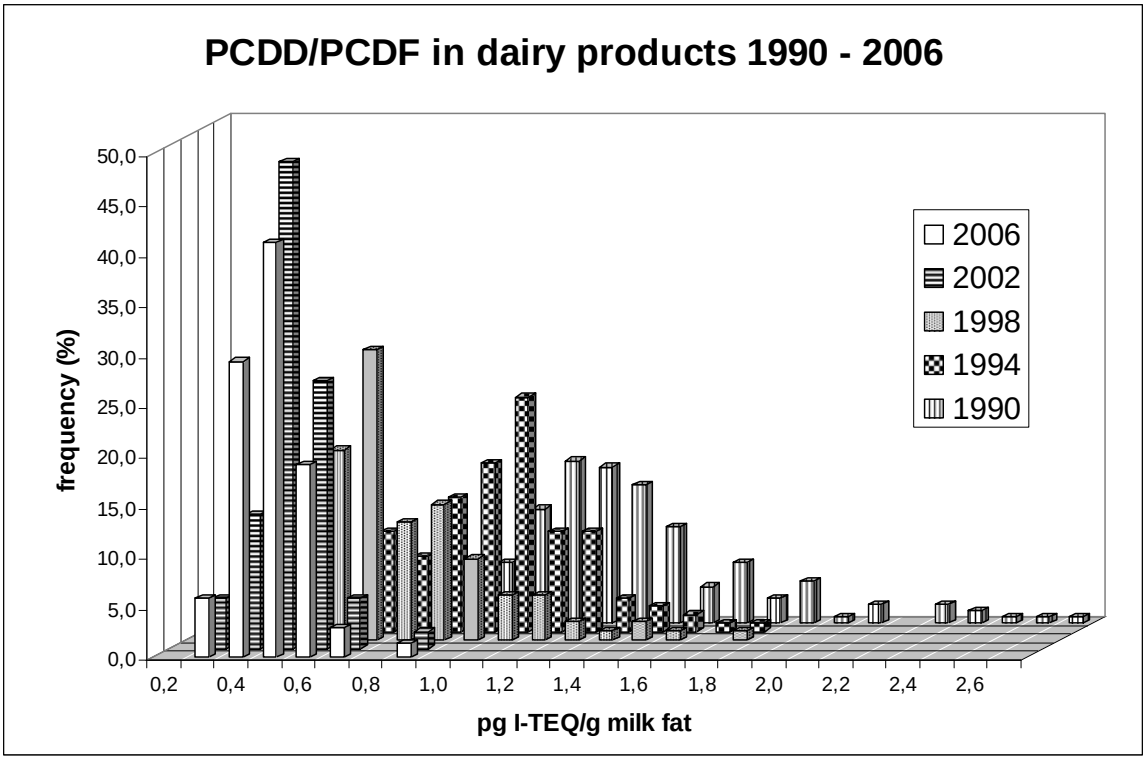


Figure 4: