# Decline of PCDD/PCDF and PCB in Dairy Products 1990-2010

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## Introduction

The major pathway of organic environmental contaminants, such as polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB) to human exposure is via food of animal origin[1,2]. In this respect contamination of dairy products, meat, eggs and fish are of special importance. In 1990 the North Rhine-Westphalian (NRW) Government conducted the first extensive survey on the contamination of dairy products from all 43 dairies with own raw milk delivery in NRW. In order to investigate whether seasonal trends exist, each dairy was sampled four times per year in March, May, July and September. Since 1990 this monitoring programme is repeated every four years following the same sampling and analytical strategy. While the survey in 1990 comprised the determination of PCDD/PCDF and the six non dioxin-like "indicator" PCB (NDL-PCB) 28, 52, 101, 138, 153 and 180, since 1998 the 12 dioxin-like PCB (DL-PCB) that were attributed a toxicity equivalent factor proposed by WHO in 1997 and published in 1998 were included as a further group of contaminants into the analysis. Since 1990 a total of 591 individual samples were analysed.

## Materials and methods

Each sample consists at least of 1 L milk. In order to avoid any potential contamination by packaging material, the samples were taken from the collection tanks in the dairies directly before processing. 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 non dioxin-like "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 with hexane. The PCDD/PCDF fraction, subsequently eluted with toluene, 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 non dioxin-like PCB are performed using capillary gas chromatography/high resolution mass spectrometry (HRGC/HRMS) on a Waters AutoSpec and/or a Thermo Fisher DFS system, each running at a resolution of R=10,000. While the gas chromatographic separation of PCDD/PCDF is performed on a DB-5 column, the separation of PCB is performed on an HT-8 column. Quantification of all analytes is based on the isotope labelled standards and multiple point calibration curves. The method applied was successfully tested in a number of national and international quality control studies and proficiency tests. The long term stability is ensured by parallel analyses of quality control samples.

## Results and discussion:

The results of the survey conducted in 2010 are summarized in Table 1. All PCDD/PCDF and DL-PCB results are given as pg $WHO_{1997}$-TEQ/g fat. According to Regulation (EC) No 1881/2006 which lays down the maximum levels for PCDD/PCDF and the sum of PCDD/PCDF and DL-PCB in various food commodities, the results are calculated as "upperbound" concentrations, i.e. congeners that are below the limit of quantification (LOQ) are included with the numerical value of the LOQ in the calculation of the total TEQ value. The results for the predominant NDL-PCB congeners are given as ng/g milk fat. For comparison, Table 1 also shows the current European maximum levels for PCDD/PCDF and the sum of PCDD/PCDF and DL-PCB in dairy products as well as the national German maximum levels for NDL-PCB. Harmonized European maximum levels for NDL-PCB in food commodities are currently in progress.

All concentrations for PCDD/PCDF and the sum of PCDD/PCDF and DL-PCB are considerably below the respective European maximum level and even below the action levels for PCDD/PCDF and DL-PCB, both laid down at 2.0 pg WHO-TEQ/g milk fat.

**Table 1**

| PCDD/PCDF and PCB in Dairy Products from North Rhine-Westphalia 2010 (n=64) | | | | | | |
|---|---|---|---|---|---|---|
| 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 | 0.20 | 0.34 | 0.60 | 0.44 | 0.64 | 0.28 |
| Maximum | 0.67 | 1.16 | 1.67 | 1.80 | 2.40 | 1.20 |
| Mean | 0.41 | 0.73 | 1.14 | 0.99 | 1.35 | 0.59 |
| Median | 0.41 | 0.71 | 1.09 | 0.97 | 1.30 | 0.57 |
| 90$^{th}$ Perc. | 0.53 | 0.94 | 1.50 | 1.37 | 1.87 | 0.79 |
| 95$^{th}$ Perc. | 0.57 | 1.09 | 1.59 | 1.49 | 2.07 | 0.85 |
| **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 (Kontaminanten-Verordnung)

The fraction of PCDD/PCDF on total TEQ ranged between 20.8 and 46.2 % with a mean value of 36.3 %. The highest contribution to total TEQ is coming from DL-PCB with more than 50 %. In case of NDL-PCB, the three persistent congeners PCB#138, 153 and 180 predominate. In contrast, the concentrations for the lower chlorinated indicator NDL-PCB#28, 52 and 101 were in almost all cases below the LOQ of 0.10 ng/g fat.

**Figure 1:**

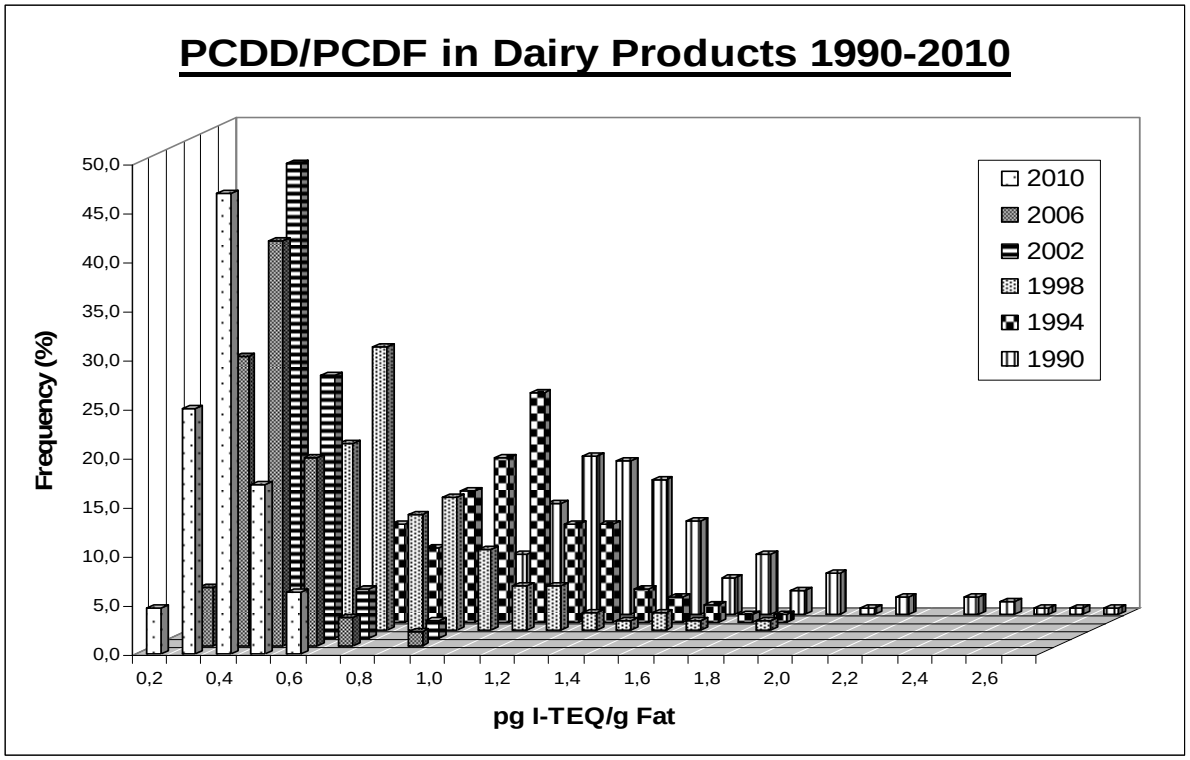
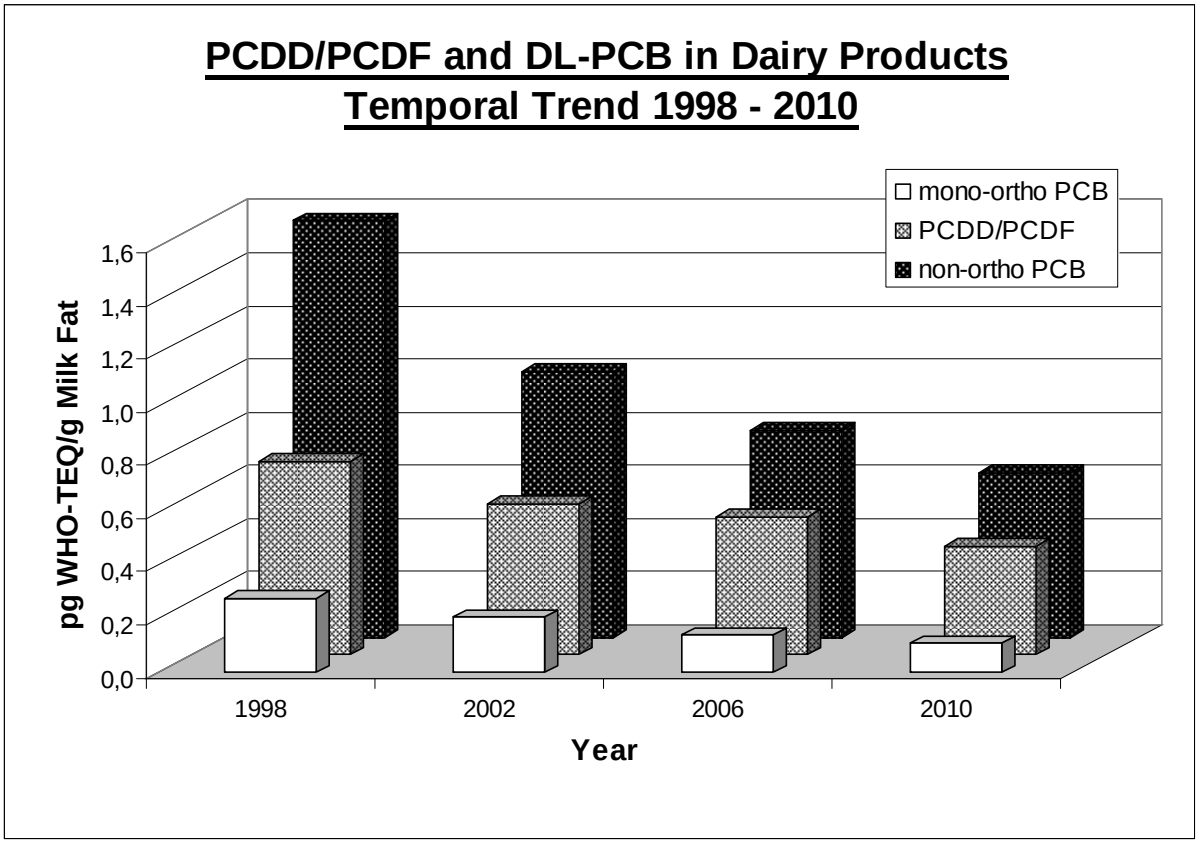


Figure 1 shows the frequencies of the PCDD/PCDF levels determined in all 591 dairy samples analysed in the surveys between 1990 and 2010. In this histogram all results are expressed as I-TEQ values calculated with the toxicity equivalent factors proposed by NATO/CCMS in 1988 and not with the $WHO_{1997}$-TEF which were only published in 1998 in order to allow a comparison of the current levels with the data of the surveys prior to 1997. Compared to the $WHO_{1997}$-TEQ, the I-TEQ values are around 15 % lower. The Figure clearly indicates that with each survey the PCDD/PCDF levels tend to lower values and the range of contamination narrows.

Figure 2 shows the temporal trend for the contamination of dairy products with PCDD/PCDF, non-ortho PCB and mono-ortho PCB between 1998 and 2010. The Figure illustrates the particular impact of non-ortho PCB on the contamination of dairy products. While the mean PCDD/PCDF levels declined by 44 % since 1998, the reduction of DL-PCB was calculated as 60 % for the same time period.

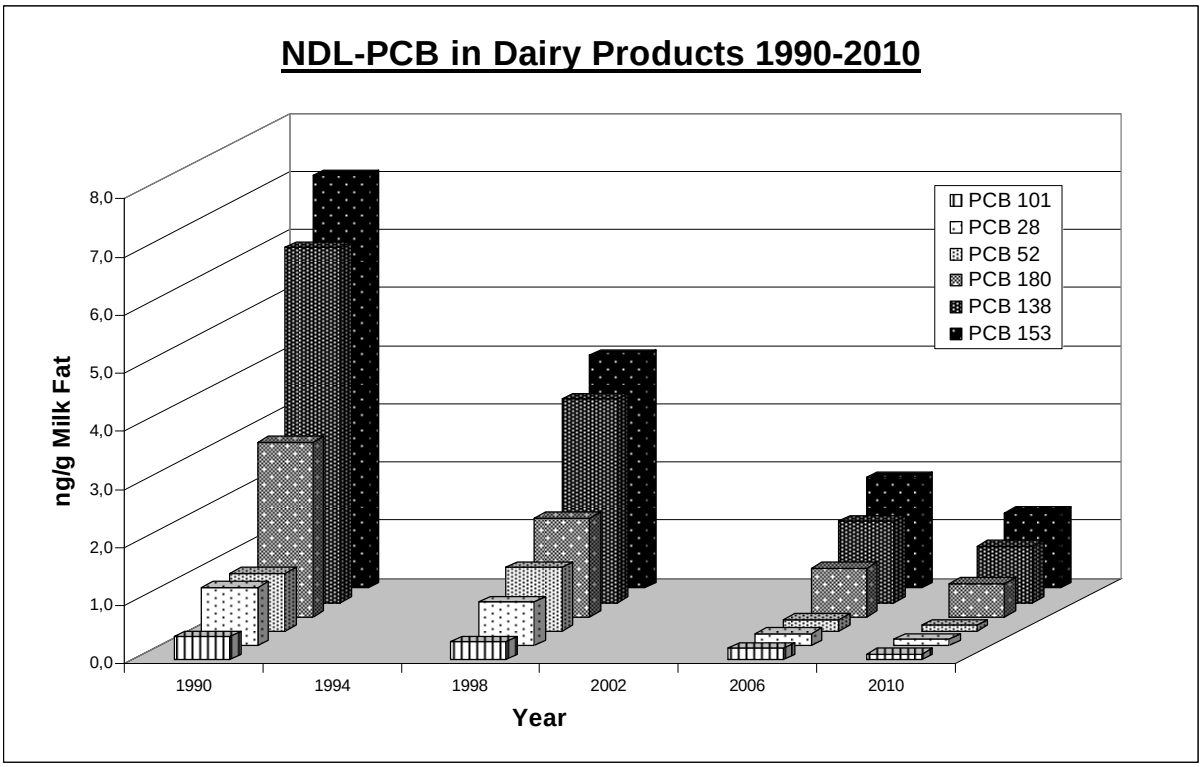
**Figure 2:**




A comparable decline was ascertained for the predominant NDL-PCB congeners 138, 153 and 180 (Figure 3). The mean values for these three congeners in the samples from 2010 were around 70 % and more than 80 % lower than the mean values determined in the dairy products from 1998 and 1990, respectively.

In summary, it can be concluded that the contamination of dairy products from North Rhine Westphalia has decreased by 75 % since 1990. Compared to 1998 where the DL-PCB were included into the survey for the first time, their mean concentrations are around 60 % lower in the samples collected and analysed in 2010. The current levels seem to reflect the background contamination of cow's milk produced in a highly industrialized region. They also demonstrate that the numerous measures to reduce the emission of PCDD/PCDF and PCB into the environment have a positive effect on the contamination of dairy products.

**Figure 3:**

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**References:**
1. Fürst P, Beck H, Theelen R. (1992); *Toxic Substances Journal, 12,* 133-150
2. EFSA Panel on Contaminants in the Food Chain (2005); *The EFSA Journal 284,* 1 - 137