LEVELS OF POLYCHLORINATED DIBENZO(p)DIOXINS, DIBENZOFURANS AND DIOXIN-LIKE PCBs IN IRISH COW'S MILK

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Introduction

To assess the presence of Polychlorinated Dibenzo(p)dioxins (PCDDs) and Dibenzofurans (PCDFs) in the Irish environment, the Environmental Protection Agency (EPA) of Ireland conducted a study on the levels of PCDD/Fs in cow's milk in 1995[1]. It was found that I-TEQs in Irish cow's milk samples from so-called background stations were lower than e.g. in other European countries. The range of lipid based levels was between 0.14 to 0,50 pg I-TEQ/g milk fat (20 samples). A set of 10 further cow's milk samples from so-called potential impact locations showed a nearly identical range of TEQs. The general absence of industry with the potential for forming dioxins as by-products was seen to be the main reason for the overall low dioxin levels in Irish cow's milk.

In 2000, the EPA of Ireland initiated a follow-up study with a similar design including this time the quantification of the 12 dioxin-like PCB congeners for which consensus TEFs were derived by a working group of the World Health Organization (WHO) in 1997[2]. The present study should indicate whether changes of PCDD/F levels in Irish cow's milk and thus the Irish environment took place in the last five years and give an indication of the PCB contribution to the TCDD TEQ.

Materials and Methods

Within the present study, a series of 24 raw milk samples was collected by the Irish EPA from so-called background stations throughout Ireland. The samples were taken in June and July 2000 from storage silos or tankers at representative regional Irish diaries[3]. Similar to 1995, a further set of 13 milk samples from so-called potential impact locations was included in the study. The milk samples were frozen in glass bottles and shipped to GfA without interrupting the cooling chain.

The cow's milk samples were analysed by GfA for PCDD/Fs and PCBs by means of fat extraction, gravimetrical determination of the fat fraction, chromatographic defatting of the fat extract, clean-up of the remaining fraction on different adsorbents, analysis of the purified extracts by means of capillary gas chromatography / high resolution mass spectrometry (HRGC/HRMS) and quantification via internal $^{13}C_{12}$-labelled standards (isotope dilution). The extract clean-up and the GC/MS analysis were carried out separately for the PCDD/F and the PCB analyses. Both analytical methods are routinely applied by GfA for the analysis of food or feeding stuff.

The dioxin/furan analyses covered the determination of the 17 PCDD/F congeners which have toxicity equivalency to 2,3,7,8-TCDD. Within the PCB analyses, the 12 dioxin-like PCB congeners for which toxic equivalency factors (TEFs) recently were revised by a working group of the WHO[2] were determined (PCBs IUPAC No. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167,

169, 189). For each native PCDD/F and PCB congener to be quantified, the corresponding $^{13}C_{12}$-labelled compound was added to the fat extract as internal standard prior to the defatting and the subsequent chromatographic clean-up. The recoveries of the internal standards through the fat separation and all clean-up steps were determined by means of further ^{13}C-labelled internal PCDD or PCB standards added to the PCDD/F and the PCB fraction before GC/MS analysis. All the ^{13}C-labelled standards were from Cambridge Isotope Labs, Endover, USA. Both, the PCDD/F and PCB analyses were performed on a HP 5890 HRGC connected to a VG AutoSpec HRMS (mass resolution > 8000). A 60 m DB-5 MS capillary column was used for the gas chromatographic PCDD/F separation and a 25 m HT-5 column for the PCB analyses. The detection limit was in the range of 0.01 pg/g fat for 2,3,7,8-TCDD and of 0.2 pg/g fat for PCB 126. Within this study, three method blanks and two duplicate analyses were performed for PCDD/Fs and PCBs, respectively. No relevant blanks were found for the 17 PCDD/Fs, while blanks were detected for some PCB congeners. Since the latter could cause a maximum contribution of up to 19% to the PCB TEQs determined for the cow's milk samples, blank corrections were made on the basis of absolute blank concentrations of these PCB congeners for the milk samples. In case of duplicate analyses, the differences in the TEQ values determined in the single PCDD/F and PCB analyses were below 15 %, which is well within the expected range. Further details of the analytical procedures are reported in reference 3.

Results and Discussion

The TEQ values determined for the 24 Irish background cow's milk samples from the year 2000 are presented in Table 1. TEQs were calculated according to the I-TEQ (PCDD/Fs only) and WHO-TEQ scheme (PCDD/F and PCB TEFs for humans). For both schemes, non-detects were included by taking one half of the detection limit. All TEQs are reported as levels in fat (pg TEQ/g milk fat). Minimum and maximum TEQ values as well as the median of the data sets are also shown in Table 1. Detailed analytical data are also reported in reference 3.

The dioxin/furan-assigned TEQs of the 24 Irish cow's milk samples were between 0.11 and 0.41 pg WHO-TEQ/g fat (0.09 - 0.35 pg I-TEQ/g fat). The median of this set of samples is 0.24 pg WHO-TEQ/g fat (0.20 pg I-TEQ/g fat). The TEQs resulting from the 12 PCB congeners lay in a similar range between 0.15 and 0.56 pg WHO-TEQ/g fat with a median of 0.23 pg TEQ/g fat. This corresponds to a PCB contribution to the total TEQ values of 39 to 66%. Consequently, the total PCDD/F and PCB WHO-TEQs of the Irish background cow's milk samples show a range of 0.26 to 0.95 pg WHO-TEQ/g fat (median of 0.45 pg WHO-TEQ/g fat). As found in 1995, the potential impact samples showed the same range of TEQs like the background samples[3].

The main constituents within the 17 determined PCDD/Fs were the higher chlorinated dioxins and 2,3,4,7,8-PentaCDF. The latter congener, the 2,3,7,8-TetraCDD and the 1,2,3,7,8-PentaCDD, however, mainly contribute to the PCDD/F WHO-TEQ, as illustrated in Figure 1. From the dioxin-like PCBs, the congeners 118, 105, 156 and 167 showed the highest concentrations. As can be seen from Figure 2, however, the PCB WHO-TEQ is dominated by PCB 126 due to its TEF of 0.1.

When comparing the PCDD/F TEQs of the Irish cow's milk samples from the current study with those of 1995, it can be seen that the low PCDD/F level found in 1995 is confirmed by the year-2000 data. As can be seen from Table 2, the range of values is even slightly lower in the background samples from 2000. I-TEQs are used for comparison since the older data were

calculated by using I-TEFs. Compared to recent cow's milk data from other European countries (e.g. France, Germany, Spain)[4,5,6,7] the dioxin levels of Irish cow's milk are still in the lowest range. The same seems to be true for the total TEQ when including the dioxin-like PCBs[7,8,9].

Tab. 1: Lipid-based TEQ values of 24 Irish raw milk background samples collected in 2000

Cow's milk Sample	Dioxins I-TEQ pg/g milk fat	Dioxins WHO-TEQ pg/g milk fat	PCBs WHO-TEQ pg/g milk fat	Dioxins and PCBs Total WHO-TEQ pg/g milk fat
1	0.14	0.16	0.16	0.32
2	0.24	0.28	0.18	0.46
3	0.33	0.39	0.56	0.95
4	0.35	0.41	0.37	0.78
5	0.13	0.16	0.24	0.40
6	0.23	0.28	0.23	0.51
7	0.14	0.18	0.19	0.37
8	0.23	0.27	0.28	0.55
9	0.21	0.24	0.18	0.42
10	0.19	0.23	0.19	0.42
11	0.20	0.24	0.22	0.46
12	0.13	0.15	0.16	0.31
13	0.16	0.19	0.19	0.38
14	0.14	0.17	0.21	0.38
15	0.17	0.20	0.24	0.44
16	0.14	0.17	0.16	0.33
17	0.18	0.21	0.24	0.45
18	0.25	0.29	0.28	0.57
19	0.32	0.38	0.38	0.76
20	0.24	0.27	0.37	0.64
21	0.09	0.11	0.15	0.26
22	0.27	0.32	0.32	0.64
23	0.17	0.20	0.38	0.58
24	0.21	0.25	0.17	0.42
Min. 1 – 24	0.09	0.11	0.15	0.26
Max. 1 – 24	0.35	0.41	0.56	0.95
Median 1 - 24	0.20	0.24	0.23	0.45

Tab. 2: Comparison of the 1995 and 2000 PCDD/F data of Irish cow's milk from background locations

Year of Sampling	Min. pg I-TEQ/g fat	Max. pg I-TEQ/g fat	Median pg I-TEQ/g fat	Mean pg I-TEQ/g fat
1995 (n=20)	0.14	0.50	0.21	0.23
2000 (n=24)	0.09	0.35	0.20	0.20

Fig. 1: Percentage of individual PCDD/F congeners to the PCDD/F WHO-TEQ of the cow's milk samples

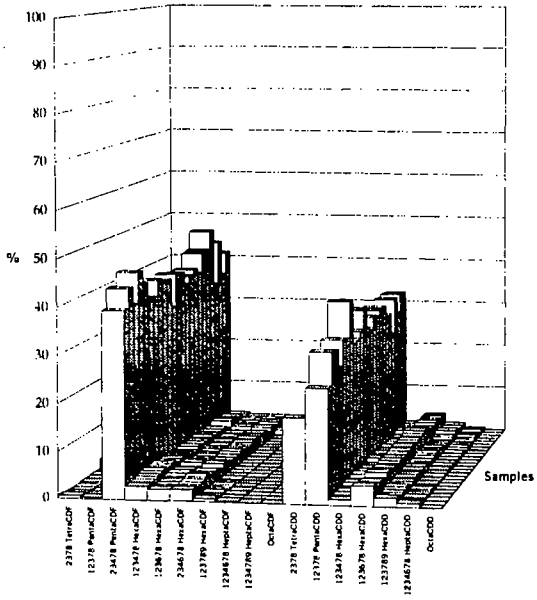
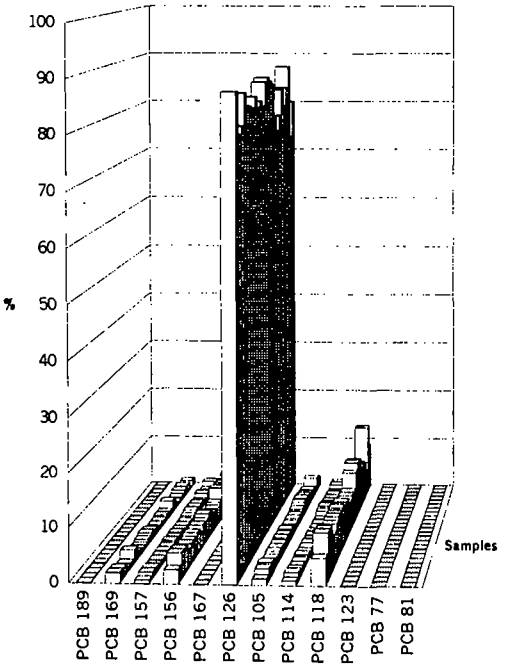


Fig 2: Percentage of individual PCB congeners to the PCB WHO-TEQ of the cow's milk samples



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