PCDDs/PCDFs AND RELATED CONTAMINANTS IN BUTTER ORIGINATING FROM 39 COUNTRIES WORLD WIDE

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are groups of global recalcitrant pollutants. Dioxins are formed as by-products in numerous processes, combustion being of major importance, and may be present in chemical products such as 2,4,5-T herbicides and in PCBs. Dependent on the inherent properties of the dioxins and of PCB several of the PCDD, PCDF and PCB congeners are accumulated in wildlife and humans. These chemicals are also present in farmed animals and hence farm products are a source for the human exposure to these contaminants[1]. Fat fish has frequently been indicated as a major source for exposure to dioxins[2]. During the 90's several countries started to analyse food baskets to calculate the intake of TEQs to compare with the tolerable daily intake (TDI) of dioxins. For example, the Swedish Dioxin Survey[3] reported a mean daily intake (MDI) of dioxins to 4.1-4.8 pg TEQ/kg bw per day (PCDDs/Fs and with an estimation of the PCB contribution), for Sweden 1990. The PCB contribution was half the TEQ value. The MDI is expected to be lower today. An investigation in Germany has shown that dairy products, meat products and fish, each contribute with around 30 % of the daily body burden via food[4, 5]. The WHOs most recent recommendation of TDI is 1-4 pg TEQ/kg bw per day[6].

Since milk and milk products are good matrices for determination of lipophilic environmental contaminants it may be useful to use butter as an indicator matrix for the contamination of persistent organic pollutants (POPs). In fact butter has been used for screening the contaminant situation in several countries[7].

The general aim of the present study was to determine any worldwide trends in dioxin concentration and levels of related pollutants. Hence butter samples from 39 countries, worldwide, have been collected and analyzed. These samples are not supposed to be representative for the general dioxin contamination of dairy products in each one of the countries from which butter has been analyzed and now reported.

Materials and methods

Sixty-seven butter samples from 39 countries were collected, during the period May 2000 - March 2001. All samples where kept in a freezer at -20°C, until investigated. The samples consisted of 10 to 300 gram and the butter was bought in ordinary stores.

Every batch analysed consisted of eight butter samples, one blank and one butter pool. All blanks had dioxin values 0.01 pg WHO-TEQ/g lipid weight (l.w.) or lower. The PCB-TEQ however had in some cases high blank levels. In no case, blank concentrations were relevant to the samples result. Five gram of butter were analysed, and one gram of each butter sample was used for gravimetric determination of the lipid content. A detailed description of the method will be given elsewhere[8]. The analytical measurement was performed using high-resolution capillary gas chromatography/ high-resolution mass spectrometry (HRGC/HRMS), of type Autospec. A DB 5

column, 60 m long, with a thickness of 0,25 mm and with a 0,1 mm film, was used. The limit of detection was set to three times the background noise. Authentic ^{13}C-labelled reference standards used for quantifications were from Promochem, Germany.

The Ergo laboratory has been included in a recent international quality assurance exercise performed by the National Institute of Public health, Norway, 2000[9]. The results from this quality control are satisfying, and confirm the reproducibility of the analytical method.

All calculations presented in this study are based on the most recent revised version of WHO-TEF values used[10].

Results

The sum-TEQs for all 67 samples are shown in increasing order in Figure 1. The origin of the samples is shown in Table 1. The total contribution of TEQ from PCDDs/Fs and of the coplanar non-*ortho*-PCBs are given in the bar diagram (Figure 1). The relative contribution of non-ortho-PCBs to the total TEQ values reported range between 9.8 % and 79 % and the mean is 41.5 %. PCDD/F concentrations were determined in 65 different samples and ranged between 0.02 pg WHO-TEQ/g l.w. (Russia) to 2.02 pg WHO-TEQ/g l.w. (Korea). The non-*ortho* PCBs had TEQ values between 0.01 pg WHO-TEQ/g l.w. (Russia) to 0.98 pg WHO-TEQ/g l.w. (Belgium). The average PCDD/F TEQ value for all samples was 0.41 pg WHO-TEQ/g l.w.. The non-*ortho*-PCBs average TEQ value for all samples was 0.29 pg WHO-TEQ/g l.w. (0.70 pg sum WHO-TEQ/g l.w.). The average TEQ value in Europe for the PCDD/F was 0.40 pg WHO-TEQ/g l.w.. The non-*ortho*-PCBs had an average TEQ value of 0.31 pg WHO-TEQ/g l.w. (0.71 pg sum WHO-TEQ/g l.w.). All samples had similar dioxin congener profiles with the highest concentrations of the high-chlorinated OCDD.

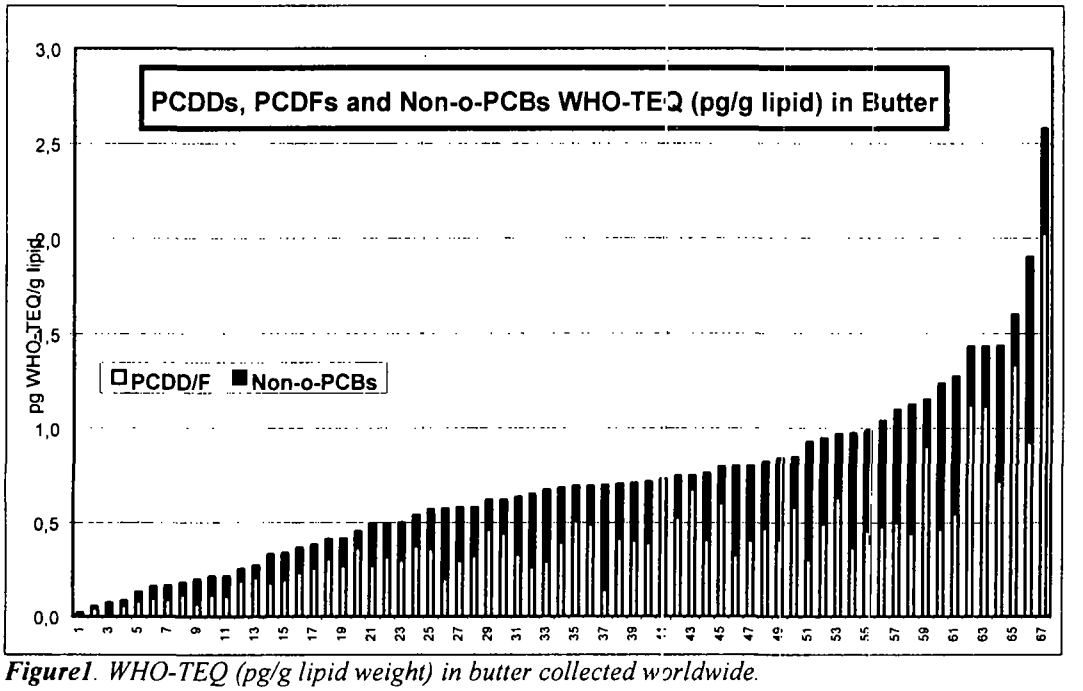

Figure1. WHO-TEQ (pg/g lipid weight) in butter collected worldwide.

Table 1. Country names in order of increasing TEQ levels in the butter samples analyzed and shown in Figure 1, above.

1	Russia	15	Sweden	29	Great Britain	43	USA	57	Belgium
2	Russia	16	Ireland	30	Great Britain	44	Belgium B	58	Ukraine
3	Egypt	17	Canada	31	Poland	45	Portugal	59	Portugal
4	Malaysia	18	USA	32	Belgium	46	Italy	60	Russia
5	Portugal	19	Scotland	33	Russia	47	German Pool	61	Belgium
6	Portugal	20	New Zealand	34	Russia	48	Belgium A	62	Korea
7	Brazil	21	Slovenia/Czech	35	Scotland	49	The Netherlands	63	Korea
8	South Africa	22	Hungary	36	Great Britain	50	Spain	64	Belgium
9	Latvia	23	Uruguay	37	Japan	51	Russia	65	Portugal
10	Finland	24	Belgium	38	Mean World	52	Bulgaria	66	Belgium
11	Norway	25	Great Britain	39	Argentina	53	Thailand	67	Korea
12	Australia	26	Russia	40	Mean Europe	54	Germany		
13	Japan	27	Austria	41	France	55	Switzerland		
14	Turkey	28	Croatia	42	Denmark	56	Belgium		

Discussion

The data indicate that countries in the northern part of the northern hemisphere have lower PCDD/F TEQs than the average TEQ value worldwide, e.g. Sweden, Norway, Finland, Latvia, Ireland, Poland, Canada. Some of the samples from Scotland, Great Britain and Russia were also lower than the average TEQ values calculated. The one sample analysed from Denmark was shown to have a higher PCDD/F TEQ value (0.53 pg WHO-TEQ/g l.w.) then the European average. A similar PCDD/F TEQ-value for Danish butter (0.52 pg WHO-TEQ/g l.w.) was recently reported from another study[11]. Still it is difficult to make any firm judgements on the basis of so few samples particularly when the data set shows highly different TEQ values in butter within the same country, e.g. the Russian samples (0.57-1.24 pg TEQ/g l.w.). As expected, low levels of TEQs were found in the southern hemisphere, e.g. Australia, New Zealand, Malaysia, South Africa and Brazil. This is in accordance with a previous report[11].

It is notable that the Korean PCDD/F TEQ-value were high, ranging between 1.12 pg /g l.w. to 2.02 pg/ g l.w., corresponding to an average of 1.42 pg WHO-TEQ/g l.w.. These values are at the highest observed in this study. The PCDD/F profile in the three Korean samples all shows higher PCDF concentration, compared to the mean world PCDD/F profile. This may indicate contamination from combustion sources in Korea (pers. commun. S. Marklund, Umeå University, Sweden), but since no further study on this matter has been performed it is impossible to make a conclusion. Almost all samples with a higher sum-TEQ than the world mean were European countries. As indicated, Korea is an exception, but also butter samples from the USA, Argentina and Thailand showed higher sum-TEQ mean levels (Figure 1).

The present study was also performed to investigate the distribution of TEQs in butter within a region or country. Nine samples were thus collected and analysed from Belgium. Sum-TEQ values between 0.54 pg/g l.w. to 1.90 pg/g l.w. were determined, with a mean of 1.06 pg /g l.w.. This gives a +/-40% variation in the levels determined among these samples. Seven of the 9 samples had TEQ-values above European mean. It is obvious that the variation in TEQ levels within one

country is rather large but still it may concluded that butter may be used for indicating the degree of dioxin contamination in dairy products.

Conclusion

The highest dioxin concentrations were found in Korea, Belgium and Portugal which had sum-TEQ above 1.4 pg WHO-TEQ/g l.w.. Butter from countries from the southern hemisphere and the northern part of the northern hemisphere had lower levels of dioxins. It can also be concluded that the chance that one butter sample shows the correct indication, i.e. above or below average value in that area, is over 50 %. That means that one butter sample cannot be said to be representative for butter concentrations from that country.

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