PCDD/Fs IN A HISTORIC BUTTER SAMPLE FROM AUSTRALIA

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Introduction

Human exposure to PCDD/Fs is primarily the result of the accumulation of PCDD/Fs in food. In Europe and North America dairy products are known to contribute on average about 20-30 % to the human intake of PCDD/Fs [3]. The accumulation of PCDD/Fs in dairy products occurs usually via the atmosphere - plant - cow - milk pathway. Studies by McLachlan and team calculated that the daily PCDD/F consumption of a lactating cow via food is equivalent to approximately 100000 m^3 of air[5]. During lactation these lipophilic chemicals partition into the milk and it has been shown that the quantity of PCBs that accumulates in 1 g of dairy lipid is equivalent to between about 2.4 and 650 m^3 of air; depending on the congener investigated[8]. Hence, analysis of dairy products may be used to estimate atmospheric concentrations of dioxin-like compounds in a given region, providing that the cows consume food from this region and food additives or dairy processing/packaging do not contribute significantly to the levels of the compounds of interest. This approach has been used in a series of studies recently. Analysis of butter samples suggested that presently atmospheric levels of PCDD/Fs are relatively low in Australia and southern Hemisphere countries and highest in South Korea, the Iberian Peninsula and a range of other industrialized countries in Europe[9,7]. To date very little information is available on historic levels of dioxins in the Australian environment. However it is noteworthy that elevated concentrations of higher chlorinated PCDDs were found in sediment core slices that were dated to prior 1800 collected from coastal areas of northern Queensland[1]. Here we present the first data of PCDD/Fs in butter from Australia to evaluate historic levels of PCDD/Fs in Australia's terrestrial environment.

Methods

The butter sample was obtained from the Australian War Memorial. It was held by the Memorial as an example of the type of food that soldiers used during World War II. A soldier had taken the butter can as a souvenir towards the end of the war; years later he donated the can to the Memorial. The butter was sealed in a 340-gram tin-coated steel container and had been sealed in this manner since manufacture. Contact was made with the dairy industry that recollected that the butter was made during World War II (that is, between 1940 and 1945), most probably towards the end of the war, with 1944 the most likely year. According to the diary workers, the milk from which the butter was made would have been drawn from all over the Australian State of New South Wales (NSW), which is located in the south-west of Australia.

To access the butter, the can was heated in a water bath and two small holes were punctured into the can. The butter was drained into a solvent washed glass jar, mixed and refrigerated until analysis. The

butter was analysed for 2,3,7,8-substituted PCDD/Fs at ERGO-Forschungsgesellschaft, Germany. Butter sub-samples (equivalent to about 10 g of lipid) were homogenised in a water bath (40 °C) and the lipophilic phase was separated then filtered through anhydrous Na_2SO_4 after which the lipid content was determined gravimetrically.

Samples were spiked with ^{13}C-labelled PCDD/Fs. For purification of the samples an automated system using activated carbon was employed, followed by an acid/base activated silica gel column (from base to top: Na_2SO_4, SiO_2, H_2SO_4/SiO_2, SiO_2, KOH/SiO_2, SiO_2, H_2SO_4/SiO_2, SiO_2, KOH/SiO_2, SiO_2, Na_2SO_4). After clean-up procedures the samples were concentrated to near dryness, transferred to vials and ^{13}C-labelled 1,2,3,4-TCDD recovery standard was added. Analysis of tetra- to octa-CDD/Fs, was performed on a GC (DB-5 fused silica column, 60 m, 0.25 mm i.d., 0.1 mm film thickness), interfaced to a VG Autospec mass spectrometer operating on a resolution of approximately 10,000. Identification of 2,3,7,8-substituted PCDD/Fs and PCBs was performed using retention times of the labeled standards and isotope ratios at M^+ and M^+2^+ or M^+4^+. For quality control the retention times of the analyte in a sample had to be within 2 s of the retention times of the internal standards. The limit of detection for PCDD/Fs in a given sample was defined by a signal to noise ratio greater than 3 times the average baseline variation and a substance quantity in the sample greater than 3 times the quantity in the respective blank.

Results and Discussion

PCDD/Fs were detectable in both analysis of the butter sample. The sum of detectable concentrations of å PCDD/Fs in the replicate analysis was 34 ± 2.7 pg g^{-1} lipid and 0.57 ± 0.02 pg WHO TEq g^{-1} lipid. PCDDs contributed to about 98 % of the å PCDD/Fs and about 76 % of the TEq value in the samples. The levels expressed on TEq basis that are found in this butter sample from the 1940s are close to the average levels that were observed in global studies on PCDD/Fs in butter carried out the last few years. Furthermore PCDD/F concentrations in the historic butter were higher than nine butter samples that were collected from various regions of Australia in the year 2000 [6]. It is particularly noteworthy that for seven of the samples collected in 2000 the concentration expressed on TEq basis (PCDD/Fs only) was less than one third of those observed in the sample from the 1940s. In comparison, PCDD/F Teq values of the butter analysed from NSW from 1940 (0.57 ± 0.02 pg WHO TEq g^{-1} lipid) was more than 4 times higher than in modern butter collected from the same state (0.15 pg g^{-1} fat and 0.08 pg g^{-1} lipid). A surprising result of the PCDD/F analysis of the historic butter relates to the PCDD/F concentration of individual PCDD/F congeners. For example the levels of OCDD and HpCDD are exceptionally high in the historic butter samples and exceed those in the more recent samples from Australia [6] and are also higher compared to butter from Europe [4] by more than an order of magnitude. Noticeably, when we analysed the recent butter samples we observed that OCDD levels were also elevated in selected modern samples (i.e. Queensland).

Analysis of archived grass samples from Europe suggested that PCDD/Fs emission and subsequent deposition in the environment started to increase from the mid 1940s due to usage of chlorinated aromatic compounds, peaked in the 1960s and since then have decreased[2]. The results of the analysis of the butter sample in this study however may provide an indication that environmental levels of selected PCDD/F congeners in Australia may have existed prior to the widespread use of chloraromatic compounds. Elevated levels of particularly higher chlorinated PCDDs have been observed in soils and sediments throughout coastal Queensland and analysis of dated sediments from North Queensland have suggestd that the source may be older than 300 years [1]. The results of the present study may be seen as new evidence that the specific source has existed in the 1940s.

On the other hand it is noteworthy that besides the 2,3,7,8-PCDD/F congeners a range of non-2,3,7,8-PCDD/Fs were detectable in the samples. Thus it is possible that the contamination may have

Table 1. Concentration of 2,3,7,8-chlorine substituted PCDD/Fs in an achieved butter sample from NSW canned in the 1940s (mean and standard deviation of replicate analysis of sub-samples taken from the same can) and from two butter samples manufactured in different regions of NSW in 2000 (mean and standard deviation).

PCDD/Fs (in pg g^{-1} lipid)	WHO-TEF	Butter from pre 1945	Butter from 2000
2,3,7,8-TetraCDD	1	0.14 ± 0.03	0.03 ± 0.01
1,2,3,7,8-PentaCDD	1	0.16 ± 0.03	0.045 ± 0.02
1,2,3,4,7,8-HexaCDD	0.1	0.17 ± 0.01	0.05 ± 0.01
1,2,3,6,7,8-HexaCDD	0.1	0.365 ± 0.007	0.07 ± 0.03
1,2,3,7,8,9-HexaCDD	0.1	0.185 ± 0.02	0.05 ± 0.03
1,2,3,4,6,7,8-HeptaCDD	0.01	6.34 ± 0.3	0.27 ± 0.2
OctaCDD	0.0001	26 ± 2.3	< 1.4
2,3,7,8-TetraCDF	0.1	0.11 ± 0.00	nd
1,2,3,7,8-PentaCDF	0.05	nd	nd
2,3,4,7,8-PentaCDF	0.5	0.2 ± 0.04	0.03 ± 0.01
1,2,3,4,7,8-HexaCDF	0.1	0.1 ± 0.00	0.02 ± 0.01
1,2,3,6,7,8-HexaCDF	0.1	0.065 ± 0.007	0.02 ± 0.007
1,2,3,7,8,9-HexaCDF	0.1	nd	nd
2,3,4,6,7,8-HexaCDF	0.1	0.06 ± 0.00	nd
1,2,3,4,6,7,8-HeptaCDF	0.01	0.14 ± 0.04	nd
1,2,3,4,7,8,9-HeptaCDF	0.01	nd	nd
OctaCDF	0.0001	0.29	nd
Total PCDD		33.5 ± 2.5	1.2 ± 1.2
Total PCDF		0.78 ± 0.24	0.06 ± 0.03
Total PCDD/PCDF		34.3 ± 2.7	1.3 ± 1.3
TEQs – WHO		0.57 ± 0.02	0.11 ± 0.05
I-TEQ		0.52 ± 0.031	0.09 ± 0.04

occurred during the manufacturing of the butter or when the can was sealed in the 1940s. At this stage we cannot elucidate the source of this contamination. Further work is underway to evaluate the composition of the butter and to locate other historic butter samples to determine whether the contamination is an artifact from the processing of the butter.

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