LEVELS OF PERSISTENT ORGANIC POLLUTANTS (PCDD/F AND DIOXIN-LIKE PCB) IN FOOD FROM THE MEDITERRANEAN DIET

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB) are three families of compounds that accumulate in animals and humans due to their properties of persistence and high lipophilia. PCDD/F are not intentionally produced, but they are formed as by-products of chemical or thermal processes. However, their bioaccumulation and biomagnification through the food chain make food the main exposition of human to these compounds (higher than 90 %)[1]. Especially, fat food and products of animal origin are those that show the highest concentrations of dioxins and PCB. Therefore, they can constitute the main input of these compounds into the diet. In 1998, World Health Organization (WHO) established the tolerable daily intake (TDI) of PCDD/F in a range of 1 to 4 pg WHO-TEQ/kg b.w./day[2]. In later revisions a tolerable weekly intake of 14 pg WHO-TEQ/kg b.w./day and a tolerable monthly intake of 70 pg WHO-TEQ/kg b.w./day have been established. Since some PCB (the twelve planar or "dioxin-like" PCB) show toxic properties similar to those of PCDD/F, WHO recommended to include them for the calculation of TEQ concentration.

In this study, we have assessed TEQ levels in fat food from the Mediterranean diet. With this purpose, dioxins, furans and dioxin-like PCB have been analysed in meat, fish, milk and dairy products, oil, butter and eggs.

Methods and Materials

Samples analysed

The samples were chosen based on two facts: firstly, the food distribution in Mediterranean diet is the one showed in Figure 1[3] and, secondly, the input of PCDD/F and PCB to the diet is higher from fat food and foodstuffs of animal origin[4].

Samples were bought in a market in Barcelona during year 2000. Following foodstuffs were analysed: milk, powder milk for children, dairy products (including yoghourts), eggs, olive oil, butter, chicken meat, pork meat, veal meat, fish (several types of fish from Mediterranean sea, including sardines).

Analytical method

Analytical methods for the determination of PCDD/F and PCB depend on which foodstuff is being analysed, especially the extraction step. However, the following scheme of analysis is shared by all the methods:

1. Homogenisation of the sample to assure that the sub-sample taken for the analysis represents the whole foodstuff.
2. Sample weighing. The weight usually depends on the fat contents of the foodstuff.

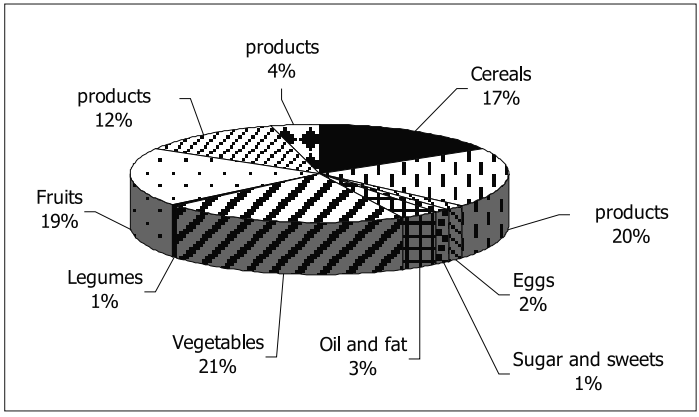

Figure 1. Composition of Catalan diet (after ENNA[3])

3. Addition of extraction internal standards labelled with ^{13}C to the sample.
4. Extraction of the fat fraction (including the compounds of interest). Extraction methodology depends on the type of sample: liquid-liquid extraction, solid-liquid extraction in Soxhlet, with homogeniser, etc. have been used.
5. Clean-up of fat extract and fractionation of PCDD/F and PCB. These steps are usually performed by liquid chromatography on different adsorbents: silica, silica modified with several reagents (sulphuric acid, sodium hydroxide, etc.), Florisil, graphitized carbon, etc.
6. Concentration of the purified extract and addition of syringe standards.
7. Instrumental analysis: It is carried out by HRGC-HRMS.
8. Quantitation: Samples are quantitated by the isotopic dilution method.

Results and Discussion

The levels of dioxin-like compounds detected in the samples analysed are summarised in Table 1. All values are expressed as upperbound concentrations (upperbound concentrations are calculated assuming that all values of the different congeners less than the limit of determination are equal to the limit of determination).

Table 1. Concentration of PCDD/F and dioxin-like PCB in foodstuffs.

Foodstuff	Concentration (pg WHO-TEQ/g lipid) PCDD/F	Non-ortho PCB	Mono-ortho PCB	Total TEQ
Milk	0.28-1.33	0.04-1.16	0.01-0.19	0.33-2.68
Dairy products	0.69-2.49	0.66-1.60	0.12-0.24	1.52-4.32
Oil and fats	0.35-0.76	0.06-0.46	0.01-0.09	0.42-1.31
Meat	0.89-2.26	0.15-0.44	0.10-0.15	1.32-2.55
Eggs	0.55	0.27	0.05	0.86
Fish	0.23-0.40[a]	0.66-1.53[a]	0.27-0.86[a]	1.16-2.79[a]

[a] Concentrations in fish are expressed in pg WHO-TEQ/g product, as it is established in new European Regulations.

The levels of dioxins detected in the samples are in the range or below those reported in the literature[5-8]. In addition, if the concentrations are compared to those established in the new European regulations (Council Regulation n. 2375/2001), in general, they are below the maximum values. Only some meat samples are close to these maximum concentrations.

Contribution of dioxin-like PCB to total TEQ values is variable but very important in all samples, as it is shown in Figure 2. For most samples, this contribution is in the range of 25-50 %. However, fish show much higher levels of dioxin-like PCB and their contribution reaches 80-85 %.

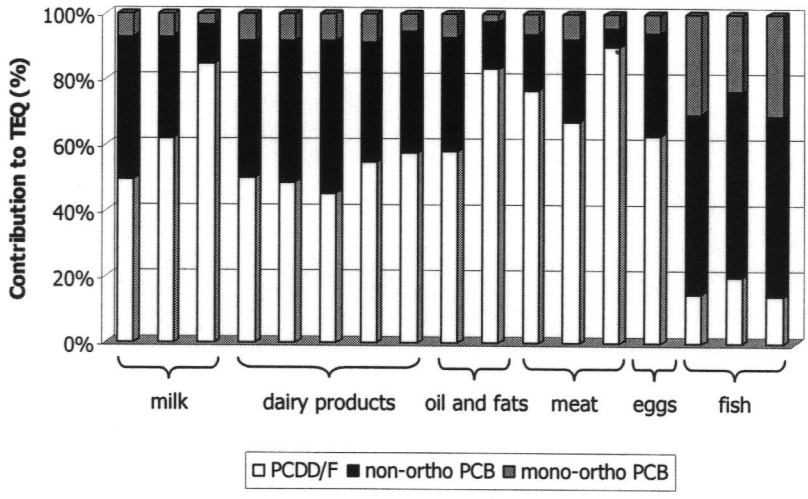

Figure 2. Contribution (%) of PCDD/F, non-ortho PCB and mono-ortho PCB to total TEQ.

In spite of the limited number of samples analysed, an estimation of the daily intake of dioxin-like compounds was calculated. For this calculation, diet data was taken from the Spanish National Study on Nutrition and Food[3] and it was assumed that the analysed food samples were the only consumed. The daily intake value obtained was 0.67 pg WHO-TEQ/kg b.w./day if only PCDD/F were considered and 2.78 pg WHO-TEQ/kg b.w./day if dioxin-like PCB were also taken into account. The main contributors to the intake were fish (78 %), followed by milk and dairy products (9.1 %) and meat (8.1 %).

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