Levels of PCDDs and PCDFs in oil components of the spanish diet

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1. Introduction and objetives.

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been found as contaminants in many different compartments of the global ecosystem[1,2] and appear to concentrate in the food chain[3]. The 2,3,7,8-substituted isomers have been detected in human adipose tissue, milk and blood samples from the general population[4,5]. The primary route of exposure in humans is via food, especially those food of animal origin[6]. The extent of such human exposure to toxic chemicals can be estimated in two ways:

1- Determination of body burdens through examination of samples of human tissues.
2- Estimation of dietary intake from measured concentrations in food.

After having examined PCDDs and PCDFs levels in different tissues from the Spanish population[7,8,9], this study was focused in the second point.

Many studies have been performed to determine the concentrations of PCDDs, PCDFs and PCBs in foods. It is most effective to base the samples studied around a typical diet, in order to reflect the trends in food consumption of the region of interest[10]. The principal components of the Spanish diet in which PCDD/Fs and PCBs are likely to be found, due to their highly lipophilic character, are: Fish, Meat, Eggs, Milk, Dairy Products and Fats and Oils used in food preparation.

In this study, fish oil capsules used as dietary supplements were selected because although not consumed by a large proportion of the population, the potential contribution via these products is worthy of investigation.

This study details the concentrations of PCDDs and PCDFs in dietary supplements on an isomer specific basis. The profiles of particular isomers observed may in future be related to specific sources of contamination.

2. Material and Methods.

Samples were collected in Madrid, SPAIN, during January 1994. Around 15 different brands of fish oil are obtainable in Madrid and the percent of the market covered for analysis was the 75%

All the samples analysed were one per brand and do not cover any seasonal or year to year variation. Fish oil capsules were stored in a cool dark cupboard.

Prior to the initial extraction of samples, a mixture of $^{13}C_{12}$ PCDDs and PCDFs internal standards was added containing one isomer from each homologue group with the exception of OCDF.

Two different procedures were used with fish oil capsules. As the main constituent of the capsule was gelatin, capsules were dissolved in warm water with stirring for a few hours in order to dissolve the gelatin and to release the oil. Cyclopentane, diethyl ether and a mixture 50/50 v/v of cyclopentane and diethyl ether were used as liquid-liquid extraction solvents. Following this procedure, the extraction step became difficult because of emulsion formation.
The alternative approach taken was to puncture the capsules and to collect the oil separately. The ratio of gelatin to oil for each type of capsule was determined gravimetrically. The aisolated oil was placed in the large silica column of the FMS (Fluid Management System, Inc.) apparatus. Internal standards were added, and the sample extracted on-column as part of the opperational cycle of the FMS cleanup system.

Cleanup followed a method based on an adaptation[11] of the Smith et al. method[12]. This comprises low pressure chromatography on neutral and base-modified silica gel, activated carbon dispersed on glass fibers, silica gel impregnated with sulfuric acid, and Florisil. Three fractions were eluted from the carbon column for each sample. These contained ortho-substituted PCBs, non-ortho-substituted CBs and PCDD/Fs respectively.

Resolution and quantification of PCDDs and PCDFs were performed by HRGC-HRMS using an VG Autospec magnetic sector instrument coupled to a Carlo Erba 5300 Mega Series Gas Chromatograph. Separation of target compounds was achieved on a Restek RTX-5 WCOT capillary column (60m x 0.25 mm i.d., 0.10μm film thickness) using Helium carrier gas at a column head pressure of 150 KPa. The MS was operated in the Voltage SIR mode. Electron Impact ionization in the positive mode was applied. Source conditions were: temperature 250°C, electron energy 50eV, trap current 800μA. The instrument was operated at a minumun resolution of 7000 (10% valley definition).

3. Results and discussion

Table 1 shows the levels of 2,3,7,8 substituted PCDD and PCDF isomers found in the different oil samples analysed.
PCDD values for the fish oil capsules are very low, ranging from 0.1 to 5.9 ppt (pg/gr) on a fat weight basis. Between the PCDDs, as usual in biological samples, it is the OCDD the isomer which exhibits the highest levels, being the medium value 6.4 ppt followed by the heptaclorinated isomer with medium values of 2.1 ppt.

Regarding to PCDFs in fish oil samples, it could be seen that the 2,3,7,8-TCDF exhibits high levels, corresponding the highest value to 31.0 ppt. It is also notable that the 2,3,4,7,8-PnCDF shows high levels.

As further studies are conducted in order to evaluate the PCDDs and PCDFs content in othes spanish fat and oil samples largely consumed by the population, this preliminary data could be used in the future to estimate the contribution of these xenobiotics to the body burden in the Spanish population. Based on a mean consumption of 5 capsules each day (0.4 grams of oil per capsule), the daily consumption would be 2.0 g/person/day on a fat weight basis. The total I-TEF is 2.11 pg TEQ/g

fat weight (see Table 1). This mean that the daily intake of PCDD and PCDF via fish oil capsules by an individual would be 4.22 pg I-TEQ/person. An individual of 60 Kg body weight, consuming 2.0 g of fish oil a day, receives a dose of 0.07 pg/I-TEQ/Kg body weight per day. Also it should be noted that analysis from the other main components of the typical Spanish diet are needs to estimate the total contribution via food.

Table 1. Levels of PCDDs and PCDFs 2,3,7,8-substituted found in the fish oil capsules on a fat weight basis (pg/g, n = 7).

ISOMER	MEAN	S.D.	RANGE	I-TEQ
2,3,7,8-T_4CDD	0.50	0.59	0.13 - 1.82	0.50
2,3,7,8-T_4CDF	5.50	11.29	0.26 - 31.02	0.55
1,2,3,7,8-P_5CDF	1.18	2.29	0.04 - 6.31	0.01
2,3,4,7,8-P_5CDF	1.05	1.40	0.11 - 3.96	0.52
1,2,3,7,8-P_5CDD	0.44	0.39	0.13 - 1.06	0.22
1,2,3,4,7,8-H_6CDF	0.50	0.61	0.08 - 1.66	0.05
1,2,3,6,7,8-H_6CDF	0.49	0.81	0.07 - 2.29	0.05
1,2,3,7,8,9-H_6CDF	0.10	0.05	0.04 - 0.15	0.01
2,3,4,6,7,8-H_6CDF	0.46	0.65	0.04 - 1.86	0.05
1,2,3,4,7,8-H_6CDD	0.11	0.30	0.09 - 0.19	0.02
1,2,3,6,7,8-H_6CDD	0.58	0.80	0.14 - 2.37	0.06
1,2,3,7,8,9-H_6CDD	0.40	0.30	0.08 - 0.83	0.04
1,2,3,4,6,7,8-H_7CDF	0.24	0.28	0.05 - 0.86	0.002
1,2,3,4,7,8,9-H_7CDF	0.24	0.12	0.11 - 0.47	0.002
1,2,3,4,6,7,8-H_7CDD	2.09	1.16	0.65 - 4.08	0.02
OCDF	0.69	0.33	0.34 - 1.27	0.001
OCDD	6.38	2.01	4.10 - 9.99	0.006

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