DIETARY INTAKES OF PCDDS, PCDFS AND PCBS IN TOTAL DIET SAMPLES FROM THE BASQUE COUNTRY (SPAIN)

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Introduction

Total Diet Studies (TDS) are used to provide information on dietary exposure of the general population and different sub-groups to nutrients and contaminants such as dioxin and dioxin-like PCBs. These studies are an essential aid to verify that exposure to these contaminants does not cause concern for human health. They are also a valuable tool to assess the effectiveness of pollution control measures that have been introduced to limit the release of these contaminants.

This study was carried out to assess the exposure to dioxins and PCBs in diets collected in the Basque Country, Spain. The study determined current levels of these contaminants in 5 food groups of the Total Diet Study[1]: Eggs, Meat and Meat products, Fish, Milk and Dairy products and Oils and Fats. The selection of these categories for the analyses was based on the fact that they include the food items with the highest reported contribution for the contaminants under study.

Methods and Materials

Sampling

The Total Diet Study of the Basque Country[1] is designed to collect 12 diets per year, approximately on a monthly basis. We selected for this assessment 8 of these diets, collected in the period 1999-2000 from 5 different locations (3 from Bilbao, 2 from Vitoria, and 1 each from Basauri, Hernani and Beasain). Samples were kept deep-frozen (-25 ºC). Sub-samples of the 5 food categories mentioned above for the 8 selected diets were shipped to the Central Science Laboratory (UK), where they performed the sample preparation (homogenisation and freeze drying) and analyses.

PCDDs, PCDFs and PCBs analytical determinations

Fat determinations were performed by a UKAS (ISO 17025) accredited laboratory on sub-samples of the freeze-dried and homogenised samples using a standard method[2]. The extraction, clean up and analysis of samples was carried out as previously described[3]. The extraction and clean up yielded three fractions: (i) ortho-PCBs, (ii) non-ortho-PCBs and (iii) PCDD/PCDFs.

The determination of non-ortho-PCBs and PCDD/PCDFs was performed by GC-High Resolution Mass Spectrometry. These analyses were carried out on a Micromass Autospec Ultima interfaced to Hewlett- Packard 6890 gas chromatograph with a Gerstal high volume injector and a CTC A200SE auto sampler.

The determination of ortho-PCBs was performed by GC- Low Resolution Mass Spectrometry on a MD800 quadrupole instrument (Fisons MassLab, UK) coupled to a GC8000 gas chromatograph fitted with a CTC A200S auto sampler.

The Limit of Reporting (LOR) applied for PCDDs, PCDFs and non-*ortho*-PCBs was the limit of determination ranging from 0.02 –2.4 ng/kg for PCDD/Fs and 0.07 – 0.15 ng/kg for non-ortho PCBs depending on the sample type and the individual congener. For the *ortho*-PCB congeners, a LOR of 0.10 ng/kg fat was applied. All analytical data were assessed for compliance with published acceptance criteria[4], using reference materials prepared by the BCR[5] as quality control samples.

WHO-TEQ and dietary intake estimations

The WHO-TEQs values were calculated by multiplying the concentration of each congener by the appropriate WHO-TEF[6] and summed to give ΣTEQ. The reporting limit for WHO-TEQ data was 0.01 ng/kg. Lower and upper bound WHO-TEQs were estimated by assigning zero and the LOR, respectively, to the congeners with concentrations below the appropriate LOR.

Whole weight basis ΣTEQs were calculated by multiplying fat weight ΣTEQs by the percentage fat content of each sample. The daily dietary intakes of PCBs, PCDDs and PCDFs were estimated by multiplying this value by the consumption data[7].

Results and Discussion

The range of the contents of dioxin and dioxin like compounds for each food category is given in Table 1.

Table 1. Concentration ranges for upper-bound WHO-TEQs (ng WHO-TEQ/kg fat)

	ng WHO-TEQ/kg fat			
Food group	**Σ PCDD/F** WHO-TEQ	**Σ non-ortho PCBs** WHO-TEQ	**Σ ortho-PCBs** WHO-TEQs	**Total** Σ WHO-TEQ
Eggs	0.68 – 1.9	0.17 – 1.2	0.22 – 0.56	1.1 – 2.7
Meat and Meat Products	0.44 – 2.3	0.15 – 1.4	0.21 – 0.62	0.95 – 4.1
Fish	1.9 – 6.1	9.1 – 39	2.6 – 13	15 – 58
Milk and dairy products	0.69 – 1.4	0.4 – 1.3	0.23 – 3.1	1.8 – 4.5
Fats and Oils	0.12 – 0.23	0.02 – 0.04	0.04 – 0.19	0.2 – 0.46

Within the TDS food categories, the fish group is found to consistently contain the highest concentrations of dioxins and PCBs. This pattern is repeated across the different studied locations.

When assessing the mean of total ΣWHO-TEQ for each of the 5 food categories (Figure 1), the fish group, as expected, contains by far the highest dioxin and PCB concentrations of all the food groups with a mean value of 26 ng/kg fat. Ortho and non-*ortho*-PCBs contribute 87 % of this value. This is in sharp contrast to the rest of the food categories where dioxins make the largest contribution to the total Σ WHO-TEQ. The fats and oils group shows the lowest concentrations with a total Σ WHO-TEQ mean value of 0.32 ng/kg with similar contribution from dioxins and PCBs. (Figure 1).

The five different locations where the samples were taken showed roughly the same pattern of total Σ WHO-TEQ distribution. The fish group dominates by at least a factor of 6 with respect to the next highest group which was milk and dairy products for all locations except Basauri. At this location,

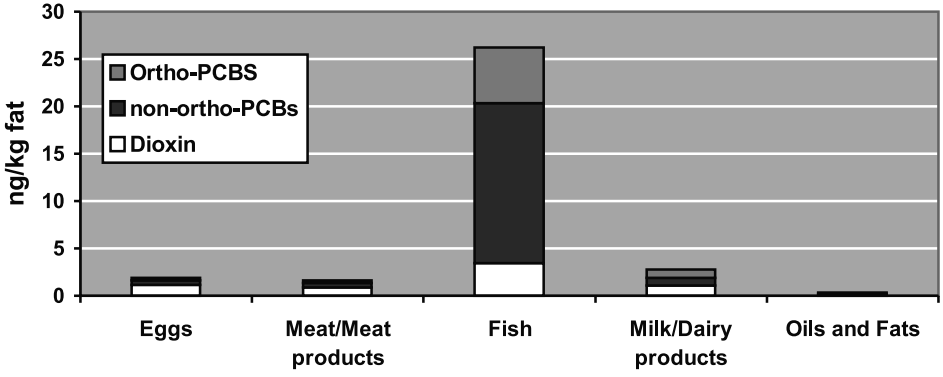

Figure 1. Mean ΣWHO-TEQ values of the 5 food categories analysed for the total diet samples under study and contribution of the different chemical fractions (Ortho-PCBs, non-ortho-PCBs and dioxin) to the total mean value

meat and meat products showed a higher value than milk and dairy products. The oils and fats group presented the lowest Σ WHO-TEQ values for all locations.

The relative TEQ content of the different food groups is similar to that found recently for other countries[8,9,10] which show that fish is one the highest dioxin and PCBs containing groups. PCDD/F data for food groups taken for another recent study from Catalonia, Spain[11] reported a similar I-TEQ content for the fish group.

The average estimated upper bound for dietary exposure to dioxins and dioxin-like PCBS through the five food groups was 175.5 pg WHO-TEQ/day (Table 2) or 2.6 pg WHO-TEQ/kg/day, assuming an average bodyweight of 68 kg[7].

Table 2. Average upper bound dietary intake in pg WHO-TEQ/day for PCDD/F, non-ortho-PCBs and ortho-PCBs

Food Group	Consum (g)	Concentration pg/g whole weight			Intake in pg WHO-TEQ/day		
		PCDD/F	non-ortho-PCBs	ortho-PCBs	PCDD/F	non-ortho-PCBs	ortho-PCBs
Eggs	41	0.11	0.04	0.03	4.51	1.64	1.23
Meat/Meat products	163	0.08	0.05	0.03	13.04	8.15	4.89
Fish	89	0.13	0.59	0.20	11.57	52.51	17.8
Milk/Dairy milk	352	0.05	0.04	0.04	17.6	14.08	14.08
Oils and Fats	45	0.17	0.03	0.12	7.65	1.35	5.4
Total					**54.37**	**77.73**	**43.4**

The estimated dietary exposure in the Basque Country is close to the Tolerable Weekly Intake (TWI) of 14 pg WHO-TEQ/kg bw proposed by the SCF of the EU[13] and to the Provisional Tolerable

Monthly Intake (PTMI) of 70 pg WHO-TEQ/kg bw proposed by the JECFA[14]. The intake is also within the range of the average intake reported for the EU[15] of 1.2-3 WHO-TEQ pg/kg/day.

Comparing dietary intakes estimated in this study to those obtained in 1997 for samples of the same Total Diet Study[12] and the same 5 food categories, the PCDD/F and the dioxin-like dietary exposure presented a decrease of at laest 60 % in the average total intake.

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