LEVELS OF PERSISTENT ORGANIC POLLUTANTS (PCB AND PCDD/F) IN PLASMA OF POPULATION FROM BARCELONA AND GIRONA (SPAIN)

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Introduction

Since the first methods to analyze PCDD/F in blood and human plasma were developed in the late 80´s, the study of levels in this kind of matrix has revealed very useful to know the exposition degree of general population. However, nowadays data from Spanish population are still scarce. Only a few studies have been published in literature [1-3]. Specifically, no data of population from Barcelona and Girona, two of the main cities in Catalonia (Spain), is available. This is the reason why our study has focused on population from these cities. Barcelona, in central coast of Catalonia, is a 90 km^2 city with up to 1.5 million of people living in it and a high industrial development. If the towns around the city are considered, then population exceeds 2.5 millions. Girona, in northern Catalonia, is a small city with 65000 people and a medium industrial activity.

Twenty four samples of human plasma have been analyzed to study the levels of exposition of this population. Half of the samples corresponded to people from Barcelona and the other half from Girona in order to test possible differences due to geographical location. In addition, the samples were chosen in such a way that allowed us to study possible trends related to the age and sex of the donors.

Following WHO recommendations, not only PCDD/F were analysed, but also “dioxin-like” PCB in order to correctly assess TEQ concentration in the samples. In addition, non-planar PCB were determined.

Methods and Materials

Sample analysis

Prior to extraction, samples (200 ml of plasma each) were spiked with $^{13}C_{12}$ labeled extraction internal standards. The extraction was performed according to a modification of Patterson´s method[4]. Extract clean-up was performed with concentrated sulfuric acid and in a multilayer silica column. Fractionation in SPE carbon tubes allowed us to separate fractions of di-ortho and higher PCB, mono-ortho PCB, non-ortho PCB and PCDD/F. After concentration under nitrogen flow and addition of syringe standards, the fractions were analyzed by HRGC-HRMS. Non-planar PCB were analyzed by HRGC-ECD.

Validation of the method

Prior to the analysis of samples, accuracy, precision and limit of detection (LOD) of the whole analytical procedure were studied. The repeatability (% RSD) was obtained from three repetitions of human plasma analysis (non-spiked sample) in different series of samples. Accuracy was expressed as the recovery obtained in the analysis of a spiked plasma sample. The LOD was calculated for each congener as the average of limits of detection (S/N=3) in the three analysis of repeatability experience.

Samples

24 plasma samples of men and women from Barcelona and Girona were analyzed. The samples were grouped by age, sex and location, as it is shown in Table 1. Blood were sampled by Centre de Transfusió i Banc de Teixits (CTBT) from volunteer donors. The conventional methodology for this kind of donation was applied to obtain plasma samples.

Table 1. Human plasma samples analyzed in this study and nomenclature used for their identification.

	Barcelona			Girona		
	18-35 yr.	36-50 yr.	51-65 yr.	18-35 yr.	36-50 yr.	51-65 yr.
Men	HBA#1	HBB#1	HBC#1	HGA#1	HGB#1	HGC#1
	HBA#2	HBB#2	HBC#2	HGA#2	HGB#2	HGC#2
Women	DBA#1	DBB#1	DBC#1	DGA#1	DGB#1	DGC#1
	DBA#2	DBB#2	DBC#2	DGA#2	DGB#2	DGC#2

Results and Discussion

Validation of the method

The results of the validation are shown in Table 2. The recoveries of PCDD/F are high (98% for the sum of 2,3,7,8 congeners). Although the validation samples were not spiked with native PCB, the recoveries of the $^{13}C_{12}$ labeled ones were also high (79-93%). RSD values were lower than 15% for most congeners

Table 2. Results of the validation study.

	Concentration[1]	Recovery (%)	Repeatability (RSD, %)	LOD[1]
Σ*PCDD/F*	479	98.5	2.1	19.9
Σ*non-ortho PCB*	113	——-[2]	6.4	4.49
Σ*mono-ortho PCB*	34.9	——-[2]	6.2	21.4
WHO-TEQ	25.9	-——[2]	7.0	8.34
Σ*di-ortho PCB*	232	——-[2]	3.4	54.3

[1] Expressed in pg/g lipid for PCDD/F, non-ortho PCB and WHO-TEQ and in ng/g lipid for mono-ortho PCB and di-ortho and higher PCB.

[2] Validation samples were not spiked with PCB. Therefore, recoveries of native PCB were unavailable.

Analysis of samples

The levels of dioxin-like compounds obtained in the samples are shown in Figure 1.

PCDD/F levels ranged from 275 pg/g lipid to 1208 pg/g lipid. As it is common in this type of samples, only 2,3,7,8-substituted congeners were detected. The most concentrated congener was always OCDD, with a contribution around 60% in most samples.

Total concentration of TEQ (including dioxin-like PCB) ranged from 9.26 pg WHO-TEQ/g lipid to 77.7 pg WHO-TEQ/g lipid for most samples. Only two samples (HBA#2 and HBC#1) showed higher concentrations (120 and 126 pg WHO-TEQ/g lipid, respectively). Dioxin levels were similar to

background concentrations in other industrialized countries[5,6]. The contribution of "dioxin-like" PCB to total TEQ was very important (Figure 2), ranging from 13-49% for non-ortho PCB and 10-40 % for mono-ortho PCB.

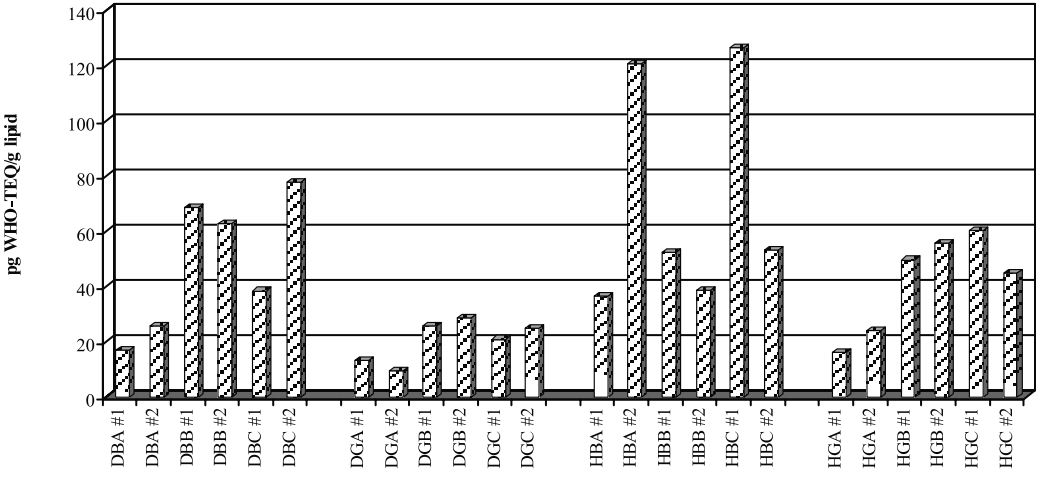

Figure 1. TEQ concentration (pg WHO-TEQ/g lipid) of the analyzed samples.

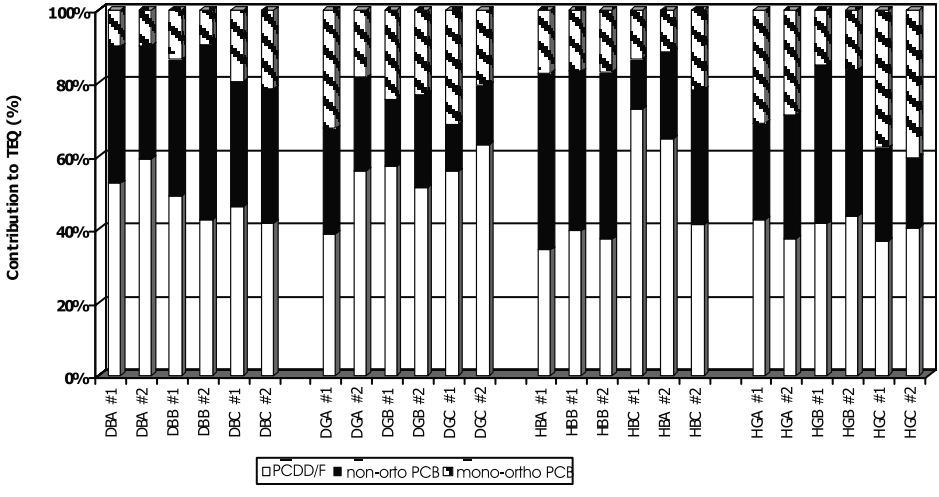

Figure 2. Contribution of PCDD/F, non-ortho PCB and mono-ortho PCB to total TEQ concentration (pg WHO-TEQ/g lipid) of the analyzed samples.

The concentration of PCB (quantified as sum of 32 congeners) in the samples were in the range of ng/g lipid (105-1060 ng/g lipid). PCB 153 and PCB 180 were the most abundants.

Statistical analysis of the samples showed some trends: (1) TEQ concentrations were lower in samples corresponding to women than in those from men, (2) samples from Barcelona showed higher TEQ values than those from Girona and (3) concentrations of PCB and PCDD/F were significantly lower in samples from the youngest group of population than in the other groups.

Acknowledgements

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