DIETARY EXPOSURE TO PCDD/Fs BY THE POPULATION OF CATALONIA, SPAIN: TEMPORAL TREND

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are among the most known and investigated POPs. PCDD/Fs are produced unintentionally due to incomplete combustion, as well as during the manufacture of certain pesticides and other chemicals. Humans are primarily exposed to PCDD/Fs by eating food contaminated by these chemicals. For that reason, in 2000 we initiated in Catalonia (Spain) a wide surveillance program focused on measuring the levels of a number of chemical contaminants (including PCDD/Fs) in various groups of foodstuffs. Dietary intake of the pollutants was subsequently estimated for various age and sex groups of the population of that country using deterministic and probabilistic methodologies[1-9]. In order to establish the temporal trend in the total dietary intake of PCDD/Fs, food items belonging to the same groups assessed in the 2000 survey were collected and analyzed in 2006, and again in 2008. We here present the concentrations of PCDD/Fs in a number of foodstuffs corresponding to this last survey, as well as human exposure through the diet of these environmental pollutants.

Materials and methods

In November-December 2008, food samples were purchased in 12 important cities of Catalonia. Samples were obtained from each locality in local markets, small stores, supermarkets, and big grocery stores. The foods selected for PCDD/Fs analysis were among the most consumed in Catalonia. Analyzed samples included: meat (veal steak, hamburger, loin of pork, pork sausage, chicken breast, and steak and rib of lamb), and meat products (boiled ham, "Frankfurt" sausage, salami, and cured ham); fish and shellfish (sardine, canned sardine, tuna, canned tuna, anchovy, mackerel, swordfish, salmon, hake, red mullet, sole, cuttlefish, squid, clam, mussel, and shrimp); vegetables (lettuce, tomato, cauliflower, string bean, onion, pepper, carrot, and eggplant); tubers (potato); fruits (apple, orange, pear, banana, mandarin, strawberry, and peach); eggs; milk (whole, and semi-skimmed); dairy products (yoghurt, cheese I - with low fat, cheese II - fat cheese, cheese III - extra fat cheese, and cream-custard-caramel); cereals (French bread, sandwich bread, rice, and pasta); pulses (lentils, haricot beans, chickpeas, and peas); oils and fats (olive oil, sunflower oil, margarine, and butter), and industrial bakery (croissant, cookie, and fairy cake). For each food item, two composite samples were prepared for analyses. Each composite sample consisted of 24 individual units. Only edible parts of each food were included in the composites.

Chemical analyses of PCDD/Fs were based on the US EPA method 8290. Appropriate 13C-labeled extraction standards were added to the homogenized samples in order to control the whole sample preparation process. Samples were extracted using hexane/acetone as solvent, being the extracts then concentrated to determine PCDD/Fs. A multi-step sample clean-up was performed to remove the matrix and to remove the potential interfering components. The cleaned extracts were injected and analyzed separately using an Agilent 6890 Capillary Gas Chromatograph equipped with a DB5-MS capillary column and coupled to a Waters Autospec Ultima High Resolution Mass Spectrometer. Following the chromatographic separation, the mass spectrometric parameters allowed to separate the PCDDs and PCDFs between the different chlorination degrees and between the 13C-labeled congeners and the native 12C-congeners. Quantification was carried out using the corresponding isotope- labeled compounds as internal standards. Toxic equivalents (TEQ) of the analyzed PCDD/Fs were calculated using the WHO-toxic equivalency factors (WHO-TEF). The limits of detection (LOD, fresh weight) were between 0.0010 and 0.5 ng/kg.

Consumption data by the general population of Catalonia of the analyzed foodstuffs were used for calculations. Data from the 24 h-recall survey were used to calculate the deterministic exposure, whereas data from the frequency questionnaires (excluding children) were used for the probabilistic assessment. The population was divided into four age groups: children (4–9 years), adolescents (10–19 years), adults (20–65 years), and seniors (>65

years). In turn, each group was subdivided according to sex. The deterministic total dietary intake of PCDD/Fs for each food group was calculated by summing the results of multiplying the PCDD/F concentration in each specific food item by the amount (proportionally estimated) consumed of that food. Finally, total dietary intake was obtained by summing the respective intakes from each food group. For calculations, when a concentration was under the respective LOD, the value was assumed to be equal to one-half of the LOD (ND = ½ LOD). Results were evaluated using the statistical software SPSS 17.0. The Levene test was applied to study the equality of variances. The statistical significance of differences was assessed by applying the Kruskal-Wallis test. A probability of 0.05 or lower ($P \leq 0.05$) was considered as significant. The probabilistic assessment was performed by a Montecarlo method, taking into account the variability associated to food intakes per unit of body weight (simulated by non-parametric distributions derived from the dietary intake data) and the uncertainty of the mean concentration of individual residues in each food (simulated by lognormal distributions). The simulations were run in an Excel© spreadsheet.

Results and discussion

Concentrations of PCDD/Fs were determined for the 17 most toxic congeners. With these concentrations and the WHO-TEF of each congener, we estimated the mean WHO-TEQ (ng/kg of fresh weight) for each food group. Those values, given in decreasing order, were the following: fish and seafood (0.120), oils and fats (0.086), milk and dairy products (0.041), eggs (0.032), bakery products (0.023), meat and meat products (0.011), cereals (0.007), pulses (0.003), fruits (0.003), and vegetables and tubers (both 0.002). In our previous surveys (2000 and 2006)[6,10], the maximum WHO-TEQ values corresponded also to the fish and seafood group, followed by oils and fats, and milk and dairy products, while the lowest PCDD/F levels were detected in vegetables and fruits. In the present study, the mean levels of PCDD/Fs found in fish and seafood were significantly higher ($P < 0.05$) than the concentrations found in the remaining food groups. In turn, PCDD/F concentrations in oils and fats were significantly higher ($P < 0.05$) than the levels found in meat and meat products, cereals, pulses, vegetables and fruits.

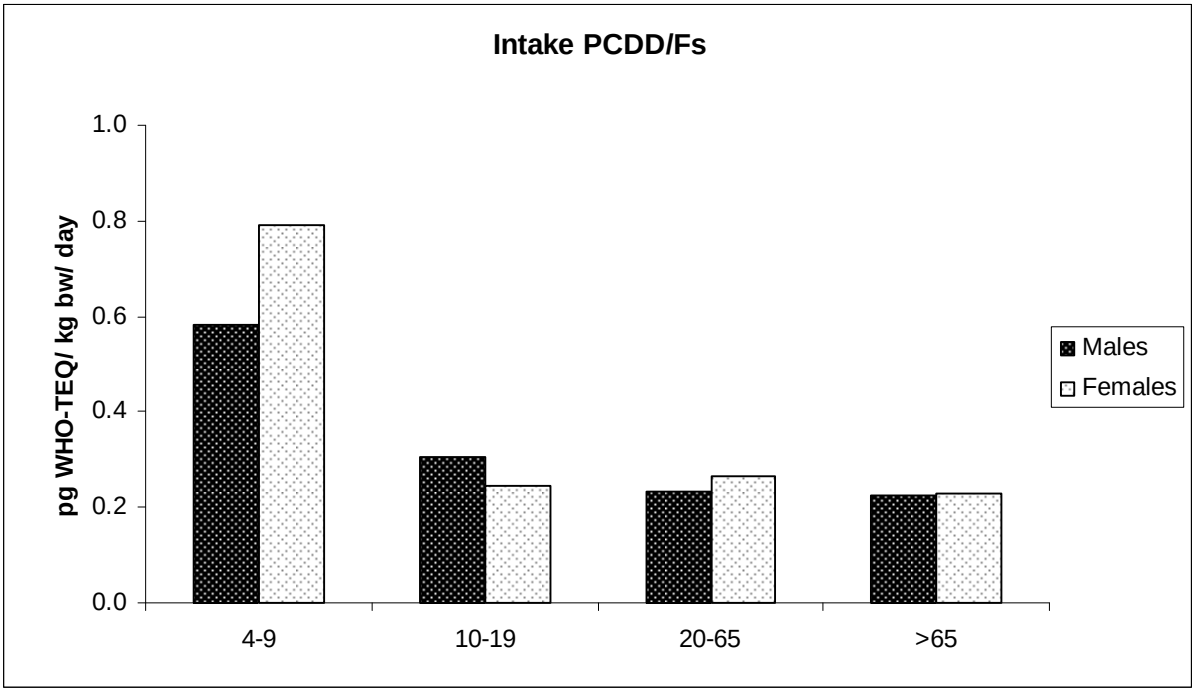

Fig. 1. Estimated dietary intake of PCDD/Fs by the general population of Catalonia, Spain, in relation to age and sex.

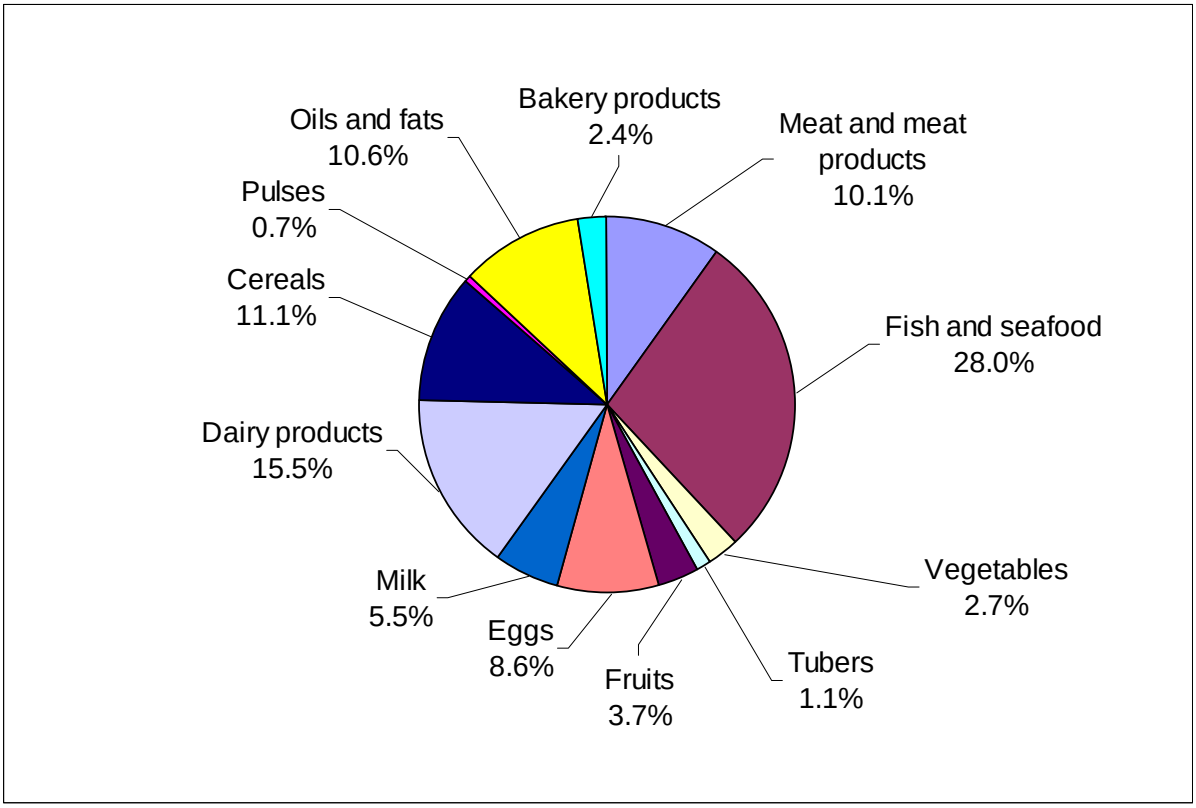

Fig. 2. Contribution (%) of food groups to the total dietary intake of PCDD/Fs for a male adult (70 kg b. wt).

Table 1. Estimated dietary intake of PCDD/Fs in Catalonia, Spain

Food group	Daily food consumption[a] (g)		PCDD/Fs intake (pg WHO-TEQ/day)		
	2000	2006 and current survey	2000	2006	current survey
Meat and meat products	185 (12.8)	172 (14.0)	12.09	2.62	1.27
Fish and seafood	92 (6.4)	68 (5.5)	28.74	6.53	3.54
Vegetables	226 (15.7)	160 (13.0)	1.67	1.28	0.34
Tubers	74 (5.1)	73 (5.9)	0.90	0.77	0.14
Fruits	239 (16.6)	194 (15.8)	2.20	0.65	0.47
Eggs	34 (2.4)	31 (2.5)	2.37	0.43	1.09
Milk	217 (15.0)	128 (10.5)	2.10	1.47	0.70
Dairy products	106 (7.3)	76 (6.2)	23.32	1.81	1.95
Cereals	206 (14.3)	224 (18.3)	13.76	6.33	1.41
Pulses	24 (1.7)	30 (2.5)	0.33	0.43	0.09
Oils and fats	41 (2.8)	27 (2.2)	7.93	2.50	1.34
Bakery products[b]		45 (3.7)		0.85	0.30
Total intake (TI)	1444 (100)	1228 (100)	95.4	25.7	15.72
TI (pg/kg/day)			1.36	0.37	0.23

Results are given for a male adult of 70 kg body weight.
[a]Food consumption data. In parentheses, percentages of total consumption. [b]Not included in the 2000 survey.

The deterministic daily dietary intake (pg WHO-TEQ per kg of body weight) of PCDD/Fs by the population of Catalonia according to 8 age/sex groups is shown in Fig. 1. As in our previous surveys, the highest intake corresponded to children (4-9 years old). It should be due to the notable different dietary habits with the rest of the population, together with the lower body weight, which influences considerably the quotient. The differences among the other 6 age/sex groups were rather scarce. The probabilistic assessment for the whole population (not including children), showed a mean daily value of 0.25 pg WHO-TEQ/kg bw (17.6 pg WHO-TEQ), being the 95 and 99 percentiles 0.39 and 0.49 pg WHO-TEQ/kg bw (29.5 and 37.9 pg WHO-TEQ), respectively.

Fig. 2 depicts the percentages of contribution of each food group to the dietary intake of PCDD/Fs for a standard male adult of 70 kg body weight. As it can be seen, the highest exposure corresponded to fish and seafood (28.0%), followed by dairy products (15.5%), and oils and fats (10.6%). In contrast, the lowest contributions corresponded to pulses (0.7%) and tubers (1.1%), followed by vegetables (2.7%) and fruits (3.7%). In comparison with our 2000 and 2006 surveys, the current estimated dietary intake (in pg/kg body weight/day) of PCDD/Fs by an adult male of 70 kg living in Catalonia showed a decreasing trend: 1.36 (2000)[6], 0.37 (2006)[10], and 0.23 (current survey). However, the difference between the 2006 study and the present survey did not reach the level of statistical significance. On the other hand, because of the notable changes in the dietary habits between the 2000 and the current surveys, it was not possible adequately comparing the notable differences observed in the PCDD/Fs intake.

Table 1 summarizes the total dietary intake of PCDD/Fs by a standard adult male (70 kg body weight) living in Catalonia during the surveys performed in 2000, 2006 and the current one. Between the 2006 and the current surveys, the highest reductions by food groups, which mainly contributed to the decrease in the total dietary intake of PCDD/Fs, corresponded to fish and seafood, and cereals. In contrast there was a slight increase in eggs and dairy products.

In summary, the results of the present study show an important decreasing trend in the dietary exposure to PCDD/Fs for the population living in Catalonia. It should be due to the general decreasing trend in the atmospheric PCDD/F levels, which has been observed in a number of countries in recent years. With respect to the health risks derived from dietary exposure to PCDD/Fs, the current total daily intake is notable lower (even considering the individuals in the extreme of the exposure distribution) than the tolerable intake established by the WHO in the range 1–4 pg WHO-TEQ/kg of body weight/day, or 14 pg WHO-TEQ/kg of body weight on a weekly basis, according to the Scientific Committee on Food (SCF) of the European Commission.

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