LEVELS OF PCBs AND HEXACHLOROBENZENE IN FOODS FROM CATALONIA, SPAIN. HUMAN EXPOSURE THROUGH THE DIET

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Introduction

Polychlorinated biphenyls (PCBs) are lipophilic organic compounds whose origin comes from a number of different sources. Like PCDD/Fs (*dioxins*), PCBs are ubiquitous and persistent environmental pollutants with a well known potential toxicity, which were included at the 1998 UN-EC POP protocol. Although human exposure to PCBs can occur by various routes, food is the primary source. A number of studies have shown that the major food sources of these pollutants are fat-containing animal products, including also fish and other seafood. On the other hand, hexachlorobenzene (HCB) is another important environmental pollutant, which until 1965 was widely used as a pesticide. The US EPA classified HCB as a probable human carcinogen (Group B2). A consistent downward trend in the environmental HCB levels has been noted over the past 25–30 years. However, this chemical is still widely distributed in the environment. As for many other environmental pollutants, exposure to HCB for the general population occurs primarily from eating low levels of this compound in contaminated food. In 2000, we initiated in Catalonia (Spain) a wide surveillance program focused on measuring the levels of a number of chemical contaminants (including PCBs and HCB) in various groups of foodstuffs. Dietary intake of all pollutants was also estimated for various age and sex groups of the population of Catalonia using deterministic and probabilistic methods[1-9]. In order to establish the temporal trend in the total dietary intake of PCBs and HCB, food items belonging to the same groups assessed in the 2000 survey were again collected and analyzed in 2006 and 2008. We here present the concentrations of PCBs and HCB in a number of foodstuffs corresponding to the last (2008) survey, as well as data on human exposure through the diet of these chemical contaminants.

Materials and methods

Details on the foodstuffs included in the study and the sampling process are given in a companion paper[10]. Samples from 12 different food groups were purchased in local markets, small stores, supermarkets, and big grocery stores of 12 important cities of Catalonia during November-December 2008. 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.

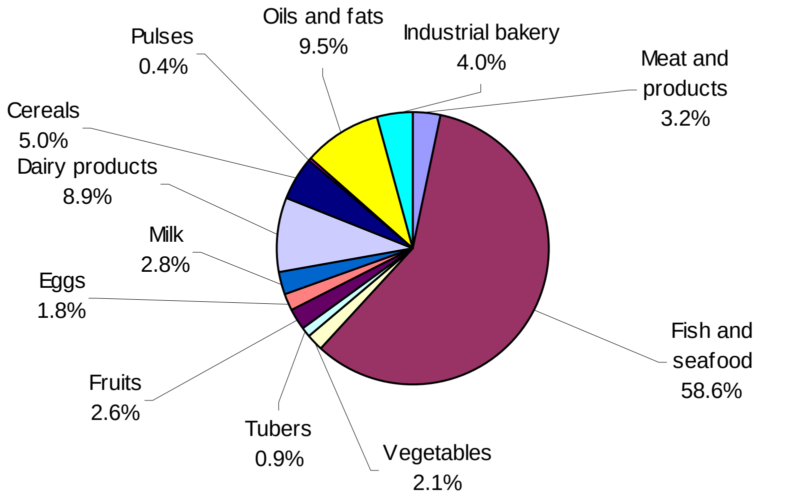
The concentrations of PCBs were determined according to the US EPA Method 1668 and JIS K 0311, while those of HCB were determined by the US EPA procedure 1625 (semivolatile organic compounds by isotope dilution gas chromatography) and the California Environmental Protection Agency Air Resources Board method 429 (1997). For PCBs and HCB determinations, C13-labeled extraction standards were added to the homogenised samples aiming to control the sample preparation process. Samples were extracted using hexane-acetone and then concentrated to determine pollutant concentrations. A multi-step sample clean-up was carried out to remove the sample matrix, as well as potential interfering compounds. The final extracts of the clean-up were injected and analysed on an Agilent 6890 capillary Gas Chromatograph equipped with a DB5-MS capillary column and coupled to a Waters Autospec Ultima High Resolution Mass Spectrometer. Measurements were done by selecting ion recording at a resolution of 10,000, two selected ions per congener group for native species and labelled components. For HCB, the detection limit (LOD) was 5 ng/kg. Toxic equivalents (TEQ) of the analysed PCBs were calculated using the WHO-toxic equivalency factors (WHO-TEF) for dioxin-like (DL) compounds. Consumption data by the general population of Catalonia of the analyzed foodstuffs were used for calculations. 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. Total dietary intake of PCBs and HCB for each food group was calculated by summing the results of multiplying the respective PCB congener or HCB 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. Results were evaluated using the statistical software SPSS 17.0. Given the non-parametric distribution of the samples, the Kruskal–Wallis or the Mann Whitney U-test were used to assess the significance of differences between food groups or age, respectively. 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.

Table 1. Estimated dietary intake of PCBs by a standard male adult living in Catalonia (Spain) and temporal variation based on data from previous surveys

	2000	**2006**	**Current study**	**% Variation 2000-current**	**% Variation 2006-current**
	pg WHO-TEQ/day				
Meat and meat products	8.85	2.24	0.84	-90.5	-62.7
Fish and seafood	82.87	38.77	15.18	-81.7	-60.8
Vegetables	1.07	0.70	0.55	-48.4	-21.2
Tubers	0.83	0.45	0.24	-70.7	-46.0
Fruits	2.10	0.79	0.68	-67.4	-13.3
Eggs	0.84	0.55	0.48	-43.3	-13.5
Milk	1.78	1.72	0.72	-59.6	-58.1
Dairy products	29.38	1.24	2.30	-92.2	85.2
Cereals	11.36	2.27	1.30	-88.6	-42.9
Pulses	0.37	0.22	0.10	-72.3	-53.4
Oils and fats	10.67	2.48	2.46	-76.9	-0.7
Industrial bakery	-	0.98	1.05		6.9
Total intake	**150.10**	**52.40**	**25.90**	**-82.7**	**-50.58**

Table 2. Estimated dietary intake of HCB by a standard male adult living in Catalonia (Spain) and comparison with results from previous surveys

	Daily consumption (g)		**HCB intake (ng/day)**		
	2000	**2006-current**	**2000**	**2006**	**Current study**
Meat and meat products	185 (12.8)	172 (14.0)	31.98	12.83	8.72
Fish and seafood	92 (6.4)	65 (5.5)	23.59	14.70	3.40
Vegetables	226 (15.7)	160 (13.0)	1.31	0.94	0.67
Tubers	74 (5.1)	73 (5.9)	0.10	0.56	0.54
Fruits	239 (16.6)	194 (15.8)	0.17	1.05	0.19
Eggs	34 (2.4)	31 (2.5)	6.26	5.47	1.18
Milk	217 (15.0)	128 (10.5)	2.80	7.57	1.64
Dairy products	106 (7.3)	76 (6.2)	92.15	8.74	6.69
Cereals	206 (14.3)	224 (18.3)	2.19	10.17	1.56
Pulses	24 (1.7)	30 (2.5)	0.01	0.42	0.05
Oils and fats	41 (2.8)	27 (2.2)	5.61	4.50	5.56
Industrial bakery	-	45 (3.7)	-	4.68	1.06
Total	**1,444 (100)**	**1,228 (100)**	**166.17**	**71.63**	**31.26**



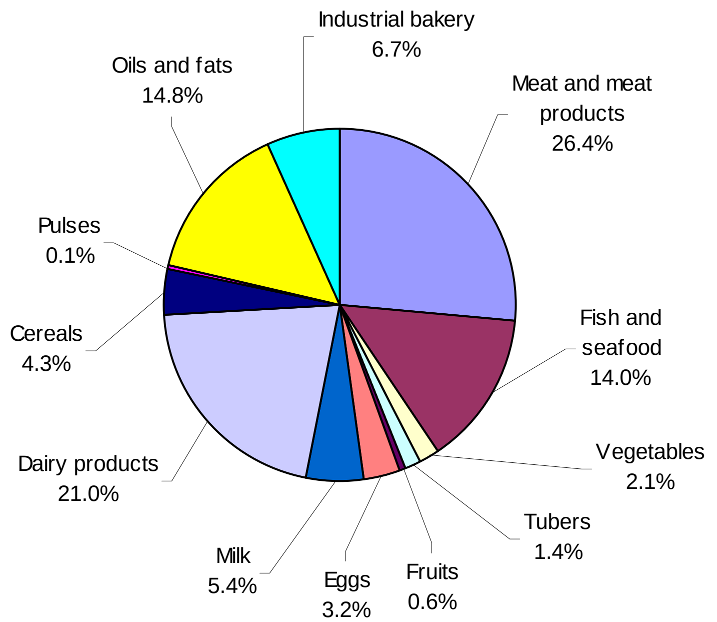


Figure 1. Contribution (%) of each food group to the total dietary intake of DL-PCBs (top) and HCB (bottom). Calculations were made for a standard male adult of 70 kg body weight

The estimated daily intakes of PCBs (pg WHO-TEQ per kg body weight) and HCB (ng) by a standard male adult of 70 kg living in Catalonia are summarized in Tables 1 and 2, respectively. As in our previous surveys[4,5,11,12], the highest intake of both, PCBs and HCB, corresponded to children (4-9 years old). However, while for PCBs, the senior groups (> 65 years) showed high levels than the groups of teenagers and adults, for HCB there was a rather decreasing tendency corresponding with increasing age. The probabilistic assessment for the whole population, not including children, showed a mean daily intake for DL-PCBs of 0.49 pg WHO-TEQ/kg bw (34.4 pg WHO-TEQ), being the 95 and 99 percentiles 0.91 and 1.23 pg WHO-TEQ/kg bw (66.7 and 94.4 pg WHO-TEQ), respectively. The daily intakes of HCB were 0.65 ng/kg bw (45.3 ng) and the 95 and 99 percentiles were 1.08 and 1.42 ng (81.2 and 109 ng), respectively.

Figure 1 depicts the percentages of contribution of each food group to the dietary intakes of PCBs and HCB for a standard male adult of 70 kg body weight. As it can be seen, the highest PCB exposure corresponded to fish and seafood (58.6%), followed by dairy products (8.9%). For HCB, the highest contribution corresponded to meat and meat products (26.4%) followed by dairy products (21.0%). The lowest percentages of contribution to the total dietary intake of PCBs and HCB, respectively, corresponded to: pulses (0.4 and 0.1%), fruits (2.6 and 0.6%) and vegetables (2.1 and 2.1%). However, the differences 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 survey, it was not possible to specifically evaluate the notable differences observed in the intakes of DL-PCBs and HCB.

In summary, the results of the present study show an important decreasing trend in the dietary exposure to PCBs for the population living in Catalonia, which has been also noted for other similar pollutants such as PCDD/Fs[10]. It should be due to the general decreasing trend in the atmospheric PCDD/F and PCB levels, which has been reported for a number of countries in recent years. Similarly, the decrease observed in the intake of HCB by the population of Catalonia is very important, having been reduced since 166 ng/day from the samples collected in 2000[5] to the current 31 ng/day.

Acknowledgements

This study was supported by the Catalan Food Safety Agency (ACSA), Department of Health, Generalitat de Catalunya, Barcelona, Catalonia, Spain.

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