

LEVELS OF PCDD/PCDFS IN FOOD SAMPLES FROM CATALONIA, SPAIN

Ana Bocio¹, Juan M. Llobet¹, Jose L. Domingo¹, Conrad Casas², Angel Teixidó² and Lutz Müller³

¹Laboratory of Toxicology and Environmental Health, School of Medicine, "Rovira i Virgili" University, San Lorenzo 21, 43201 Reus, Spain

²Department of Health and Social Security, Generalitat de Catalunya, 08028 Barcelona, Spain

³Department of Analytical Laboratory, MPU GmbH, 10829 Berlin, Germany

Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) are a lipophilic group of organic compounds, which are ubiquitous environmental pollutants¹. Due to the notable toxic properties of PCDD/PCDF^{2,3}, human exposure to these contaminants raises a great public concern. Because of their persistence in the environment, PCDD/PCDFs are found at every level of the food chain. Therefore, although exposure to these pollutants can occur by various routes, food is the primary source. A number of studies have reported that > 90-95% of PCDD/PCDF exposure is from food⁴, with fish, shellfish and fat-containing animal products being the major food sources of PCDD/PCDFs^{5,6}. Recent episodes such as the Belgian dioxin and PCB contamination of feeding stuff in 1999⁷, or the incident of the citrus pulp pellets in 1998⁸, show that PCDD/PCDF can still mean important risks of accidental contamination of the food chain.

In 1996, food samples were obtained from local markets and supermarkets of Tarragona Province (Catalonia, Spain) and the concentrations of PCDD/PCDFs were determined⁹. Recently, the European Commission has proposed maximum limits, target levels and action limits for PCDD/PCDFs in food and feed, in order to establish protective measures in public health at the level of the food and feed chain¹⁰. The aim of the present study has been to determine the current concentrations of PCDD/PCDFs in food samples collected in various areas of Catalonia, and to compare the results with those of our previous survey⁹ and with the maximum limits proposed by the European Commission.

Methods and Materials

In June-August 2000, food samples were randomly acquired in local markets, big supermarkets, and grocery stores from seven different cities of Catalonia with populations between 150,000 and 1,800,000 inhabitants. A total of 108 samples were analyzed. For collection of food samples, two groups were made up. The first group included meats of beef (steak, hamburger), pork (loin, sausage), chicken (breast) and lamb (steak); fish (hake, sardine) and shellfish (mussel); vegetables (lettuce, tomato, potato, green beans, cauliflower); fresh fruits (apple, orange, pear), and eggs. The second group included cow milk (whole, semiskimmed) and dairy products (yogurt, cheese); cereals (bread, pasta, rice); pulses (lentils, beans); fats (margarine) and oils (olive, sunflower); tinned fish (tuna, sardine), and meat products (ham, hot dogs, salami). Because most products in the first group are usually retailed, their origins could be very diversified in the different cities. Therefore, in that group 4 composite samples were analyzed for each food item. Each composite was made up by 10 individual samples. In contrast, most food items included in the second group corresponded to brands/trademarks that could be acquired in many places. Consequently, in this group only 2 composite samples were analyzed for each food item. Each composite was made up by 8 individual samples.

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Food analyses were performed in series of 5 samples and 1 blank. Analytical methods, including preparation of samples for analysis and clean-up, were described previously⁹ and are not repeated in detail here. Measurement and quantification were performed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), model Fisons 8000 GC coupled with a VG Autospec Ultim system (EI and multiple ion determination mode resolution 10000). Quantitative determinations were carried out using internal standards. For TEQ calculations the WHO-98 toxicity equivalent factors (TEF) were used. It was assumed that non-detected isomer concentrations would be equal to the respective limit of detection (ND = LOD).

Results and discussion

Table 1 shows the concentrations of PCDD/PCDFs in eight groups of food samples. Results are presented for each of the 17 most toxic congeners. The sum for PCDDs and PCDFs, the ratio sum PCDD/sum PCDF, as well as the WHO-TEQ for each food group are also shown. Values are given in ng/kg wet weight. TCDD, the most toxic congener, was not detected in pulses, cereals and fruits. By contrast, fats and oils showed the greatest level (0.054 ng TCDD/kg wet weight) of this congener, followed by eggs (0.021 ng/kg wet weight) and fish and shellfish (0.017 ng/kg wet weight). OCDD was the predominant congener in all food groups. The highest OCDD values corresponded to meats (2.249 ng/kg wet weight), eggs (1.819 ng/kg wet weight) and fats and oils (1.673 ng/kg wet weight). Notwithstanding, 1,2,3,7,8-PeCDD and 1,2,3,7,8,9-HxCDD were only detected in fish and shellfish, meats, eggs, and milk and dairy products. Fruits, followed by pulses and cereals, were the food groups in which more congeners were under their respective detection limits. The greatest sumPCDD/sumPCDF ratio corresponded to eggs (6.536), meats (2.755), fats and oils (1.697), and edible vegetables (1.112), while in the remaining groups the ratios were < 1. Fish and shellfish showed the highest WHO-TEQ concentration, 0.321 ng/kg wet weight, followed by fats and oils (0.303 ng/kg wet weight) and milk and dairy products (0.124 ng/kg wet weight).

The concentrations of PCDD/PCDF (WHO-TEQ values) in a number of food groups collected in Catalonia are summarized in Table 2. Data are given in both ng/kg fat and pg/kg wet weight. Based on the PCDD/PCDF levels expressed in pg WHO-TEQ/kg wet weight, blue fish (656.3) reached the highest WHO/TEQ values, followed by margarine (351.5), shellfish (303.1), oil (278.9), tinned fish (265.8), and dairy products (234.9). However, when the results were expressed in ng WHO-TEQ/kg fat the greatest value corresponded to shellfish (10.82). Table 2 also shows maximum limits and action levels proposed by the European Commission. In relation to it, only chicken and chicken products reached concentrations (1.56 ng WHO-TEQ/kg fat) over the proposed action levels, while the remaining food items were under these levels.

In general terms and in comparison with our previous survey⁹, a substantial decrease in the concentrations of PCDD/PCDFs has been noted for most food items analyzed. It agrees well with the continued reduction in the environmental PCDD/PCDF levels found in most surveys carried out in recent years¹¹⁻¹⁴. According to this, additional important decreases in the current PCDD/PCDF values in foods are still expected in future surveys.

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Table 1. PCDD/PCDF concentrations in food samples from Catalonia, Spain^a

Congener	<i>Vegetables</i> (n=20)	<i>Pulses and cereals</i> (n=12)	<i>Fruits</i> (n=12)	<i>Fish and shellfish</i> (n=16)	<i>Meats</i> (n=30)	<i>Eggs</i> (n=4)	<i>Milk and dairy products</i> (n=8)	<i>Fats and oils</i> (n=6)
2378-TCDD	0.002	<0.013	<0.003	0.017	0.008	0.021	0.011	0.054
12378-PeCDD	<0.004	<0.024	<0.006	0.034	0.016	0.016	0.027	<0.100
123478-HxCDD	0.004	<0.027	<0.006	0.015	0.020	0.018	0.021	<0.107
123678-HxCDD	0.004	<0.027	<0.006	0.036	0.037	0.042	0.048	<0.107
123789-HxCDD	<0.004	<0.027	<0.006	0.018	0.017	0.015	0.020	<0.107
1234678-HpCDD	0.016	0.049	0.007	0.160	0.387	0.409	0.122	0.256
OCDD	0.071	0.203	0.024	0.844	2.249	1.819	0.418	1.673
2378-TCDF	0.008	0.042	0.005	0.402	0.039	0.043	0.069	0.092
12378-PeCDF	0.003	0.024	0.003	0.148	0.023	0.017	0.036	0.056
23478-PeCDF	0.003	0.019	0.003	0.254	0.022	0.020	0.071	0.055
123478-HxCDF	0.010	0.061	0.012	0.634	0.152	0.027	0.147	0.246
123678-HxCDF	0.005	0.031	<0.006	0.097	0.039	0.012	0.065	0.139
123789-HxCDF	<0.004	<0.027	<0.006	0.028	0.019	<0.009	0.022	<0.107
234678-HxCDF	0.008	0.040	0.009	0.082	0.049	0.025	0.075	0.233
1234678-HpCDF	0.013	0.051	0.008	0.198	0.121	0.031	0.156	0.182
1234789-HpCDF	0.004	0.027	<0.006	0.057	0.032	0.012	0.046	<0.107
OCDF	0.021	0.092	0.018	0.334	0.207	0.045	0.206	0.321
Sum PCDD	0.137	0.462	0.035	1.668	2.905	2.674	0.943	2.588
Sum PCDF	0.123	0.538	0.061	4.850	1.054	0.409	1.896	1.525
SumPCDD/ sumPCDF	1.112	0.858	0.561	0.344	2.755	6.536	0.498	1.697
VHO-TEQ	0.012	0.078	0.016	0.321	0.080	0.071	0.124	0.303

^aResults are given in ng/kg wet weight; n=number of samples analyzed; ND=LOD.

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Table 2. Concentrations of PCDD/PCDF in a number of foodstuffs acquired in various locations of Catalonia, Spain

Food Group	ng WHO-TEQ/kg fat	pg WHO-TEQ/kg wet weight	Maximum limits ^a	Action levels ^a
Vegetables	4.98	12.3	—	0.4*
Pulses	1.44	22.9	—	0.4*
Cereals	8.52	105.6	—	0.4*
Fruits	9.56	15.7	—	0.4*
White fish	6.41	115.4	4*	3*
Shellfish	10.82	303.1	4*	3*
Tinned fish	2.17	265.8	4*	3*
Blue fish	6.98	656.3	4*	3*
Pork and pork products	0.39	89.9	1	0.6
Chicken and chicken products	1.56	63.8	2	1.5
Beef and beef products	0.52	72.9	3	2
Lamb	0.49	57.9	3	2
Eggs	0.59	71.5	3	2
Dairy products	1.33	234.9	3	2
Whole milk	0.44	16.7	3	2
Semiskimmed milk	0.70	11.3	3	2
Oil	0.28	278.9	0.75	0.5
Margarine	0.43	351.5	0.75	0.5

^aValues are given in pg WHO-TEQ/g fat. Those marked with an asterisk are expressed in pg WHO-TEQ/g wet weight.

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