DIETARY INTAKE OF PCDD/Fs BY THE POPULATION LIVING IN THE VICINITY OF A HAZARDOUS WASTE INCINERATOR IN CATALONIA, SPAIN

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Abstract
The levels of PCDD/Fs were measured in a number of foodstuffs randomly acquired in various locations from Tarragona County (Catalonia, Spain) near a hazardous waste incinerator (HWI). A total of 36 "composite" samples belonging to 11 different food groups were analyzed. The dietary intake of PCDD/Fs by the population living near the HWI was subsequently determined. The current PCDD/F intake through the diet (27.8 pg WHO-TEQ/day) was considerably lower than that found in the baseline survey performed in 1996-1998 (210 pg I-TEQ/day), and also notably lower than that found in a previous (2002) survey (63.8 pg WHO-TEQ/day). Eggs was the only food group whose contribution to total WHO-TEQ increased, decreasing that of the remaining ten groups.

Introduction
Incineration has been demonstrated to be a commercially available technology for hazardous waste disposal. In 1999, the first and to date the only HWI in Spain, began to operate in Constantí (Tarragona County). Because of the potential health risks of the emissions of the HWI, especially PCDD/Fs, previously, and during the period of construction of the facility, there was a notable concern among the population living in the area. Therefore, the regional/local authorities decided to perform a wide preoperational environmental and biological monitoring program for metals and PCDD/Fs. This program included measurements of the baseline levels of metals and PCDD/Fs in soil and herbage samples, as well as the baseline concentrations of blood, breast milk and adipose tissue of subjects living near the new facility. The surveillance program has continued without interruption since 1999. Every year various measurements have been performed.[1]

For non-occupationally exposed subjects, dietary intake is the main path of exposure to PCDD/Fs. Consequently, the assessment of the intake of PCDD/Fs through the diet was also included in the monitoring program. The update of PCDD/F intake from food is essential to establish clearly whether any potential increase in the PCDD/F levels in biological tissues of individuals living in the vicinity of the facility might be due to the emissions of PCDD/Fs by the HWI, or due to increases of PCDD/F levels in foodstuffs. During the construction of the facility (1996-1998), a baseline food survey was also performed, followed by a second survey in 2002.[2,3] We here present the results of the third survey concerning PCDD/F levels in a number of foodstuffs, as well as the dietary intake of these pollutants by the population living near the HWI. A comparison of the dietary intake of PCDD/Fs with those corresponding to the previous studies (baseline: 1999, and 2002) is also presented.

Materials and Methods
Sampling. In July 2006, food samples were randomly acquired in local markets, large supermarkets, and grocery stores from various locations of Tarragona County. Most of them were not local products and might be potentially of any origin. A total of 36 "composite" samples formed by subsamples were analyzed. The following food items were included: beef (steak, hamburger), pork (sausage, hot dogs, steak, hamburger, ham), chicken (breast, thighs, sausage), lamb (steak), white fish (hake, whiting blue, sea bass, monkfish), seafood (mussel, shrimp), tinned fish (tuna, sardine, mussel), blue fish (salmon, sardine, tuna), milk (whole, semiskimmed), dairy products (light fresh cheese, early cheese, seminature cheese, yogurt, "petit-Swiss", cream caramel, custard), vegetables (lettuce, tomato, green bean, spinach), pulses (lentils, beans, chick-peas), cereals (rice, spaghettis, bread), fruits (apple, orange, pear, banana), oils and fat (olive oil, sunflower oil, corn oil, margarine), and eggs . For the preparation of the composite samples, the quantity of each food in each subsample was added according to the dietary habits of the population of the area under evaluation.[3] Ten individual samples of each food were collected in 10 different markets and stores. Each sample was part of a composite of its respective kind of food, in a representative percentage of the consumption by the population of the area. Two composites of each food were made and analyzed for PCDD/Fs.

Analytical Methods and Instrumentation. Food samples were homogenized and lyophilized. Analyses of PCDD/Fs were performed according to the German VDI 3499 and US EPA 1925 methods. Measurement and quantification of PCDD/Fs were performed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), Model Fisons CE 8000 GC coupled with a VG Autospec Ultim system (EI and multiple ion determination mode resolution >10000). More details about extraction, clean-up, quality control, etc. were previously reported.[3, 4]

PCDD/F intake. Toxic equivalents (TEQ) were calculated using the toxicity equivalent factors established by the WHO in 1998 (WHO-TEF). Estimates of average daily food intake were obtained from a nutritional study carried out in the same area in a healthy population aged 2-80 years old. A total of 1358 individuals participated in that survey, which was performed during 3 days with the 24-h recall method. For calculation of PCDD/F intake, if the concentrations were under the limit of detection (LOD), the value was assumed to be one-half of the respective LOD (ND= ½ LOD).

Results and Discussion

Table 1 summarizes the concentrations of PCDD/Fs in the 11 groups of analyzed foodstuffs. Results are presented for each of the 17 most toxic congeners for the 2002 and for the current survey. The WHO-TEQ values for each group of food samples are also shown for both surveys. It can be seen that with the exception of pulses for which the WHO-TEQ values were rather similar in both studies, there were important decreases in the current PCDD/F levels compared with the previous (2002) ones. In 2002, the highest WHO-TEQ values corresponded to fish (0.270 ng/kg fresh weight), oils and fats (0.238 ng/kg fat weight), seafood (0.123 ng/kg fresh weight), and dairy products (0.083 ng/kg fresh weight), whereas the lowest WHO-TEQ values corresponded to vegetables and fruits: 0.006 and 0.008 ng/kg fresh weight, respectively. In the current survey, the order was the following: oils and fats (0.147 ng/kg fat weight), eggs (0.134 ng/kg fresh weight), fish (0.086 ng/kg fresh weight), and seafood (0.069 ng/kg fresh weight). Again, the lowest WHO-TEQ values corresponded to vegetables and fruits: 0.004 and 0.003 ng/kg fresh weight, respectively.

In oils and fats, the current group showing the highest WHO-TEQ, the greatest PCDD/F concentrations corresponded to the congener OCDF followed by OCDD, whereas 2,3,7,8.-TCDD was under the respective detection limit. In the 2002 survey, the main contributors to WHO-TEQ were also OCDD and OCDF, but the order was OCDD > OCDF. With respect to eggs, which were currently the second group in terms of WHO-TEQ, the highest contributors were again OCDF and OCDD. The increase in the concentrations of various PCDD/F congeners found in eggs is possibly one of the most striking findings of the present survey.

The estimated dietary intake of PCDD/Fs for individuals of the general population living near the HWI from Constantí (Catalonia, Spain) is given in Table 2. Data corresponding to the 2002 survey are also given. The current intake was estimated to be 27.81 pg WHO-TEQ/day. The most remarkable contribution to total WHO-TEQ intake corresponded to fish and seafood (7.91 pg WHO-TEQ/day), followed by oils and fats (6.01), dairy products (3.02), and eggs (4.59). In comparison with the 2002 survey (63.80 pg WHO-TEQ/day), a very notable reduction was noted. In percentage terms, the reduction meant a 43.6% of the 2002 value. The most important decreases were observed in fish and seafood, with a considerable reduction from 21.50 to 7.91 pg WHO-TEQ/day. Very important were also the reductions in cereals (9.20 vs. 1.42), and milk (4.10 vs. 0.62) and dairy products (8.80 vs. 3.02). In contrast, there was a notable increase in the contribution of eggs (1.30 vs. 4.59) to the total WHO-TEQ, which is not easy of explaining taking into account that the average consumption has been basically the same. The percentages of contribution from each food group to the total dietary intake (pg WHO-TEQ/day) of PCDD/Fs by the population of Constantí living near the HWI are depicted in Fig.1. It can be seen that fish and seafood (28%), oils and fats (22%), and eggs (17%) were the main contributors to that intake, whereas the lowest contribution corresponded to pulses (1%), milk (2%), and vegetables and fruits (3% each), respectively.

Table 1. PCDD/PCDF concentrations in food samples collected in different locations from Tarragona County (Catalonia, Spain) near to the HWI[a]

Congener	Vegetables (n=2)		Pulses (n=2)		Cereals (n=2)		Fruits (n=2)		Fish (n=6)		Seafood (n=2)		Meat (n=7)		Eggs (n=2)		Milk (n=4)		Dairy products (n=2)		Oil and fats (n=4)	
	2002	2006	2002	2006	2002	2006	2002	2006	2002	2006	2002	2006	2002	2006	2002	2006	2002	2006	2002	2006	2002	2006
2378-TCDD	< 0.001	< 0.001	< 0.005	0.003	< 0.019	< 0.003	< 0.004	< 0.001	0.015	0.014	0.008	0.005	< 0.006	0.002	< 0.005	0.022	< 0.002	0.0003	< 0.007	< 0.002	< 0.050	< 0.039
12378-PeCDD	< 0.001	0.001	< 0.005	0.006	< 0.019	< 0.003	0.004	< 0.001	0.036	0.020	0.019	0.014	< 0.006	0.002	< 0.005	0.076	0.002	0.001	0.010	0.008	< 0.100	0.046
123478-HxCDD	< 0.003	0.001	< 0.011	< 0.004	< 0.038	< 0.003	< 0.007	0.001	0.014	0.008	0.008	0.014	0.009	0.002	0.008	0.016	< 0.004	0.0004	< 0.015	0.005	< 0.100	0.049
123678-HxCDD	< 0.003	0.001	< 0.011	< 0.004	< 0.038	< 0.003	< 0.007	< 0.001	0.030	0.026	0.034	0.020	0.027	0.007	0.015	0.017	0.010	0.001	0.029	0.010	< 0.100	0.026
123789-HxCDD	< 0.003	< 0.001	< 0.011	0.003	< 0.038	0.003	< 0.007	< 0.001	0.011	0.014	0.013	0.017	< 0.012	0.003	< 0.009	0.016	0.005	0.001	< 0.015	0.006	< 0.100	< 0.039
1234678-HpCDD	0.011	0.006	0.013	< 0.019	0.034	0.013	0.010	< 0.006	0.155	0.077	0.166	0.100	0.143	0.038	0.070	0.025	0.031	0.002	0.131	0.031	0.343	< 0.193
OCDD	0.062	0.023	0.187	< 0.074	0.501	< 0.066	0.062	< 0.022	1.061	0.218	1.673	0.645	0.635	0.119	0.305	0.140	0.131	< 0.010	0.431	0.066	2.209	1.465
2378-TCDF	0.005	0.003	< 0.005	< 0.008	< 0.019	< 0.007	0.004	0.002	0.276	0.221	0.360	0.120	0.009	0.009	0.033	0.020	0.007	0.001	0.027	0.007	0.088	0.046
12378-PeCDF	0.004	0.001	< 0.005	< 0.004	< 0.019	0.003	< 0.004	0.002	0.135	0.070	0.050	0.033	0.014	0.004	0.023	0.023	0.008	0.001	0.038	0.004	0.165	0.056
23478-PeCDF	0.004	0.002	< 0.005	0.004	0.016	< 0.003	< 0.004	0.001	0.269	0.061	0.081	0.036	0.017	0.004	0.024	0.027	0.017	0.001	0.078	0.023	0.120	0.047
123478-HxCDF	0.006	0.003	< 0.011	0.009	< 0.038	0.006	0.006	0.003	0.236	0.054	0.039	0.022	0.027	0.012	0.050	0.031	0.021	0.003	0.102	0.021	0.236	0.185
123678-HxCDF	0.004	0.002	< 0.011	0.003	< 0.038	< 0.003	< 0.007	0.001	0.098	0.026	0.011	0.018	0.016	0.007	0.026	0.071	0.010	0.002	0.043	0.016	0.133	0.073
123789-HxCDF	< 0.003	< 0.001	< 0.011	< 0.004	< 0.038	< 0.003	< 0.007	0.001	< 0.010	0.004	< 0.007	0.006	< 0.012	< 0.002	0.008	0.024	< 0.004	< 0.0005	0.015	0.002	< 0.100	< 0.039
234678-HxCDF	0.003	< 0.001	< 0.011	0.004	0.035	< 0.003	0.007	< 0.001	0.066	0.029	0.038	0.010	0.021	0.002	0.036	0.018	0.011	0.001	0.037	0.006	0.207	0.027
1234678-HpCDF	0.010	0.014	0.014	0.043	0.042	0.036	0.007	0.015	0.279	0.081	0.048	0.090	0.067	0.050	0.052	0.054	0.020	0.015	0.079	0.052	0.312	0.725
1234789-HpCDF	0.003	< 0.005	0.011	< 0.019	0.038	< 0.017	< 0.007	< 0.006	0.046	0.019	< 0.007	< 0.029	0.010	0.007	0.010	0.018	< 0.004	0.003	< 0.015	< 0.012	< 0.200	0.121
OCDF	0.031	0.104	0.062	0.325	0.137	0.270	0.020	0.104	0.123	0.315	0.138	0.500	0.089	0.294	0.058	0.325	0.020	0.100	0.084	0.320	0.600	5.125
WHO-TEQ	**0.006**	**0.004**	**0.011**	**0.015**	**0.045**	**0.007**	**0.008**	**0.003**	**0.270**	**0.086**	**0.123**	**0.069**	**0.030**	**0.012**	**0.037**	**0.134**	**0.019**	**0.003**	**0.083**	**0.029**	**0.238**	**0.147**

[a]Results are given in ng/kg fresh weight excepting oils and fats are given in ng/kg fat; *n* , number of analyzed samples.

Table 2. Estimated daily intake of PCDD/PCDF by the general population living near a hazardous waste incinerator in Tarragona County, Catalonia (Spain)

Food group	Consumption rate[a](g)	pg WHO-TEQ/day	
	2002 and 2006	2002	2006
Vegetables	226 (15.7)	1,40	0,86
Pulses	24 (1.7)	0,30	0,36
Cereals	206 (14.3)	9,20	1,42
Fruits	239 (16.6)	2,00	0,75
Fish and seafood	92 (6.4)	21,50	7,91
Meat and meat products	185 (12.8)	5,60	2,26
Eggs	34 (2.4)	1,30	4,59
Milk	217 (15.0)	4,10	0,62
Dairy Products	106 (7.3)	8,80	3,02
Oils and fats	41 (2.8)	9,70	6,01
Total intake	**1370 (100)**	**63,80**	**27,81**

[a]In parentheses: percentage of the total consumption.

The estimated dietary intake of PCDD/Fs according to the different sex and age groups of the population living near the HWI is depicted in Fig. 2. Intake is given in pg WHO-TEQ/kg body weight/day. Boys and girls aged 4-9 years, reached the highest intake of these pollutants, showing a considerable difference with the remaining age groups, which in general terms were rather similar. Moreover, sex differences were not especially relevant in any age groups (Fig. 2). For human consumption**,** the tolerable daily intake (TDI) for PCDD/Fs plus dioxin-like-PCBs was established in the range 1-4 pg WHO-TEQ/kg body weight/day and in 70 pg WHO-TEQ/kg body weight/month by the WHO by the Joint FAO/WHO Expert Committee on Food Additives (JECFA), respectively, for non-carcinogenic effects. The present results show that this TDI was not exceeded for any age or sex group.

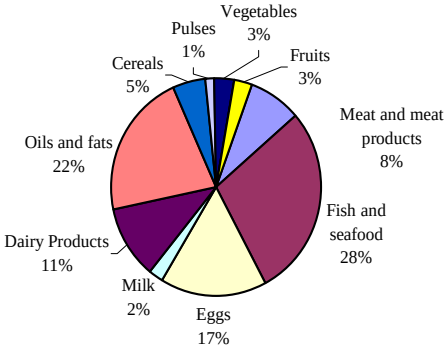

Fig 1. Percentatges of contribution from each food group to the total daily intake (pg WHO-TEQ/day) of PCDD/PCDFs by the population of Tarragona County (Catalonia, Spain).

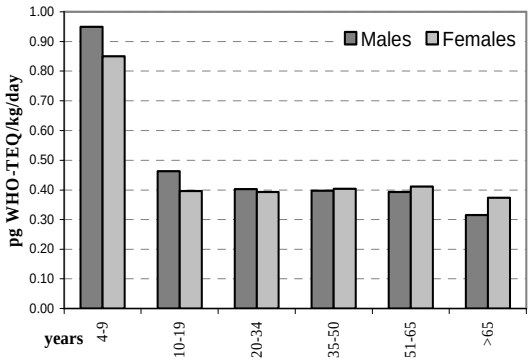

Fig. 2. Estimated daily intake (pg WHO-TEQ/kg body weight/day) of PCDD/PCDFs by the general population of Tarragona County (Catalonia, Spain) according to sex and age.

During the period of construction of the HWI (1996-1998), a baseline survey concerning the dietary intake of PCDD/Fs was carried out in the area under potential influence of the emissions of the facility. Total dietary intake by the population of that area was estimated to be 210 pg I-TEQ/day, which is considerably higher than the current one (27.8 pg WHO-TEQ/day), and than that of the previous (2002) survey (59.6 pg I-TEQ/day or 63.8 pg WHO-TEQ/day).[2,3] These results agree quite well with recent data concerning the levels of PCDD/Fs in blood samples of the workers of the HWI. The mean baseline concentration of PCDD/Fs in blood of the HWI workers was 26.7 ng I-TEQ/kg lipid, being the current one (2006 survey) 2.9 ng I-TEQ/kg (unpublished data); that is to say, a relationship of 9.2 vs. approximately 7.6 in the dietary intake of PCDD/Fs.[5] This is an important finding, as clearly indicates that dietary intake of PCDD/Fs is much more important than the potential occupational exposure to PCDD/Fs for the HWI workers. The notable decrease in the atmospheric levels of PCDD/Fs over the world, would explain the notable differences between the results in the dietary intake of this pollutants in the baseline, 2002, and 2007 surveys.

In conclusion, the continued decrease found in the dietary intake of PCDD/Fs which has been noted in the present investigation is quite in agreement with the results of other recent studies also performed in Catalonia.[6, 7]

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