DIETARY INTAKE OF POLYCHLORINATED NAPHTHALENES (PCNs) AND POLYCHLORINATED DIPHENYL ETHERS (PCDEs) IN CATALONIA, SPAIN

Llobet Juan M.[1], Martí-Cid Roser[2] and Domingo José L.[2]

[1]GRET-CERETOX, School of Pharmacy, University of Barcelona, Avgda. Diagonal, 08028 Barcelona, Spain; [2]Laboratory of Toxicology and Environmental Health, School of Medicine, "Rovira i Virgili" University, San Lorenzo 21, 43201 Reus, Spain

Introduction

Polychlorinated naphthalenes (PCNs) are chemicals used in a variety of industrial products and commercial goods, such as cable insulation, wood preservatives, engine oil additives, electroplating masking compounds, and in dye production[1, 2]. Although production and use of PCNs were banned in the USA and Europe in the 1980s, they are still present in the environment due to their persistent, lipophilic, and bioaccumulative properties[1]. On the other hand, polychlorinated diphenyl ethers (PCDEs) are also a group of halogenated aromatic compounds that have been detected in a number of environmental samples[3, 4]. Their widespread occurrence in the environment is mainly the result of their presence as impurities in chlorophenol preparations[5-7]. In this study, the concentrations of PCNs and PCDEs were determined in samples of foodstuffs widely consumed by the population of Catalonia, Spain. The dietary intake of PCNs and PCDEs was also estimated for the population of this Spanish region. The results were compared with those of a previous survey performed during 2000.

Materials and methods

Sampling

In March-June 2006, food samples were randomly acquired in local markets, big supermarkets, and grocery stores from 12 representative cities of Catalonia. For collection of samples, 2 groups were made up. The first group included meat of beef (steak, hamburger), pork (loin, sausage), chicken (breast), and lamb (steak); vegetables and tubers (lettuce, tomato, cauliflower, string bean, potato); fruits (apple, orange, pear, banana), and eggs. Because in the first group, most products are usually retailed, their origins could be very diverse in the different cities. Therefore, in that group, for each food item 4 and 2 composite samples were analyzed for PCNs and PCDEs, respectively. The second group included cow milk (whole, semi-skimmed) and dairy products (yoghurt, cheese); cereals (French and sandwich bread, pasta, rice); pulses (lentil, haricot bean); oils (olive, sunflower) and fats (margarine, butter); meat products (boiled ham, hot dogs, salami), and bakery products (croissant, cookie, fairy cake).

Chemical analysis

PCNs and PCDEs were determined based on the US EPA method 1625 (semi volatile organic compounds by isotope dilution GC-MS) and CARB Method 429. The sample was extracted using hexane/acetone as solvents. The extract was then concentrated to determine the levels of PCNs and PCDEs. The cleaned extracts were analyzed by HRGC/HRMS using Agilent GCs (5890 and 6890) coupled to Waters Autospec Ultima HRMS systems with selected ion recording at resolution 10000. Depending on the specific samples, the limits of detection (LOD) ranged 0.8-2.1 ng/kg ww for PCNs, and between 0.2 and 0.4 ng/kg ww for PCDEs.

Dietary exposure estimates

Consumption data by the general population of Catalonia of the analyzed foodstuffs were taken from Serra-Majem et al.[8]. The results concerning to fish and seafood (sardine, tuna, anchovy, mackerel, swordfish, salmon, hake, red mullet, sole, cuttlefish, squid, clam, mussel and shrimp) were taken from a recent study[9, 10]. For each food group, total dietary PCN and PCDE intake was estimated by summing the results of multiplying the PCN and PCDE concentrations in each specific food item by the amount (proportionally established) consumed of that item. Total dietary intake of PCNs and PCDEs was obtained by summing the respective intakes from each food group. When a concentration was under the respective limit of detection (LOD), daily intakes were calculated

assuming the respective values would be equal to one-half of that LOD.

Results and discussion

Concentrations of PCNs

In our previous (2000) market basket study, the highest concentrations of ΣPCNs were found in oils and fats (447 ng/kg of wet weight), cereals (71 ng/kg ww), fish and seafood (39 ng/kg ww), and dairy products (36 ng/kg ww)[11]. In the present study, the highest mean level of ΣPCNs corresponded to fish and seafood (47 ng/kg ww), followed by oils and fats (22 ng/kg ww), dairy products (12 ng/kg ww), and bakery products (15 ng/kg of wet weight). This last group was not included in the 2000 study[11]. In both surveys, the lowest concentrations of ΣPCNs were observed in milk (0.4 ng/kg ww in 2000, and 0.8 ng/kg ww in the present study) and fruits (0.7 ng/kg ww in 2000, and 1.2 ng/kg ww in the current study). TetraCNs and pentaCNs were again the groups of homologues showing the greatest contribution to ΣPCNs, with the exception of fish and seafood, group where the highest contribution corresponded to pentaCNs. In both studies, the lowest contribution in most food groups corresponded to OCN.

Concentrations of PCDEs

In the 2000 survey, PCDEs could only be detected in the samples of fish and seafood[12]. In the present study, the highest ΣPCDEs corresponded also to this food group, with an average level of 1094.7 ng/kg of wet weight. In comparison to this notable level, the ΣPCDEs found in the remaining food groups were almost irrelevant, ranging between 0.4 ng/kg ww in fruits and 8.3 ng/kg ww in oils and fats. In the present survey, hexaCDEs and tetraCDEs were again the groups of homologues showing the highest and lowest contribution, respectively, to ΣPCDEs in the fish and seafood group.

Dietary exposure estimates

Data on food consumption and dietary intake of PCNs and PCDEs for a standard male adult of 70 kg body weight are shown in Table 1. The current total intake of PCNs was 7.25 ng/day (or 0.10 ng/kg body weight/day), while that of PCDEs was 51.68 ng/day (or 0.74 ng/kg body weight/day). In the 2000 study, total dietary intakes were 45.78 ng/day (or 0.65 ng/kg body weight/day) and 41.04 ng/day (or 0.59 ng/kg body weight/day) for PCNs and PCDEs, respectively. In both surveys, the daily intakes of PCNs and PCDEs were calculated assuming that ND=LOD/2. The very notable decrease observed in the current dietary intake of ΣPCNs with respect to the previous one is in part due to the reduction in the total consumption of the different foodstuffs included in both studies, which has decreased from 1444 g/day to the current 1228 g/day, a percentage of 15%. However, it is obvious that this can not be the only reason to explain the very important reduction in the daily intake of PCNs, which reached a value of 84%. Quantitatively, the greatest decreases corresponded to two groups: oils and fats (18.33 vs. 0.56 ng/day) and cereals (14.64 vs. 1.92 ng/day).

In contrast to PCNs, the dietary intake of PCDEs showed an increase between the 2000 and the current survey: 41.04 and 51.68 ng/day (or 0.59 and 0.74 ng/kg/body weight/day), respectively. As expected according to the 2000 results, this increase (26%) was mainly due to the contribution of the fish and seafood group. Although the consumption of marine species from this group by an adult male was currently 26% lower than in 2000, the contribution of this consumption to PCDE intake increased in 31% (38.43 vs. 50.24 ng/day). It is also important to remark that in the 2000 survey only three fresh marine species (sardine, hake and mussel) and two tinned species (sardine and tuna) were analyzed vs. the current 14 fresh marine species. On the other hand, the estimated intake of PCNs and PCDEs (ng/kg body weight/day) for the population of Catalonia according to age and gender is depicted in Figure 1. The highest PCN and PCDE intake corresponded to the group of children (boys > girls) between 4 and 9 years old. By contrast, the lowest PCN intake corresponded to females > 65 years old, whereas that of PCDEs was observed in males aged 10-19 years.

Data on PCNs in foodstuffs are currently very limited, an exception being fish and other seafood, as well as our recent data from Catalonia on food concentrations and dietary intake[1, 13]. Most of the existing information concerning the levels of organohalogenated pollutants in food has been mainly focused on PCDD/PCDFs and PCBs, while that concerning PCN is basically limited to a few marine species and sampling areas[12]. The dietary

intake of PCNs for a standard male adult (70 kg body weight) of Catalonia was 45.8 ng/day. Recently, Jiang et al.[14] determined the concentrations of organochlorine contaminants (PCDD/PCDFs, PCBs and PCNs) in common seafood in two Chinese coastal cities, and assessed the health risk due to the daily consumption of contaminated seafood belonging to five categories. Concentrations of PCNs in seafood were 10 to 1000-fold lower than total PCBs and ranged from 93.8 to 1300 ng/kg of lipid weight, while in fish PCN levels ranged between 137 and 545 ng/kg of lipid weight. Total intake of PCNs was 15.1 pg/kg body weight/day (∑PCNs, ND=0) or 19.6 pg/kg body weight/day (∑PCNs, ND=LOQ). In a survey on PCN levels in fishes from the Detroit River, Kannan et al.[15] found that the contribution of these pollutants to sum TEQs was similar or greater than that of coplanar PCBs, which suggested that in industrialized locations contribution of PCNs to TEQs might be greater enough to be of concern. However, in a recent study in mussels from the Qingdao coastal Sea (China), Pan et al.[16] reported that the total TEQs of PCNs were generally lower than that of PCBs.

In relation to PCDEs, to the best of our knowledge only our previous study[12] has determined quantitatively the levels of PCDEs in various food groups and evaluated the dietary intake of PCDEs by a general population. In that study, the concentrations of PCDEs were measured in a number of food groups. With the exception of the samples of fresh fish (hake and sardine), shellfish (mussels), and tinned fish (tuna and sardine), the concentrations of PCDEs in the other food groups were for all homologues (tetra- to octaCDE) under the respective detection limits[12]. In the present study, PCDEs (mainly tetraCDEs) could be also detected in other food groups. However, the most important contribution to PCDE intake corresponded again to fish and seafood, whilst the intake from the remaining groups was significantly lower.

The results of the present study show a very notable decrease in the dietary exposure to PCNs by the population of Catalonia, Spain, which was mainly due to the reductions in the contribution of cereals, and oils and fats to the total PCN intake. By contrast, exposure to PCDEs through the diet increased since our previous study[16] due to the increase observed in the fish and seafood group. Although it has been reported that since the toxicity point of view, PCNs and PCDEs can act as dioxin-like compounds, the current lack of well characterized TEFs for the different congeners of these compounds prevents the estimation of the TEQ of both pollutants. On the other hand, the lack of data from other regions or countries on the dietary intakes of PCNs and PCDEs prevents establishing whether the current intakes may be considered as “normal values”.

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

References
1. Falandysz J. *Food Addit Contam* 2003; 20: 995.
2. Noma Y., Yamamoto T. and Sakai S. I. *Environ Sci Technol* 2004; 38: 1675.
3. Koistinen J. Vol. 3, part K; *Paasivirta, J., (Ed.), Springer-Verlag*: Berlin, Germany, 2000.
4. Koistinen J., Kukkonen J. V., Sormunen A., Mannila E., Herve S. and Vartiainen T. *Chemosphere* 2007; 68: 1382.
5. de Boer J. and Denneman M. *Rev Environ Contam Toxicol* 1998; 157: 131.
6. Frankki S., Persson Y., Tysklind M. and Skyllberg U. *Environ Sci Technol* 2006; 40: 6668.
7. Hayward D. *Environ Res* 1998; 76: 1.
8. Serra-Majem L., Ribas L., Salvador G., Castells C., Serra J., Jover L., Treserras R., Farran A., Román B., Raidó B., Taberner J. L., Salleras L. and Ngo J. *Generalitat de Catalunya*, Barcelona, Spain, 2003.
9. Domingo J. L., Bocio A., Falcó G. and Llobet J. M. *Environ Sci Technol* 2006; 40: 4394.
10. Llobet J. M., Falcó G., Bocio A., Domingo J. L. *Chemosphere* 2007; 66: 1107.
11. Domingo J. L., Falcó G., Llobet J. M., Casas C., Teixidó A. and Müller L. *Environ Sci Technol* 2003; 37: 2332.
12. Bocio A., Llobet J. M. and Domingo J. L. *J Agric Food Chem* 2004; 52: 1769.
13. Domingo J. L. *J Chromatogr A* 2004; 1054: 327.
14. Jiang Q., Hanari N., Miyake Y., Okazawa T., Lau R. K., Chen K., Wyrzykowska B., So M. K., Yamashita N. and Lam P.K. *Environ Pollut* 2007; 148: 31.

15. Kannan K., Yamashita N., Imagawa T., Decoen W., Khim J. S., Day R. M., Summer C. L. and Giesy J. P. *Environ Sci Technol* 2000; 34: 566.
16. Pan J., Yang Y. L., Xu Q., Chen D. Z. and Xi D. L. *Chemosphere* 2007; 66: 1971.

Table 1: Estimated dietary intake of PCNs and PCDEs by the adult population of Catalonia, Spain[a]

food group	daily consumption[b] (g)		PCN intake[c] (ng/day)		PCDE intake[c] (ng/day)	
	2000	This study	2000	This study	2000	This study
meat and meat products	185 (12.8)	172 (14.0)	3.25	0.42	0.34	0.18
fish and seafood	92 (6.4)	68 (5.5)	3.63	1.95	38.43	50.24
Vegetables	226 (15.7)	160 (13.0)	0.76	0.40	0.12	0.13
Tubers	74 (5.1)	73 (5.9)	0.21	0.16	0.08	0.05
Fruits	239 (16.6)	194 (15.8)	0.17	0.25	0.19	0.08
Eggs	34 (2.4)	31 (2.5)	0.80	0.13	0.04	0.05
Milk	217 (15.0)	128 (10.5)	0.08	0.12	0.13	0.11
dairy products	106 (7.3)	76 (6.2)	3.82	0.35	0.23	0.06
Cereals	206 (14.3)	224 (18.3)	14.64	1.92	1.01	0.43
Pulses	24 (1.7)	30 (2.5)	0.08	0.29	0.03	0.02
oils and fats	41 (2.8)	27 (2.2)	18.33	0.56	0.45	0.24
bakery products		45 (3.7)		0.69		0.09
total	**1444 (100)**	**1228 (100)**	**45.78**	**7.25**	**41.04**	**51.68**
			0.65[d]	**0.10[d]**	**0.59[d]**	**0.74[d]**

[a]Results are given for a male adult of 70 kg body weight. [b]In parentheses, percentages of total consumption. [c]Data were calculated assuming that when a congener was below the detection limit, the concentration was equal to one-half of the respective limit of detection (ND=LOD/2). [d]Total intake expressed in ng/kg body weight/day.

Figure 1: Estimated daily intake of PCNs (left) and PCDEs (right) through the diet of children, adolescents, adults, and seniors of Catalonia, Spain.