Bull. Environ. Contam. Toxicol. (1993) 51:160–164
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Environmental Contamination and Toxicology

Organochlorine Pesticide Residues in the Population of Catalonia (Spain)

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Concentrations of organochlorine residues in the adipose tissue of the general human population are good indicators of the environmental and food related exposition to these ubiquitous pollutants. In this paper, levels of organochlorine pesticide residues in some populations of several areas of Catalonia (NE Spain) are reported. Results are compared with those obtained: a) in other Spanish populations, and b) in a previous study developed during the years 1982-83 (To-Figueras et al. 1986).

Major concern is devoted to hexachlorobenzene (HCB) residues because of: a) the very high levels previously determined in some Spanish populations, particularly in Barcelona (To-Figueras et al. 1986; Planas et al. 1990); b) the several potential sources proposed to explain the origin of HCB in the environment (Tobin, 1986); c) the possible risks to human health due to the porphyrinogenic and carcinogenic potential of this chemical (Krewski et al. 1986; Enriquez de Salamanca et al. 1990).

MATERIALS AND METHODS

Human adipose tissues were obtained from individuals living in four different geographical areas (Table 1). Samples were taken from the abdominal wall from corpses subjected to judicial autopsy or from patients submited to abdominal surgery. Residence in the area was the only selection criterium applied. Samples were stored at -30°C in glass containers until analyzed. Register forms including data about the sample donors -age, sex, occupation, cause of death (if necropsy), and length of residence in the area- were annexed. Geographical and socioeconomic characteristics of the areas are explained in Table 2.

About 0.3 g of fresh tissue was homogenized and dehydrated with anhydrous sodium sulfate and extracted twice with hot hexane. Clean-up was performed with sulphuric acid (Veierov and Aharonson, 1978) for the determination of all residues, except for dieldrin. For the analysis of dieldrin an aliquot of the extract was cleaned by partition with acetonitril and elution through florisil (A.O.A.C. 1980).

Gas chromatography with electron capture detection was utilized for the quantification of residues (Hewlett-Packard 5890 and/or Varian 3700); identification was confirmed by GC-MS in some samples. Packed (2.5%

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Table 1. Samples: origin, number (N), sampling period (SP), mean age of donors ± S.D. (Age) and males/females ratio (M/F)

Origin	N	SP	Age	M/F
Barcelona (Necropsies)	68	1987-1988	57±22	41/27
Olot-Garrotxa (Biopsies)	50	1986-1988	54±22	23/27
Tarragona (Biopsies)	85	1987-1988	55±18	35/50
Lleida (*) (Necropsies)	53	1985-1987	51±22	41/12

(*) Results from the area of Lleida have been previously published (Camps et al., 1989)

Table 2. Geographical and socioeconomic characteristics of the populations studied

	residents (x1000)	location	main economic activities
Barcelona	2500	coastal, urban	industry, services
Olot-Garrotxa	45	mountain, rural	cattle, agriculture (corn, pasture), alimentary and textile industry
Tarragona	153	coastal	agriculture (vineyard, olive)
		urban & rural	petrochemical industry, tourism
Lleida	200	inland, rural	agriculture (fruit trees and cereals), alimentary industry

OV-17, 1.95% OV-210) and capillary (SPB-5, 30m long, 0.32mm ID) columns were used. Aldrin was added as internal standard and results were expressed in ppm (μg/g) on a lipid basis. All solvents were of pesticide residue analysis grade and the purity of all reagents was carefully checked.

RESULTS AND DISCUSSION

Table 3 summarizes the results. Detectable concentrations of every residues were found in each of the samples studied (N=256), but quantification of DDD and dieldrin was only possible in 205 and 222 respectively. The four populations showed a very similar pattern: pp'-DDE was present in higher concentration than the other residues; second place was occupied by HCB; ß-HCH was third and pp'-DDT was fourth. These four pesticide residues were the majoritary ones in lipid tissue of the populations under study; lindane, DDD, dieldrin and some others occasionaly identified are present in very lower levels. Other organochlorine residues, as PCBs, are not included in this report because of the particular characteristics of its quantification, but partial results for the population of Barcelona have been reported elsewhere (Gómez-Catalán et al. 1991). Lower levels of the DDT group residues were determined in the Olot-Garrotxa population ($p<0.01$ compared to Barcelona); higher levels of HCB were found in Lleida (rural population) than in Barcelona (urban) ($p<0.01$); ß-HCH in Lleida was higher than in the rest of populations. The rest of residues did not show any significant difference among the populations studied. Considering the whole population, the more outstanding result is the high level of HCB when compared with the world-wide literature; e.g., mean

Table 3. Concentration of organochlorine residues in fat tissue (mean ± S.D. μg/g extracted lipid)

	Barcelona	Olot-Garrotxa	Tarragona	Lleida	mean
HCB	2.42±1.34	3.11±1.60	3.00±1.46	3.58±2.56	2.99±1.77
pp'-DDE	6.98±6.85	3.73±2.37	6.03±5.32	6.84±6.13	6.00±5.64
Lindane	0.07±0.04	0.06±0.04	0.05±0.03	0.08±0.05	0.06±0.04
ß-HCH	1.63±1.11	1.16±0.69	1.62±0.93	3.74±5.92	1.97±2.95
pp'-DDD	0.06±0.07	0.03±0.02	0.04±0.04	0.08±0.07	0.05±0.06
pp'-DDT	1.35±0.80	0.69±0.35	1.20±0.84	1.40±0.85	1.18±0.80
Dieldrin	0.06±0.07	0.08±0.08	0.06±0.06	0.08±0.08	0.07±0.07

concentrations reported in USA and in United Kingdom were 0.05 ppm (Robinson et al. 1986; Abbott et al. 1981). However, levels of HCB of the same order that our results were determined in some Italian and German populations (Focardi et al. 1986; Bertram et al. 1986) and in other populations of Spain, both in adipose tissue (Ferrer et al. 1992) and in human milk (Conde, 1990).

This high incidence of HCB contamination in Spain is very intriguing. Main potential sources of HCB can be classified in three types (Tobin, 1986): a) direct use as a fungicide (seeds preservative); b) impurity of other pesticides and c) subproduct in some industrial procedures, mainly production of chlorinated solvents. Which of these sources is the main responsible for the residues in our country is not known but there are some contradictory pieces of evidence:

a) Mean levels in Barcelona have fallen from 5.55 ppm in years 1982-83 (To-Figueras et al. 1986) to the the current (1987-88) value of 2.42 ppm ($p<0.001$). This decrease coincides with the withdraw of HCB containing formulations and a more rigorous control in pesticide use.

b) Our results suggest a major incidence in agrarian areas (Lleida) than in urban areas (Barcelona), but difference is too small to take definitive conclusions. However in an study on human milk clearly higher levels of HCB were found in samples from an agrarian area devoted to cereal crops and provided with big grain storage plants (Conde, 1990).

c) A chemical factory that produced an average of 150 tons/year of HCB during the latter seventies and earlier eighties is present in Catalonia, near to the Tarragona area (IARC, 1979) and contributed to the contamination of the Ebre River (Grimalt et al. 1988).

Evidences a) and b) suggest an agrarian (pesticide) origin, whereas c) indicates that industrial sources may be very significant.

ß-HCH levels were also higher in our population than in most of the occidental populations studied (Abbott et al. 1981 and 1985). Incidence of ß-HCH -specially high in the agrarian population (Lleida)- reflects the past and present use of lindane-containing pesticides: lindane has a short half life in the environment whereas the ß isomer, present as an impurity in technical lindane, is a persistent residue.

High and homogenous levels of DDE are the result of past heavy use of DDT in Spain. The ratio DDE/DDT increases with time after exposure or after use restriction of DDT. DDT and DDE correlated significantly ($r=0.650$, $p<0.001$) and the ratio was 5.27 ± 3.55. DDE mean concentration in Barcelona has fallen from the 1982-83 study: 8.06 ppm to 6.98 ppm but difference is not significant.

Residue levels in male and female populations did not show any statistically significant difference. This result is in accordance with those of many studies; however, some others suggest the existence of some sex-linked factor in the accumulation of organochlorine residues (Ferrer et al. 1992).

Concentrations of HCB, pp'-DDE, ß-HCH and pp'-DDT correlated positively with age ($p< 0.01$). This is an habitual finding usually explained by the longer exposure time and the long half-life of the residues. Also positive correlations between the majoritary residues were found and only partially explained by the common correlation with age; for instance there was a strong correlation between HCB and ß-HCH ($r=0.493$, $p<0.001$) that could be interpreted as a result of a possible metabolic relation between HCB and HCH isomers as proposed by some authors (Gopalaswamy and Aiyar, 1984). We think that a more feasible explanation for correlation among residues come from its commom pathways in the biosphere and, specially, in the trophic chains.

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Received August 20, 1992; accepted February 2, 1993.