EXPOSURE TO HEXACHLOROBENZENE THROUGH FISH AND SEAFOOD CONSUMPTION IN CATALONIA, SPAIN

Falcó G[1], Llobet JM[1], Bocio A[2], Nadal M[2], Domingo JL[2]

[1]Toxicology Unit, University of Barcelona, Av. Joan XXIII s/n, 08028 Barcelona, Catalonia, Spain; [2]Laboratory of Toxicology and Environmental Health, "Rovira i Virgili" University, Sant Llorenç 21, 43201 Reus, Catalonia, Spain

Introduction

Until 1965, hexachlorobenzene (HCB) was widely used as a pesticide.[1] Although a consistent downward trend in the environmental HCB levels has been noted over the past 20 years, this chemical is still widely distributed in the environment.[2] For the general population, exposure to HCB occurs primarily from eating low levels of this organic compound in contaminated food.[1]

Recently, we performed a wide survey in which the concentrations of a number of environmental contaminants (metals, PCDD/Fs, PCBs, PCNs, PBDEs PCDEs, PAHs and HCB) were determined in 11 groups of foodstuffs acquired in Catalonia (Spain). In general terms, the highest levels of most inorganic and organic pollutants were detected in fish and seafood. This food group showed the greatest contribution to the daily intake of As, Hg, Pb, PCDD/Fs, PCBs, PBDEs and PCDEs. Fish and seafood was also an important contributor to the daily intake of HCB, only preceded by dairy products and meats.[3]

Because of the important contribution of edible species to the dietary intake of the above pollutants, as well as the rather reduced number of previously analyzed species (3 fresh plus 2 tinned), recently we performed a new study aimed at extending the data of the previous survey. In this study, the 14 marine species that are most consumed by the population of Catalonia[4] were analyzed for the same pollutants, and their daily intakes estimated. The results concerning HCB are here reported.

Materials and Methods

Sampling. In March-April 2005, edible marine species were randomly acquired in local fish markets, big supermarkets and grocery stores from six important cities of Catalonia. Selected fish and seafood species were the following: sardine, tuna, anchovy, mackerel, swordfish, salmon, hake, red mullet, sole, cuttlefish, squid, clam, mussel and shrimp. A total of 42 composite samples (3 for each species) were analyzed for HCB levels. Composite samples were made up of 20 individual samples of each respective species.

Analytical Methods and Instrumentation. HCB was determined as previously reported.[3] In brief, after homogenization of samples, extraction was done with hexane:dichloromethane (1:1). Clean-up and fractionation of each sample was carried out using adsorption chromatography and gel permeation chromatography. The cleaned extract was analyzed by HRGC/HRMS using a Fisons CE 8065 GC coupled with VG AutoSpec Ultima system. HCB quantification was carried out using internal standards. The detection limit was 5 ng/kg.

Dietary Exposure Estimates. The daily intake of HCB through fish and seafood consumption was calculated by multiplying the respective concentration in each species by the weight of that specie consumed by an average individual from Catalonia[4]. When the levels were under the limit of detection (LOD), the concentration was assumed to be one-half of the LOD (ND = ½ LOD).

Results and Discussion

HCB concentrations in the 14 marine species are summarized in Table 1. The highest HCB levels were found in salmon and mackerel: 1.68 and 0.80 ng/g wet weight, respectively. Red mullet and sole showed also high HCB concentrations (0.59 and 0.55 ng/g ww, respectively). In contrast, the lowest HCB levels were found in cuttlefish, mussel and shrimp (0.02, 0.03 and 0.04 ng/g ww, respectively). In general terms, these results are within the range of data reported in recent years by a number of authors. Yang et al. (2006) found an average HCB concentration of 0.38 ng/g wet weight (range: 0.01-2.28 ng/g ww) in a wide variety of fish and shellfish from local fish markets from 3 Chinese cities.[5] In turn, El-Nemr and Abd-Allah (2004) reported a range of average concentrations of HCB in fish samples obtained of local fishermen from 4 sites in Egypt between ND (detection limit 0.3 ng/g) and 38.6 ng/g ww[6], while Campos et al. (2005) found mean HCB values in sardine (6.5 ng/g ww) and mackerel (2.7 and 5.0 ng/g ww) from Portugal,[7] which are notably higher than those of the current study. Similar HCB ranges to those of our survey were reported by Nakata et al. (2002) and Marcotrigiano and Storelli (2003) in various fish and shellfish species from China (0-02-0.09 ng/g ww)[8] and Italy (ND-4.55 ng/g ww)[9], respectively. In turn, a lower value than the current one was reported as the mean HCB in several pools of edible clams from different Italian and European markets (mean: 0.06, range 0.03-0.15 ng/g ww).[10] Recently, Naso et al. (2005) determined HCB levels in a number of edible marine species from the Gulf of Naples, Italy.[11] Some of the species analyzed were also measured in the present study. However, these results could not be compared with our current data, as they were expressed on a different basis (lipid weight versus wet weight).

Table 1. Concentrations of hexachlorobenzene in edible marine species

Species	HCB (ng/g wet weight)	Species	HCB (ng/g wet weight)
Sardine	0.18	**Tuna**	0.11
Anchovy	0.18	**Mackerel**	0.80
Swordfish	0.17	**Salmon**	1.68
Hake	0.11	**Red mullet**	0.59
Sole	0.55	**Cuttlefish**	0.02
Squid	0.06	**Clam**	0.10
Mussel	0.03	**Shrimp**	0.04

Table 2. Intake of HCB (ng/day) through edible marine species by the population of Catalonia, Spain

Species	m.adult	f. adult	boys	girls	m.adol.	f.adol.	m.senior	f. senior
Sardine	0.69	0.54	N	0.34	0.19	0.39	0.64	0.97
Tuna	1.13	0.95	0.80	0.46	0.85	1.20	0.55	0.35
Anchovy	0.37	0.34	0.02	N	0.41	0.19	0.61	0.22
Mackerel	0.91	1.02	N	N	0.29	0.26	0.40	2.30
Swordfish	0.01	0.01	N	N	0.01	0.01	0.01	0.01
Salmon	3.02	5.05	1.95	N	5.54	1.68	3.75	1.91
Hake	1.73	1.61	1.99	1.78	0.92	1.23	2.56	1.60
Red mullet	0.20	0.19	N	N	0.13	0.13	0.21	0.16
Sole	3.01	3.09	2.88	1.29	3.42	2.04	2.01	2.84
Cuttlefish	0.07	0.05	N	0.05	0.04	0.02	0.10	0.03
Squid	0.19	0.19	0.11	0.03	0.11	0.31	0.19	0.05
Clam	0.03	0.06	0.01	0.03	0.02	N	0.02	0.02
Mussel	0.03	0.05	0.01	0.01	0.03	N	0.05	0.02
Shrimp	0.14	0.16	N	0.03	0.13	0.12	0.11	0.07
Total (ng/day)	11.5	13.3	7.8	4.0	12.1	7.6	11.2	10.6
Total (ng/kg/day)	0.16	0.24	0.32	0.17	0.23	0.14	0.17	0.18

m: males; f: females; adol: adolescents. N: negligible.

On the other hand, the comparison of the current results with those of our previous study for the species analyzed in both surveys show a decrease of HCB levels in sardine (0.18 vs, 0.78 ng/g ww), an increase in hake (0.11 vs 0.04 ng/g ww), and analogous values in mussels.[3] In a total diet study concerning food surveillance in the Basque Country (Spain) performed in 1990-1991, the levels of HCB in all fish samples were below 1 ng/g,[12] which is in accordance with the present results (with the exception of salmon).

The daily HCB intake through fish and seafood was estimated for four age groups of the population of Catalonia: children, adolescents, adults and seniors, which were in turn divided according to sex. The highest and lowest HCB intake (ng/day) corresponded to female adults (13.3) and girls (4.0), respectively. For most age/sex groups, salmon and sole were the species showing the highest contribution to HCB intake. When HCB intake was calculated according to the average body weight of the individuals in each group, the highest and lowest values corresponded to boys (0.32 ng/kg/day) and female adolescents (0.14 ng/kg/day). For all groups, HCB intake is considerably lower than the WHO tolerable daily intake (TDI), which is 0.17 µg/kg/day for non-cancer effects and 0.16 µg/kg/day for neoplastic effects in humans.[1] Fon cancer effects, daily HCB intake due to fish and seafood consumption represents a maximum of 0.20% of TDI (boys), and a minimum of 0.09% (female adolescents). In conclusion, the current results indicate that intake of HCB through fish and seafood should not be of concern for the health of the consumers.

Acknowledgements
This study was supported by the Catalan Food Safety Agency, Generalitat de Catalunya, Spain. The authors thank Dr. L. Serra-Majem and co-workers for providing their data about fish and seafood consumption by the general population of Catalonia.

References

1. Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Hexachlorobenzene 2002*. Atlanta, GA: US Department of Health and Human Services, Public Health Service.
2. Barber JL, Sweetman AJ, van Wijk D, Jones KC. *Sci Total Environ* 2005;349:1.
3. Falcó G, Bocio A, Llobet JM, Domingo JL, Casas C, Teixidó A. *Sci Total Environ* 2004;322:63.
4. Serra-Majem L, Ribas L, Salvador G, Castells C, Serra J, Jover L, Treserras R, Farran A, Román B, Raidó B, Taberner JL, Salleras L, Ngo J. *Avaluació de l'estat nutricional de la població catalana 2002-2003. Evolució dels hàbits alimentaris i del consum d'aliments i nutrients a Catalunya (1992-2003).* Direcció General de Salut Pública. Departament de Sanitat i Seguretat Social 2003. Generalitat de Catalunya, Barcelona, Spain (in Catalan).
5. Yang N, Matsuda M, Masahide M, Wakimoto T. *Chemosphere* (in press).
6. El Nemr A, Abd-Allah AMA. *Chemosphere* 2004;54:1401.
7. Campos A, Lino CM, Cardoso SM, Silveira MIN. *Food Addit Contam* 2005;22:642.
8. Nakata H, Kawazoe M, Arizono K, Abe S, Kitano T, Shimada H, Li W, Ding X. *Arch Environ Contam Toxico.* 2002;43:473.
9. Marcotrigiano GO, Storelli MM. *Vt. Res Commun* 2003;27(suppl 1):183.
10. Binelli A, Provini A. *Mar Pollut Bull* 2003;46:879.
11. Naso B, Perrone D, Ferrante MC, Bilancione M, Lucisano A. *Sci Total Environ* 2005;343:83.
12. Urieta I, Jalón M, Eguileor I. *Food Addit Contam* 1996;13:29.