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Health risks arising from the dietary intake of chemical contaminants: a case study of the consumption of edible marine species in Catalonia, NE Spain

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Resum

Actualment, està ben establert que la ingesta dietètica és la principal via d'exposició humana a metalls i compostos orgànics persistents (COP). L'any 2000, el nostre laboratori va començar una exhaustiva investigació sobre l'exposició dietètica a diversos metalls i contaminants orgànics per la població general de Catalunya. Entre els onze grups d'aliments analitzats, els nivells més elevats de la major part dels contaminants es van trobar, en termes generals, al peix i marisc. Aquest grup va suposar les contribucions més elevades de la ingesta d'As, Hg i Pb, dioxines i furans (PCDD/PCDF), policlorbifenils (PCB), difenil èters polibromats (PBDE) i difenil èters policlorats (PCDE). El peix i marisc va ser també un contribuent important en la ingesta de Cd, hexaclorobenzè, hidrocarburs aromàtics policíclics (PHA) i naftalens policlorats (PCN). Tanmateix, els nivells dels contaminants es van determinar solament en tres espècies de peix fresc i en dues de conservat, la qual cosa suposava un factor limitant per tal de poder establir recomanacions sobre el consum de peix i marisc. Per això, recentment hem dut a terme un estudi addicional amb la intenció d'incrementar les dades de l'anterior investigació. Els resultats són aquí presentats. En termes generals, la major part d'espècies marines analitzades no haurien de suposar efectes adversos sobre la salut dels consumidors. Tanmateix, el tipus de peix, la freqüència de consum i la quantitat consumida són aspectes essencials per a establir un equilibri entre els beneficis i els riscos d'un consum regular de peix.

Paraules clau: contaminants químics, ingesta dietètica, espècies marines comestibles, riscos per a la salut humana, NE Espanya

Abstract

Dietary intake is the main means of human exposure to toxic metals and persistent organic pollutants (POPs). In 2000, our laboratory initiated research into dietary exposure to a number of metals and organic pollutants. Among 11 food groups analyzed, the highest levels of most pollutants were detected in fish and seafood. This group contributed most to the intake of As, Hg and Pb, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated diphenyl ethers (PCDEs). Fish and seafood also made an important contribution to the daily intake of Cd, hexachlorobenzene, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated naphthalenes (PCNs). However, the levels of contaminants were only determined in three species of fresh fish and in two species of tinned fish, which was a limiting factor for the purposes of establishing recommendations concerning human consumption of fish and other seafood. Taking into account the potentially important contribution made by marine species to the dietary intake of environmental pollutants, as well as the reduced number of species analyzed, we recently performed additional research to extend our previous study. This paper presents our results from both the preliminary and the extended studies. In general terms, most marine species analyzed do not pose adverse health risks for consumers. However, the type of fish, frequency of consumption, and meal size are essential factors in balancing the health benefits and risks of regular fish consumption.

Keywords: chemical contaminants, dietary intake, edible marine species, human health risks, NE Spain

Although the association between diet and health is well recognized, it is frequently difficult to establish a causal relationship between a particular dietary component and a specific health issue. This is particularly so for environmental contaminants, as most of them reach humans through the food chain. Among inorganic pollutants, toxic elements such as arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) are widely dispersed in the environment and persist for long periods in different media. These elements have no beneficial effects on humans, and there is no known homeostasis mechanism for them. Toxicity and threats to human health from any contaminant are a function of concentration. However, it is well known that chronic exposure to As, Cd, Hg and Pb at relatively low levels can cause

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adverse effects [11,13]. Few individuals are primarily exposed to such toxic elements in the workplace, and for most people the main exposure to these elements comes from their diet [8,10,28]. Consequently, information about dietary intake is essential to assess the human health risks they pose.

Persistent organic pollutants (POPs) are lipophilic, bioaccumulative and semi-volatile toxic compounds. Some POPs are produced deliberately in a number of industrial activities, while others are formed accidentally or released as by-products of various activities, such as combustion [14,15,22]. POPs are found in several worldwide ecosystems in complex mixtures, as a result of agricultural, industrial and other human activities. They pose a significant health problem due to bioaccumulation through the food web and their potentially highly toxic effects. The carcinogenic nature of some POPs is well established, while others are endocrine disruptors with a number of adverse effects on hormone homeostasis [27,34,35].

Potential public health risks from environmental exposure to metals and POPs continue to be the subject of much research, regulation, and debate [12]. Human exposure to metals and POPs occurs via various routes: dermal absorption, air inhalation, ingestion of contaminated soils, and daily intake of foodstuffs.

In recent years, according to various studies, more than 90-95% of the toxic metals and POPs to which humans are exposed originate in food and roughly 90% of this normally comes from animal sources [3,12,14-16]. In general, fish and other seafood represent only relatively small percentages of the human diet. However, it has been demonstrated that frequent consumption of fish and seafood is one of the major routes for chemical pollutants to enter the human body [7,8,17].

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), together with polychlorinated biphenyls (PCBs) are among the most well-known and studied POPs. PCDD/PCDFs are among the most hazardous environmental contaminants. These organic pollutants are toxic in extremely tiny amounts and bioaccumulate in humans [4,27]. In turn, PCBs are ubiquitous in the environment, and are found in the adipose tissue, and blood of the general population as well as in breast milk [1]. Recently, the World Health Organization (WHO) identified various PCB congeners whose toxicity levels were similar to those of PCDD/PCDFs and assigned them toxic equivalency factors (TEFs) for the calculation of toxic equivalents (TEQ) [41]. According to recent research, PCBs seem to be even more important than PCDD/PCDFs with regard to human health. Exposure to PCDD/PCDFs and PCBs can occur by various routes, though food is the primary source.

Although they have been studied much less than PCDD/PCDFs and PCBs, polychlorinated naphthalenes (PCNs), polychlorinated diphenyl ethers (PCDEs) and polybrominated diphenyl ethers (PBDEs) are other polyhalogenated POPs with long half-lives. Several PCN congeners display toxicities similar to the most toxic and well-studied dioxin, 2,3,7,8,-TCDD, through mechanisms mediated by aryl hydrocarbon receptor (AhR) [14]. In turn, although research is still clearly necessary, the major toxicity mechanism of PCDEs can also be related to their ability to bind to and activate AhR [16]. PBDEs are a class of brominated flame retardants that has been produced in notable quantities and widely used in a variety of consumer products. In recent years, a marked increase has been observed in some countries in the levels of PBDEs in human tissues and fluids, especially breast milk [15]. As with other structurally similar classes of POPs, at least some PBDE congeners are endocrine disrupters [15]. Although information is still rather scarce, for non-occupationally exposed individuals dietary intake is very probably the main route of exposure to PCNs, PCDEs, and PBDEs (as it is for metals, PCDDs, PCDFs, and PCBs) [5,6,14-16].

Preliminary Study of human exposure to chemical contaminants in Catalonia, NE Spain

Method

In recent years, monitoring programs have been developed in various countries to determine the presence of chemical contaminants in foodstuffs and to assess human health risks resulting from dietary exposure to them. In Spain, until recently, data were only available from one exhaustive dietary study (in the Basque Country) involving various contaminants [37,38]. From 2000 to 2002 an extensive study was performed in our laboratory to determine the daily intake of several chemical pollutants by the general population of Catalonia, NE Spain. We included in the study inorganic elements such as As, Cd, Hg and Pb [28], POPs such as hexachlorobenzene [23], PCNs [18], PCDD/PCDFs [29], PCBs [30], PBDEs [5] and PCDEs [6], as well as polycyclic aromatic hydrocarbons (PAHs) [24].

From June to August 2000, food samples were acquired in local markets, supermarkets, and grocery stores in seven large cities (Barcelona, Tarragona, Lleida, Girona, l'Hospitalet de Llobregat, Badalona, and Terrassa). The food was divided into various groups: meat and meat products (beef steaks, hamburgers, pork loin, ham, sausages, salami, chicken breast, and lamb); fish and shellfish (fresh hake, sardines and mussels, together with tinned tuna and sardines); vegetables (lettuce, tomatoes, potatoes, green beans and cauliflower); tubers; fresh fruit (apples, oranges and pears); eggs; cow's milk (whole and semi-skimmed); other dairy products (yogurt and cheese); cereals (bread, pasta and rice); pulses (lentils and beans); and fats (margarine) and oils (olive and sunflower). Composite samples were analyzed for each foodstuff. Each composite sample was made up of 8-10 individual samples. After the formation of the respective composites, a total of 108 samples were analyzed for the inorganic and organic pollutants indicated above, with the exception of PBDEs and PCDEs for which 54 composite samples were analyzed.

The daily intakes of the chemical contaminants from each foodstuff were calculated by multiplying the concentration in a specific item by the estimated daily consumption of the respective food group. Finally, the total dietary intake of each pollutant was calculated by summing each product over all the food groups. For calculation purposes, when the concentration of a contaminant was under the limit of detection (LOD), the value was either taken to be half the LOD (ND = 1/2 LOD) or to be zero (ND = 0).

Results

What follows is a summary of the dietary intake of the metals and organic pollutants analyzed for the average adult man in Catalonia.

The intakes of As, Cd, Hg, and Pb were 223.6, 15.7, 21.2 and 28.4 µg/day, respectively (Table 1). For each of these four elements, fish and shellfish was the food group showing the highest contribution to their intakes [28]. Total dietary intake of PCDD/PCDFs was estimated to be 95.4 pg WHO-TEQ/day (78.4 pg I-TEQ/day), with fish and shellfish (31%), dairy products (25%), cereals (14%) and meat (13%) contributing the most. The contribution of all the other food groups to the total dietary intake of PCDD/PCDFs was less than 20% (Fig. 1) [29]. The highest level of most of the PCB congeners analyzed (IUPAC No. 28, 52, 77, 101, 105, 118, 126, 138, 153, 169, and 180) was also found in fish and shellfish: 11.864 [[5]]g/kg of wet weight (ww). The next highest concentration, which was substantially lower, was detected both in milk and in dairy products (674.50 ng/kg ww).

Table 1. Food intake, and intake of arsenic, cadmium, mercury, and lead through the diet of adult men in Catalonia, Spain

Food group	*Food intake (g/day)*	*As intake (µg/day)*	*Cd intake (µg/day)*	*Hg intake (µg/day)*	*Pb intake (µg/day)*
Vegetables	226	0.34	1.13	0.11	3.68
Pulses	24	0.04	0.01	0.01	0.18
Cereals	206	8.65	6.80	6.18	4.94
Tubers	74	0.96	1.47	0.22	1.92
Fruit	239	0.36	0.22	0.12	3.01
Fish and Seafood	92	203.32	3.33	8.92	4.71
Meat	185	4.44	1.11	2.22	4.44
Eggs	34	0.51	0.27	0.27	0.51
Dairy Products	106	2.44	0.64	1.27	2.44
Milk	217	1.30	0.43	0.65	1.30
Fats and Oils	41	1.23	0.33	1.23	1.23
Total	1444	223.59	15.73	21.22	28.37

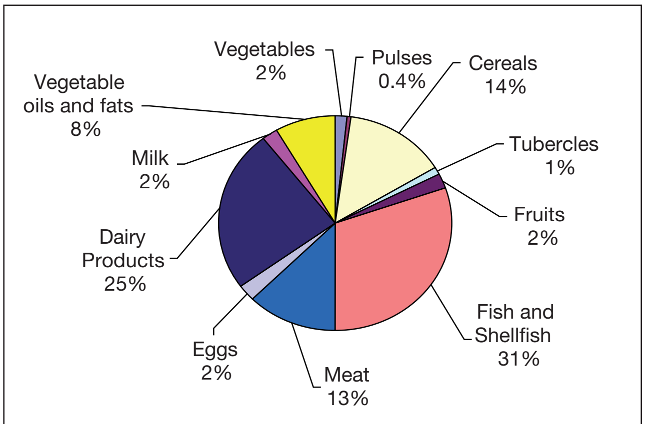

Figure1. Percentage contributions from each food group to the total dietary intake of PCDD/PCDFs for the population of Catalonia, Spain.

The estimated daily intake of PCBs was 150.13 pg WHO-TEQ/day, with the largest contributions to this intake corresponding to fish and shellfish, and dairy products: 82.87 and 29.38 pg WHO-TEQ/day, respectively (Table 2) [30].

The highest concentration of PCNs was found in fats and oils (447 pg/g), followed by cereals (71 pg/g), fish and shellfish (39 pg/g), and dairy products (36 pg/g). In general, tetraCNs were the predominant PCN homologue in all food groups except fruit and pulses, which had greater proportions of hexaCNs. The largest contribution to the daily PCN intake corresponded to fats and oils, and to cereals, with the remaining food groups contributing considerably less (Table 3) [18]. With the exception of fish and shellfish (Table 4), the concentrations of PCDEs were below the LOD. Taking half the LOD as the average concentration of undetected PCDE congeners, the estimated total dietary intake of PCDEs was 41 ng/day [6]. In contrast, the highest PBDE levels were found in fats and oils, fish and shellfish, meat and meat products, and eggs. The dietary intake of PBDEs was 97.3 or 81.9 ng/day (assuming ND = 1/2 LOD or ND = 0, respectively). TetraBDEs and pentaBDEs were the homologues contributing most to total PBDEs (Fig. 2) [5].

Table 2. Estimated daily intake of PCBs for a 70-kg man (20-65 years old) living in Catalonia, Spain

Food group	*Consumption rate[a] (g/day)*	*Intake of PCBs (pg WHO-TEQ/day)*
Vegetables	226 (15.7)	1.07
Tubers	74 (5.1)	0.83
Pulses	24 (1.7)	0.37
Cereals	206 (14.3)	11.36
Fruit	239 (16.6)	2.10
Fish and seafood	92 (6.4)	82.87
Meat	185 (12.8)	8.85
Eggs	34 (2.4)	0.84
Milk	217 (15.0)	1.78
Dairy products	106 (7.3)	29.38
Fats and oils	41 (2.8)	10.67
Total Intake	1444 (100)	150.13

[a]In parentheses: percentage of total consumption.

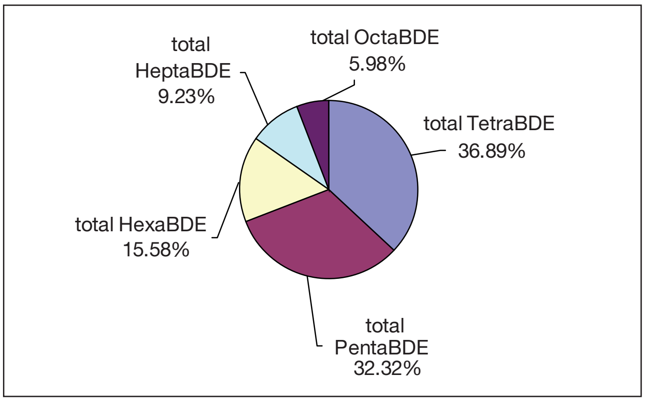

Figure 2. Percentage contribution of the different congeners to the total dietary intake of PBDEs (ng/day). Calculations assuming ND = 0.

Table 3. Food intake and estimated dietary intake of PCNs for adult men of Catalonia, Spain

Food group	Food intake (g/day)	PCN *(ng/day)*
Meat and meat products	226	0.76
Fish and seafood	24	0.08
Vegetables	206	14.64
Tubers	74	0.21
Fruit	239	0.17
Eggs	92	3.63
Milk	185	3.25
Dairy products	34	0.80
Cereals	106	3.82
Pulses	217	0.08
Fats and oils	41	18.33
ng/day		45.78
ng/kg/day		0.65

Table 6. Food intake (g/day) and hexachlorobenzene (HCB) intake (ng/day) for adult men in Catalonia, Spain

	Adult men	
Food group	*Food intake*	*HCB*
Meat and meat products	185	31.98
Fish and seafood	92	23.59
Vegetables	226	1.56
Tubers	74	0.10
Fruit	239	0.17
Eggs	34	6.26
Milk	217	2.80
Dairy products	106	92.15
Cereals	206	2.19
Pulses	24	0.01
Fats and oils	41	5.61
Total HCB intake		
(∝g/day)		0.166
(μg/kg/day)		0.0024

Table 4. PCDE concentrations (ng/kg of fresh weight) in different fish and seafood samples bought in Catalonia, Spain

	Hake N = 2	*Mussel N = 2*	*Sardine N = 2*	*Tuna in vegetable oil N = 1*	*Sardine invegetable oil N = 1*
TetraCDEs	0.3–1.5	0.7–4.6	4.8–5.9	0.2	5.0
PentaCDEs	2.3–12.8	6.5–12.1	9.8–115	0.2	5.2
HexaCDEs	18.4–270	39.8–76.8	209–1531	1.5	27.2
HeptaCDEs	10.6–150	4.4–5.7	72.0–140.3	0.4	16.7
OctaCDEs	14.4–272	8.1–8.4	104–914	1.0	17.9
Total PCDEs	45.9–707	59.8–107	400–2707	3.3	71.9

Table 5. Mean dietary intake of polycyclic aromatic hydrocarbons by adult men living in Catalonia, Spain. Contribution from different food groups

PAHs	*Food groups*											*Total dietary intake*	
	Meat and meat products	*Fish and seafood*	*Vegetables*	*Tubers*	*Fruit*	*Eggs*	*Milk*	*Dairy products*	*Cereals*	*Pulses*	*Fats and oils*	*μg / day*	*μg / kg/ day*
BaP	0.018	0.022	0.003	0.005	0.003	0.001	0.002	0.008	0.054	0.001	0.011	0.128	0.002
Σ carcin. PAHs[a]	0.331	0.178	0.052	0.059	0.025	0.010	0.072	0.108	0.601	0.021	0.095	1.552	0.022
Σ 16 PAHs	2.485	0.727	0.200	0.267	0.222	0.083	0.331	0.703	2.979	0.065	0.356	8.418	0.120

[a] Σ carcin. PAHs include benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene and indenol[1,2,3-c,d]pyrene, which are probable human carcinogens according to the US EPA [40].

Furthermore, for the general population, we calculated the dietary intakes of 16 PAHs, as well as that of hexachlorobenzene (HCB). Among the PAHs analyzed, phenantrene (16.7 μg/kg) and pyrene (10.7 μg/kg) were predominant. By food group, the highest levels of total PAHs were detected in cereals (14.5 μg/kg), and in meat and meat products (13.4 μg/kg). The mean estimated dietary intake of the sum of the 16 PAHs was 8.4 μg/day for a 70-kg adult man, of which 1.6 μg/day were carcinogenic PAHs (including benzo[a]pyrene) (Table 5) [24]. HCB residues in foods were generally rather low, except for dairy products with a mean concentration of 0.869 ng/g of ww. For adult men, total dietary intake of HCB was calculated as 0.166 μg/day. Dairy products, meat and meat products, and fish and shellfish were the main contributors to this intake (Table 6) [23].

Conclusions

These results show that the highest levels of most inorganic and organic pollutants were, in general terms, detected in fish and other seafood, which contributed most to the intake of As, Hg and Pb [28], as well as to that of PCDD/PCDFs [29], PCBs

[30], PBDEs [5] and PCDEs [6]. Fish and seafood was also an important contributor to the daily intake of Cd (second contributor) [28], HCB (third contributor) [23], PAHs (third contributor) [24], and PCNs (fourth contributor) [18]. However, in spite of the considerable magnitude and scope of the previous survey, for technical and economic reasons the total number of samples analyzed for the different groups of foodstuffs was limited to 108. Moreover, the levels of contaminants were only determined in three species of fresh fish and two of tinned fish. There is no doubt that these are limiting factors for the purposes of establishing recommendations concerning human consumption of fish and other seafood (frequency and size of meals). Taking into account the important contribution of marine species to the dietary intake of environmental pollutants, we decided to perform an additional study aimed at extending the fish and seafood data.

Extended study

Materials and methods

Sampling

From March to April 2005, samples of fish and seafood were acquired in local markets, supermarkets, and grocery stores in six important cities (Barcelona, Tarragona, Lleida, l'Hospitalet de Llobregat, Terrassa and Girona). Fish and seafood samples consisted of: six species of oily fish (sardine [*Sardine pilchardus*], tuna [*Thunnus thynnus*], anchovy [*Engraulis encrasicholus*], mackerel [*Scomber scombrus L.*], swordfish [*Xiphias gladius*] and salmon [*Salmo salar L.*]); three species of white fish (hake [*Merluccius merluccius L.*], red mullet [*Mullus surmuletus*] and sole [*Solea vulgaris*]); and five species of cephalopods and shellfish (cuttlefish [*Sepia esculenta*], squid [*Loligo vulgaris*], clam [*Tapes decussatus*], mussel [*Mytilus galloprovincialis L.*] and shrimp [*Penaeus setiferus*]). According to recent studies by the Spanish Ministry of Agriculture and Fishery [33], all these 14 species are included in those most consumed in Spain. A total of 42 composite samples (3 for each species) were analyzed for all the chemical pollutants listed above in the preliminary study. For analytical purposes, composites were made up of 20 samples from individuals of each species. Therefore, 840 individual fish and seafood samples were processed. For small species (such as, sardine, anchovy, clam, etc.) the entire edible part of each individual was included to prepare the composite sample. However, for larger species (such as hake, swordfish or tuna) only fillets of the edible parts of each individual were collected and included in the respective composite samples.

Analytical methods and instruments

Details of the analysis of metals, POPs and PAHs, (including preparation of samples for analysis, clean-up, etc.) are described in recent reports [5,6,18,23,24,28-30].

Dietary exposure estimates

Data regarding the human consumption of the analyzed species of fish and seafood in Catalonia were obtained from Serra-Majem et al. [36]. The daily intake of the chemical pollutants from each edible species was calculated by multiplying the respective concentration in each species by the average daily consumption of the eight groups (4 age ranges x 2 sexes) into which the population was divided. When pollutant concentrations were under the LOD, the value was taken to be half the LOD (ND = 1/2 LOD).

Results and discussion

For all the population groups, the main contribution to As intake comes from hake, which accounts for 23.6 and 60.1 % of the total As intake from fish and seafood consumption for adolescents boys and girls, respectively The contribution from sole is also notable. For Cd, elderly men are the group with the highest intake; 1.34 μg/day. The lowest intake corresponds to boys; 0.48 μg/day. For all groups, cuttlefish contributes most to Cd intake. Adult men show the highest Hg intake (9.89 μg/day), while girls and elderly women are the groups with the lowest Hg intake through fish consumption; 5.60 and 5.99 μg/day, respectively. In all groups the main contribution to these intakes comes from tuna. Hake also makes an important contribution to Hg intake (ranging from 22.6% for adolescent boys to 54.2% for girls). Finally, elderly men have the highest Pb intake through fish and seafood consumption; 2.48 μg/day. Girls have the lowest Pb intake; 1.27 μg/day. For all groups, hake is the species with the highest contribution to Pb intake, with percentages ranging from 29.0% for adolescent boys to 69.4% for girls. The daily intake through fish and seafood consumption of these elements is compared with the provisional tolerable weekly intakes (PTWI). The intake of As, Cd, Pb and total Hg for the population is below the respective PTWI values. However, the estimated intake of methyl mercury for boys (1.96 μg/kg/week) exceeds the PTWI. Table 7 summarizes these data concerning fish and seafood consumption, and shows mean daily intakes of As, Cd, Hg and Pb for adult men in Catalonia [25].

The highest levels of PBDEs (the sum of tetra– to octaBDEs) were found in salmon (2015 ng/kg) followed by mackerel, swordfish, and red mullet (1124, 978 and 769 ng/kg, respectively). The lowest PBDE concentrations were observed in cuttlefish (16 ng/kg) and shrimp (20 ng/kg), followed by clam (79 ng/kg). The differences between PBDE levels in salmon and those in the remaining species were quite considerable. In most species, tetraBDEs were the main contributors to total PBDEs, followed by pentaBDEs [19]. The highest PCDE concentrations (ng/kg wet weight) were observed in red mullet (7088) followed by four species of oily fish: sardine (1829), anchovy (1606), tuna (1292) and mackerel (1031). However, the differences with the PCDE levels found in red mullet were only slight. By contrast, shrimp (27), clam (48) and cuttlefish (50) were the species showing the lowest total PCDE content. In some samples of shrimp and cuttlefish some PCDE congeners fell below the analytical LOD. With the exception of clam and mussel (for which tetraCDE was the predominant group) there was a predominance of hexaCDE [19].

Fish and seafood consumption and the intake of PBDEs and PCDEs for the average adult man living in Catalonia are shown

Table 7. Intake of arsenic, cadmium, mercury, and lead from fish and seafood consumption by adult men in Catalonia, Spain

		Intake (μg/day)			
Species	*Consumption (g/day)*	*As*	*Cd*	*Hg*	*Pb*
Sardine	3.8	14	0.03	0.31	0.13
Tuna	10.1	12	0.10	4.91	0.16
Anchovy	2.0	9.5	0.02	0.17	0.03
Mackerel	1.1	4.7	0.01	0.11	0.02
Swordfish	0.1	0.12	Na	0.11	N
Salmon	1.8	3.4	0.02	0.08	0.18
Hake	15.8	65	0.15	2.94	0.86
Red mullet	0.3	5.5	N	0.08	0.01
Sole	5.5	33.4	0.05	0.45	0.19
Cuttlefish	4.5	13.3	0.31	0.11	0.05
Squid	3.2	13.5	0.17	0.18	0.16
Clam	0.3	0.60	0.04	N	0.02
Mussel		2.2	0.13	0.02	0.15
Shrimp	3.5	22	0.07	0.42	0.04
Total	52.9	198.5	1.10	9.89	2.00

[a] N: negligible value.

Table 8. Estimated PBDE and PCDE intake from fish and seafood consumption by the adult population of Catalonia, Spain[a]

	Daily consumption (g)	*PBDE intake (ng/day)*	*PCDE intake (ng/day)*
Sardine	3.8	2.68	6.91
Tuna	10.1	5.66	13.1
Anchovy	2.1	1.25	3.29
Mackerel	1.1	1.27	1.16
Swordfish	0.06	0.06	0.01
Salmon	1.8	3.62	0.67
Hake	15.8	3.49	7.26
Red mullet	0.33	0.25	2.34
Sole	5.5	1.32	1.07
Cuttlefish	4.5	0.07	0.22
Squid	3.2	0.65	3.10
Clam	0.27	0.02	0.01
Mussel	0.97	0.34	0.15
Shrimp	3.5	0.07	0.10
Total	52.9	20.8	39.4

[a]Results are given for a 70-kg adult man.

in Table 8. Total PBDE intake through edible marine species is estimated to be 20.8 ng/day. The highest contributions (ng/day) to this intake correspond to tuna (5.7), salmon (3.6) and hake (3.5), while the lowest PBDE intakes correspond to clam (0.02), swordfish (0.06), and cuttlefish and shrimp (both with 0.07). The ranking of PBDE concentrations and the contributions to daily intake of PBDEs show important differences. These differences are due to the differences in the amounts of each species consumed, which range from 15.8 g/day for hake to 0.06 g/day for swordfish. This explains why species with high levels of PBDEs (such as swordfish or red mullet) contribute a relatively small amount to total PBDE intake from fish consumption. Total PCDE intake from fish and seafood is 39.4 ng/day. The highest contributions (ng/day) to this intake come from tuna (13.1), hake (7.3) and sardine (6.9), while the lowest PCDE intake is from clam (0.01), shrimp (0.10) and mussel (0.15). As for PBDEs, PCDE intakes from edible marine species show important differences from the level of their presence in the different species, according to the average daily consumption. Thus, the species with the highest levels of PCDEs, red mullet, makes a lower contribution to the total daily PCDE intake than other less contaminated species such as squid, tuna, sardine, or anchovy. Although currently there is no evidence that PBDEs behave like dioxins, further research is necessary to assess whether long-term exposure to PBDEs (mainly through diet) may have adverse effects on humans. With respect to PCDE congeners, establishing TEF values would be of great assistance in evaluating human health risks [19].

Mussel, clam and shrimp were the species showing the highest PAH concentrations (22.4, 21.5 and 15.9 ng/g fresh weight, respectively). In contrast, sole (2.5 ng/g fresh weight), and both cuttlefish and squid (3.0 ng/g fresh weight) showed the lowest mean total concentrations of PAHs. The highest

Table 9. Mean intakes from the consumption of 14 edible marine species by the average adult man (70 kg body weight) living in Catalonia, Spain, of the seven PAHs considered probable human carcinogens by the US EPA. Benzo[a]pyrene equivalents (B[a]P) and percentage contributions to the total intake of B[a]P equivalents

PAH	*Intake (∝g/day)*	*TEF*	*Intake of B[a]P equivalents (∝g/day)*	*B[a]P (%)*
Benzo[a]anthracene	0.007	0.1	0.0007	5.2
Chrysene	0.009	0.001	0.00001	0.1
Benzo[a]pyrene	0.006	1	0.006	44.5
Benzo[b]fluoranthene	0.011	0.1	0.0011	8.2
Benzo[k]fluoranthene	0.007	0.01	0.0001	0.5
Dibenzo[a.h]anthracene	0.005	1	0.005	37.1
Indeno[1,2,3-c,d]pyrene	0.006	0.1	0.0006	4.5
Total	0.051		0.0135	100

Table 10. Concentrations (ng/g of wet weight) of hexachlorobenzene in edible marine species

Species	*HCB*	*Species*	*HCB*
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 11. Fish and seafood consumption and estimated intake of PCNs by the average adult man (70 kg body weight) in Catalonia, Spain

	Consumption (g/day)	*PCN intake (ng/day)*
Sardine	3.8	0.11
Tuna	10	0.24
Anchovy	2.1	0.05
Mackerel	1.1	0.11
Swordfish	0.06	0.004
Salmon	1.8	0.41
Hake	16	0.20
Red mullet	0.33	0.02
Sole	5.5	0.28
Cuttlefish	4.5	0.01
Squid	3.2	0.05
Clam	0.27	0.005
Mussel	0.97	0.02
Shrimp	3.5	0.02
Total	52.9	1.53

PAH intake corresponds to adult women and girls (5.3 and 5.2 ng/kg/day, respectively), while adolescent women and elderly women are the groups with the lowest PAH intake (3.3 ng/kg/day in both cases). Intakes of the seven PAHs considered as probable human carcinogens [40] from fish and seafood consumption by an adult man (70 kg body weight) are shown in Table 9. The benzo[a]pyrene (B[a]P) equivalents and the contribution of these seven PAHs to B[a]P equivalents are also shown. To calculate B[a]P equivalents, the TEFs adopted by the US EPA [40] were used. According to the current results, the estimated daily intake of seven PAHs (benzo[a]pyrene and six other probable human carcinogens) through the consumption of 14 edible marine species would be associated with a $0.27/10^6$ increase in the risk of developing cancer in an adult man (body weight of 70 kg) [31].

HCB concentrations in the 14 edible marine species are summarized in Table 10. The highest HCB levels were found in salmon and mackerel: 1.68 and 0.80 ng/g wet weight, respectively. Red mullet and sole also showed 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). The highest and lowest HCB intakes (ng/day) correspond to adult women (13.3) and girls (4.0), respectively. For most groups, salmon and sole are the species contributing most to HCB intake. When HCB intake is calculated according to average body weight for each group, the highest and lowest values correspond to boys (0.32 ng/kg/day) and adolescent girls (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 [2]. For cancer effects, the daily HCB intake due to fish and seafood consumption represents a maximum of 0.20% of TDI (boys), and a minimum of 0.09% (adolescent girls). These results indicate that the intake of HCB through fish and seafood should not be a health concern for consumers [26].

The highest concentration (ng/kg of ww) of total PCNs was observed in salmon (227), followed (at a considerable distance) by mackerel (95) and red mullet (68). By contrast, cuttlefish (3) and shrimp (5) showed the lowest concentrations of total PCNs [32]. With the exception of cephalopods and shellfish (squid, cuttlefish, mussel, clam and shrimp)–species for which tetraCN was the predominant homologue–there was a predominance of pentaCN. The mean percentage contribution of this group to total PCNs is 60%, followed by that of tetraCN, 33%. The fish and seafood intake of PCNs for the average adult man living in Catalonia is given in Table 11. Total PCN intake is 1.53 ng/day. The highest contributions (ng/day) to this intake correspond to salmon (0.41), sole (0.28) and tuna (0.25), while the lowest PCN intakes correspond to swordfish (0.004) and clam (0.005). By fish and seafood groups, oily fish (sardine, anchovy, tuna, mackerel, swordfish and salmon) contribute 60% to the daily intake of PCNs, followed by white fish (hake, red mullet and sole), and cephalopods and shellfish (squid, cuttlefish, clam, mussel and shrimp); 33% and 7%, respectively. Although these results do not seem to suggest any health risks arising from exposure to PCNs through fish and seafood consumption, the paucity of information concerning PCN toxicity, as well as the lack of information on the contribution of individual PCN congeners to total TEQ clearly indicate the necessity to research these important issues. To estimate the contributions of PCNs to total TEQs it is essential to assess human health risks derived from exposure to dioxin-like POPs [32].

In the case of PCDD/PCDFs and PCBs, the highest levels for both groups of these POPs were found in red mullet, followed by salmon and mackerel for PCDD/PCDFs, and by sardine and anchovy for PCBs. The lowest PCDD/PCDF and PCB concentrations were detected in cuttlefish and shrimp, respectively. The highest total TEQ values corresponded to red mullet followed by anchovy and sardine, while the lowest values were found in cuttlefish, and shrimp and clam. In general terms, the species of oily fish showed higher concentrations of PCDD/PCDFs and PCBs than those of white fish, cephalopods, and shellfish [9]. The intakes (pg WHO-TEQ/day) of PCDD/PCDFs and dioxin-like (DL)-PCBs through fish and other seafood consumption were estimated for the eight population groups. Adult men, followed by adult women and elderly men have the highest intake of PCDD/PCDF plus DL-PCBs: 36.5, 33.3 and 33.1 pg WHO-TEQ/day, respectively. In con-

Table 12. Estimated intake of PCDD/PCDFs and DL-PCBs (pg WHO-TEQ/day) from fish and seafood consumption by the average adult man (70 kg body weight) living in Catalonia, Spain

Consumption (g/day)		*PCDD/PCDFs*	*DL-PCBs*	*PCDD/PCDF/ DL-PCBs*
Sardine	3.78	0.83	4.50	5.33
Tuna	10.1	1.90	11.9	13.8
Anchovy	2.05	0.39	2.54	2.93
Mackerel	1.13	0.26	1.00	1.26
Swordfish	0.06	0.004	0.03	0.03
Salmon	1.80	0.43	1.56	1.99
Hake	15.8	0.58	5.41	5.99
Red mullet	0.33	0.16	1.37	1.53
Sole	5.48	0.69	1.31	2.00
Cuttlefish	4.46	0.13	0.08	0.21
Squid	3.17	0.30	1.93	2.23
Clam	0.27	0.01	0.01	0.02
Mussel	0.97	0.13	0.24	0.37
Shrimp	3.53	0.20	0.12	0.32
Total	52.94	6.02	31.98	38.0

trast, the lowest daily intakes correspond to children: 20.4 and 16.2 pg WHO-TEQ for boys and girls, respectively. However, when the daily intakes of PCDD/PCDFs plus DL-PCBs are estimated according to average body weight for each group, children (0.85 and 0.71 pg WHO-TEQ/kg body weight/day for boys and girls, respectively) show the highest values, whereas the elderly women and adolescents boys have the lowest intakes of PCDD/PCDFs plus DL-PCBs. On average, for the average adult man (70 kg body weight), the daily intake of PCDD/PCDFs and DL-PCBs from fish and seafood consumption is estimated to be 6.02 pg WHO-TEQ for PCDD/PCDFs, 31.98 pg WHO-TEQ for DL-PCBs, and 38.0 pg WHO-TEQ for the sum of both PCDD/PCDFs and DL-PCBs (Table 12). Tuna, followed by hake and sardine, contribute most to total TEQ intake. Considering only the intake of DL-PCBs, a similar sequence could be observed. PCDD/PCDFs show a different profile in the contribution of marine species to total TEQ intake. Tuna showed the highest contribution, followed by sardine and sole. Although red mullet was the species with the most important concentrations of PCDD/PCDFs and PCBs, this white fish does not make an important contribution to total TEQ intake (Table 12). The highest contribution to the daily intake of PCDD/PCDFs and DL-PCBs (pg WHO-TEQ/day) corresponds to oily fish, 67% of total TEQ, followed by white fish (25%) [9].

Conclusions

Calculations based on dietary data from Catalonia [36], show that the estimated daily intakes by the average 70-kg adult man of As, Cd, Pb and Hg from fish consumption are below the respective PTWI values [28]. With respect to the organic pollutants, the intake of PCDD/PCDFs plus DL-PCBs is estimated to be 38.0 pg WHO-TEQ/day, being tuna, hake, and sardine the main contributors. The TDI for these compounds established by the WHO for non-carcinogenic effects is 1-4 pg TEQ/kg body weight. PBDE and PCDE intakes are 20.8 and 39.4 ng/day, respectively. The highest contributions correspond to tuna, salmon, and hake for PBDEs, and tuna, hake, and sardine for PCDEs. PCN intake is 1.53 ng/day, with salmon, sole, and tuna contributing the most. TDI values for PBDEs, PCDEs and PCNs have not yet been established. HCB intake is estimated to be 11.5 ng/day. This value is considerably lower than the WHO-TDI: 0.17 μg/kg/day for non-cancer effects, and 0.16 μg/kg/day for neoplastic effects [2]. Finally, PAH (16 compounds) intake is 268 ng/day. The intake of benzo[a]pyrene and six other PAH probable human carcinogens through consumption of the above species is associated with a $0.27/10^6$ increase in the risk of developing cancer over a 70-year lifespan. The main contributions to the intake of the carcinogenic PAHs come from shrimp, hake, and tuna.

Most marine species analyzed here should not cause adverse health effects for consumers [20]. However, the type of fish, the frequency of consumption, and the meal size are essential issues for weighing up the health benefits and risks of regular fish consumption. To quantitatively compare the intake of chemical pollutants (risks) versus that of the omega-3 fatty acids eicosapentaenoic acid (EPA) and docosohexaenoic acid (DHA) (benefits), we have designed a simple computer program, RIBEPEIX. The concentrations of EPA, DHA, and the chemical pollutants were introduced into the program. RIBEPEIX may be easily used as a tool to optimise fish consumption: most suitable species, frequency of consumption, and size of meals. RIBEPEIX can be useful not only for professionals (cardiologists, general physicians, nutritionists, toxicologists, etc.), but also for the general public. It is available at: htpp://www.fmcs.urv.cat/portada/ribepeix/ [21].

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