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Organochlorine Residues in Fish Oil Dietary Supplements.

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INTRODUCTION

Fish oil accounts for around 2% of the total world production of oils and fats, currently estimated at 80 million tonnes[1]. The largest use of fish oil is in the partially hydrogenated form in the baking industry, principally in Europe. Pharmaceutical grade nutritional supplements commanded a market of 50 million pounds sterling in 1992 in the UK[2]. Total 1992 UK production of refined fish oils was estimated at 108.6kt (Burt pers. comm.) for all uses.

In the case of cod liver oil, 3 basic grades are produced. Concentrates can be also be produced by extraction of the oils from the comminuted bodies of whole fish[3] and these are used for a range of purposes similar to fish liver oils. Organochlorine contaminants present in fish oils available from retail outlets have not apparently been subjected to independent scrutiny. This study reports the results of analysis of 22 samples of oil obtained through retail outlets in a number of countries as sold for dietary purposes and industrial applications. These values are compared with those obtained from fish oils reported in other studies. The potential contribution of fish oils to dietary intakes of organochlorines under normal conditions and under prescribed medical regimes is discussed.

MATERIALS AND METHODS

5ml of HPLC grade hexane (Rathburn Chemicals) were added to 1ml of fish oil sample contained in a precleaned glass universal and shaken to effect complete dissolution. 2ml of concentrated Aristar grade sulphuric acid was added to the vessel, mixed thoroughly to ensure destruction of the lipid content and the mixture allowed to stand until the hexane and acid layers separated. This extract was cleaned up on a column packed with 0.8g active, neutral, Brockmann grade 1 aluminium oxide (BDH, Poole). The column was eluted with hexane until 5ml of eluate had been collected and 1ml of this was transferred to a glass vial. To this an internal standard of 2,6-dichlorobenzonitrile was added to give a concentration of 0.04 $\mu g\ ml^{-1}$ and the extract analysed. Chromatographic analysis was carried out using a Varian 3400 gas chromatograph (GC) equipped with an 8035 autosampler and electron capture detector (ECD). The GC was fitted with two 30m DB210 columns (J&W Scientific) of 0.253mm internal diameter and 0.25µm phase thickness, connected in series using a 4m deactivated retention gap.

Identification and quantification of analytes was by comparison with prepared calibration standards. ΣPCB values were derived from comparison with a standard of the PCB formulation Aroclor-1254. Recoveries of analytes from the alumina columns were checked and exceeded 96% in every case. In addition, analyses were conducted of cod liver oil standard reference materials (SRM) using the same analytical methodology. In order to facilitate comparisons between the data expressed here in µg/l with previously published data expressed in µg/kg, densities of oils were determined gravimetrically. These were found to lie between 0.911 and 0.937 g ml^{-1}.

RESULTS

With the exception of sample 16, a marine lipid concentrate, all samples of fish oils examined contained detectable residues of organochlorine contaminants. Mean values, standard errors and ranges of the specific analytes are shown in TABLE 1. The values obtained for cod liver oil are generally lower by an order of magnitude than those reported for the Baltic[4]. The oil (Sample 18) derived from the Iceland Shelf is described as a fish oil and is not therefore directly comparable with the previously published values (see: TABLE 1). The highest overall contaminant concentrations were found in a salmon oil preparation (Sample 9). This may not be representative of the natural content of salmon oil since this oil may be extracted using pilchard or Greyfish oil[5] followed by simple centrifugation to separate the oil mixture. More probably, however, this reflects the use of farmed salmon reared in coastal waters and fed on synthetic foods which contain between 15 and 30% added fish oil (Sargent pers. comm.). In addition, it is common practice to feed farmed salmon the viscera of processed individuals.

ANALYTE	HCB	α-HCH	γ-HCH	ΣDDT	ΣPCB
Range	N/D-46	N/D-93	N/D-20	N/D-148	N/D-1132
Mean	9.1	13.1	3.0	66.0	479.0
SError	2.4	4.4	1.0	11.8	89.0
Slce	73-100	42-71	5-9	650-950	1.9*
Mean	87	53	6	860	-
SBalt	170-370	280-400	100-160	3100-12000	8100-16000
Mean	280	320	140	6300	10

TABLE 1: Values of the range, mean and standard error about the mean for organochlorine contaminants present in fish oil shown in µg/l. N/D denotes analyte undetected. n=22 (17 pharmaceutical grade, 4 industrial grade, 1 veterinary grade). Lower section of table shows comparative values in µg kg^{-1} for fish oils sampled between 1984 and 1989 from the Shelf of Iceland (Slce) and Southern Baltic (SBalt) (Ref 6). * Denotes a single value. ΣDDT values not directly comparable due to summation of different isomers in each case.

After the salmon oil, cod liver oil samples were the most highly contaminated, although this group of 8 also contained the second least contaminated oil (Sample 3). Products described as fish oils (Samples 1,2,3,4 & 5), including an industrial grade sandeel oil, had intermediate to low levels of contamination together with the halibut liver oil (Sample 12). According to the list of ingredients the packaging for Sample 12, this oil was a mixture of unknown proportions of halibut liver oil and soya oil. The levels of contaminants found therefore cannot be regarded as representative of halibut liver oil alone. No organochlorine contaminants were detected in Sample 16. Comparatively low concentrations were found in Sample 11, another marine lipid concentrate, comparable with Sample 3.

Quantitatively, the dominant contaminants were the PCBs, followed by DDT and its metabolites DDE and TDE. Hexachlorobenzene (HCB) and hexachlorcyclohexane (HCH) isomers were lesser components of the overall contaminant content and were absent from many samples. The levels of contaminants present in the industrial and veterinary grade oils do not appear markedly different from concentrations present in those oils designated as pharmaceutical grade.

DISCUSSION

Results from the analysis of fish oils indicate that none exceed the 2.0 ppm regulatory limits specified for foodstuffs by a number of authorities including the US Food and Drug Administration (see:[7]) although in some cases the 1.0 ppm limit specified in Switzerland is exceeded. In the UK there are no specific legal requirements relating to the PCB content of food, including fish oils, except for the general provision enshrined in the Food Safety Act (1990) that commodities should be safe for human consumption. Further, there appear to be no specific limits set for pesticide residues for fish oils in the UK. Similarly, the Codex Alimentarius published by the United Nations World Health Organisation appears to contain no recommendations for limits on organochlorine pesticides or PCBs in fish oils although oils derived from fish and marine mammals are recognised as a commodity group[8].

The results obtained in this study suggest that despite controls on the use of persistent organochlorine substances and the possible introduction of manufacturing refinements to remove them, appreciable quantities of these contaminants are found in pharmaceutical and industrial grade oils available on the open market. There appears to be little regulatory control and few advisory limits appear to have been published. Many of these oils are intended for dietary uses by the healthy consumer.

TABLE 2 shows the manufacturer's recommended daily consumption of fish oil as indicated on the relevant packaging together with an intake figure for total PCBs and DDT calculated from the results obtained by analysis of the specific packaged products. TABLE 3 shows published estimated daily intakes of PCBs from dietary sources[9].

On the basis of the calculated results presented in TABLE 2, consumption of fish oil at manufacturers recommended levels can result in daily intakes of PCBs between 0.009 and 4.5 μg day^{-1} or between 0.12×10^{-3} and 0.064 μg kg body $weight^{-1}$ day^{-1}. This excludes Samples 3, 5 and 16 in which PCBs were not detected. At the highest level this exceeds many of the estimates presented in TABLE 3. At intermediate levels of recommended intake or with excedence of recommended consumption levels, fish oils could account for a significant proportion of estimated PCB intakes. The wide variation in contaminant levels in the oils together with the varied recommended intakes means that a meaningful comparison using the mean value calculated is not possible. On the basis that Sample 9 of salmon oil represents a worst case at an intake of 0.064μg kg body $weight^{-1}$ day^{-1}, then this represents a potential contribution of between 7 and 12800% of the estimated daily intakes given in TABLE 3. This also constitutes 6.4% of the US FDA Maximum Consumption Guideline of 1μg kg body $weight^{-1}$ day^{-1} [9]. This estimate considers only the possible contribution from fish oils used as dietary supplements.

NO	COUNTRY OF ORIGIN	TYPE	RECOMMENDED DAILY INTAKE (ml)	ΣPCB DAILY INTAKE (μg)	ΣDDT DAILY INTAKE (μg)
1	Norway	FO	5-7	2.85-3.99	0.74-1.036
2	Norway	FO	5	2.2	0.32
3	Norway	CL	5	N/D	0.01
4	Japan	FO	0.25	0.08	0.02
5	Japan	FO	0.3	N/D	0.0005
6	Spain	CL	0.2-1.2	0.05-0.31	0.01-0.08
7	Spain	CL	-	-	-
8	UK	CL	1	0.99	0.12
9	UK	SO	4	4.5	0.56
10	UK	CL	0.25	0.12	0.02
11	UK	MLC	1-6	0.01-0.06	0.004-0.024
12	UK	HL	0.25	0.009	0.0007
13	UK	CL	0.54	0.56	0.074
14	UK	CL	1	0.014	0.006
15	UK	CL	0.54	0.57	0.074
16	UK	MLC	2-8	N/D	N/D
17	UK	CFO	1-4	0.92-3.66	0.058-0.232

TABLE 2: Daily dietary intakes of pharmaceutical grade fish oil recommended by product manufacturers. Total PCB and DDT intake are shown as calculated from the analytical determinations presented in TABLE 1. (-) Indicates that recommended dosage is not known. Abbreviations: FO: Fish oil; CL: Cod liver oil; MLC: Marine Lipid Concentrate; HL: Halibut liver oil; CFO: Fish oil concentrate; SO: Salmon oil. Descriptions are those given by the manufacturer/supplier.

COUNTRY	YEAR	ESTIMATED INTAKE (μg kg b.w^{-1} day^{-1})	CALCULATED TOTAL (μg day^{-1})
AUSTRALIA	1987	0.002	0.14
FINLAND	1984	0.21	14.7
	1993*	0.25	15.0
	1994*	0.03	2.3
GUATEMALA	1988	0.012	0.84
JAPAN	1988	0.045	3.15
NETHERLANDS	1984	0.2	14.0
NEW ZEALAND	1982	0.9	63.0
SWITZERLAND	1983	0.12	8.4
UK	1981	0.0005	0.035
	1995**	0.0076	0.53
USA	1988	0.001	0.07

TABLE 3: Estimated intake of PCBs in μg kg body weight^{-1} day^{-1} and calculated total intake of PCBs based upon data submitted as part of the UNEP/FAO/WHO Food Contamination and Assessment Programme and reported in Reference 9. Body weight figure of 70kg assumed in the calculation except for (*) where 60kg applies. * & + denote estimates derived by two different research groups in Finland (*: Reference 10; +: Reference 11. ** Values taken from Reference 12.

Fish oils have also been identified as of potential therapeutic value due to their high content of omega-3 fatty acids and their contents of vitamin A, D & E. The treatment of rickets and promotion of wound healing using fish oil is well known[4] but fish oils have also been investigated as agents for the treatment and prevention of *inter alia* cardiovascular disease[13,14,15,16] rheumatoid arthritis[17], hypertension[18,19,20], psoriasis[21] and colon cancer[22]. The quantities of fish oil used in therapeutic applications may contribute substantially to intake of organochlorine contaminants even when the oils are only moderately contaminated. Excluding the emulsion supplied intravenously, daily volumes prescribed range between 6 and 50ml of oil. At the highest contamination level of 1132 μg l^{-1} this translates to a total intake of up to 56.6 μg day^{-1} or about 80% of the US FDA Consumption Guideline. Again, this does not consider intakes from other dietary sources.

CONCLUSION

In conclusion, the levels of organochlorine contaminants present in fish oils from various sources could constitute a significant contribution to daily intakes of these compounds, particularly the PCBs used as an example in this case. This is without consideration of other potential dietary sources of PCBs and other organochlorines. Those consuming large quantities of fish oils for therapeutic purposes may have substantially higher intakes. It follows that contamination of fish oils requires careful monitoring if they are intended for use as a dietary supplement, therapeutic agent or in the preparation and manufacture of other foodstuffs.

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