

Persistent Organochlorine Residues in Canned Cod-Livers of the Southern Baltic Origin

Jerzy Falandysz, ¹ Kurunthachalam Kannan, ² Shinsuke Tanabe, ² and Ryo Tatsukawa ²

¹Research Group of Environmental Chemistry and Toxicology, Department of Chemistry, University of Gdańsk, ul. J. Sobieskiego 18, PL 80-952, Gdańsk, Poland and ²Department of Environment Conservation, Ehime University, Tarumi 3-5-7, Matsuyama 790, Japan

The use of organochlorine compounds in industry and agriculture has led to the contamination of foodstuffs, especially those having Codfish liver from the Baltic Sea, which higher fat contents. 35% of lipid, remained unfit contains more t.han for human consumption from 1969 until recently because \mathbf{of} contamination by PCBs, DDTs, HCHs and HCB residues (Falandysz Hence processing of the livers of Baltic cods was banned in Poland in the early 1980s (Falandysz 1986). However, the cod-livers "Watróbka Kaukasku" rybna po appeared again in the Polish market. We have previously reported the presence of considerable levels of toxic coplanar PCB congeners in these products (Falandysz et al. 1992).

A recent investigation of cod-liver oils of the southern Baltic origin reported a steady state in the residue levels of most of the organochlorine pesticides except DDTs, implying a continuous input of certain organochlorine contaminants from eastern European countries (Kannan et al. 1992a). This situation prompted us to examine a wide range of organochlorine pollutants in the canned cod-livers marketed recently.

MATERIALS AND METHODS

Canned cod-livers, Watróbka rybna po Kaukasku, examined in this study were processed commercially by a company, Zakłady Rybne, in Gdańsk, Poland. Basic ingredients in the net weight of 105 g container included tomato concentrate, garlic paste and table salt. The cod-livers used for processing were taken during January - March 1990 from cod caught in the Polish exclusive economic zone in the Baltic Sea.

Contents of the cans were well ground and ca 15-20 g sample was used for the analysis of PCBs, DDTs, HCHs, HCB, aldrin, dieldrin, heptachlor, heptachlor epoxide and chlordanes. Details of the analytical procedure have been mentioned elsewhere (Kannan et al. 1992b). In short, the method consists of Soxhlet extraction with

Send reprint requests to Prof. J. Falandysz at the above address.

diethyl-ether and hexane for 7 h followed by the removal of fat by eluting through a dry Florisil column. Clean up and fractionation were performed using silica gel packed in a glass column. Samples were then treated with 5% fuming sulfuric acid and injected into a capillary GC-ECD for quantification.

RESULTS AND DISCUSSION

High concentrations of PCBs and DDTs were recorded in all the three samples even though the values observed for other organochlorine pesticides are lower (Table 1).

Table 1. Organochlorine pesticide and PCB contents (ng/g wet wt; n=3) of canned cod-livers from the southern Baltic

Compound	X ± SE	Range
 PCBs	2,000 ± 400	1,200-2,600
DDTs	$1,000 \pm 140$	830-1,400
o,p'-DDT	1.8 ± 0.1	1.6-1.9
p,p'-DDT	0.7 ± 0.2	0.4 - 1.0
p,p'-DDD	320 ± 36	270-410
p,p'-DDE	740 ± 100	560-990
HCB	60 ± 6	50-76
HCHs	54 ± 3	51-61
α-HCH	22 ± 1	19-24
B-HCH	26 ± 2	22-30
γ -HCH	3.4 ± 0.1	3.3-3.5
δ-HCH	3.2 ± 0.6	1.8-4.1
CHLs	24 ± 5	12-30
α-chlordane	5.3 ± 1.2	2.6-7.1
γ-chlordane	1.3 ± 0.2	1.0-1.8
cis-nonachlor	8.0 ± 1.7	3.8-11
trans-nonachlor	1.9 ± 0.2	1.3-2.2
oxychlordane	7.0 ± 1.6	3.1-9.6
Heptachlor	<1.0	<1.0
Heptachlor epoxide	4.2 ± 0.1	3.9-4.4
Aldrin	7.3 ± 0.4	6.7-8.3
Dieldrin	56 ± 2	50-60
Fat (%)	42 ± 1	41-43

The livers of cod from the southern part of the Baltic Sea, because of the extensive contamination by PCBs and DDTs residues have been banned as a food item at first in Sweden (Westöö and Norén 1970) and soon after in Denmark (Dybern and Jensen 1978) and in Poland in 1983 (Falandysz 1984). The tolerance limits established for seafoods, particularly cod-livers in different countries have been: 2,000 ng/g (USA) or 5,000 ng/g (in Sweden) for PCBs; 500 ng/g (Finland) or 5,000 ng/g (Denmark, Sweden, Germany and Canada) for DDTs; 100 ng/g (Finland) or 200 ng/g

Table 2. Estimated annual intake of organochlorines from codlivers in Poland (μ g/person/annum)

Compound	per e	per capita consumption (g/yr)			
	10	105*	95-160 [*]		
PCBs	20	210	190-320		
DDTs	10	105	95-160		
HCB	0.60	6.3	5.7-9.6		
HCHs	0.54	5.7	5.1-8.6		
CHLs	0.24	2.5	2.3-3.8		
Heptachlor	<0.01	<0.11	<0.1-<0.2		
Heptachlor epor	xide 0.042	0.44	0.4-0.67		
Aldrin	0.07	0.77	0.7-1.2		
Dieldrin	0.56	5.9	5.3-9.0		

^{*105}g for Watróbka rybna po Kaukasku and 95-160g for other kinds of canned cod-liver products. The these two consumption quantities are calculated based on cod-liver production and the existing population.

Table 3. Reported concentrations (ng/g wet wt) of PCB and DDT residues in cod-livers from different parts of the world

Locality	Year	PCBs	DDTs	Reference
Halifax, Nova Scotia	1980	240-4,300	530	Freeman et al. (1984)
Antarctic	1977	10	37	Ballschmiter and Zell (1980)
North Sea	1987	-	800	Boer (1989)
Norwegian fjord	1982	450	1,100	Skåre et al. (1985)
Northern Baltic	1985	1,370	490	Haahti and Perttilä (1988)
Baltic proper	1983	7,200	2,600	Falandysz (1986)
Southern Baltic	1981	3,700-65,000	220-15	,000 Falandysz (1984)
Southern Baltic	1990	2,000	1,000	present study

(Sweden) or 500 ng/g (Germany - fat wt basis) for HCHs; 100 ng/g (Finland and Sweden) or 1,000 ng/g (Germany - fat wt basis) for aldrin and dieldrin; 200 ng/g (Sweden) or 500 ng/g (Germany - fat wt basis) for HCB; 10 ng/g (Germany) or 100 ng/g (Finland) for chlordanes and 50 ng/g (Germany) or 100 ng/g (Finland) for heptachlor and its epoxide (refer NPRLF 1990; SFR 1983). In light of these tolerance limits, it is explicable that the PCBs and chlordanes have exceeded the prescriptions (i.e., concentrations recorded in few samples in this study are above 2,000 and 10 ng/g respectively). The concentrations recorded for other organochlorine pesticides are high especially with regard to aldrin and dieldrin, considering their greater mammalian toxicity.

The proportion of α -HCH in the total HCH concentration is relatively large indicating a recent input of HCH to the southern Baltic. In fact, earlier studies also indicated such a greater α -to γ -HCH ratio in cod liver oils and biological samples from the southern Baltic (Kannan et al. 1992a). Probably, HCH transported through atmosphere from point source areas is deposited in this region. Local contamination arising from the use of HCH in the southern Baltic nations is also a source.

It had been reported that the production of canned cod-livers in Poland in 1978-82 was between 181 and 466 tonnes annually, with the average consumption per capita being 10g (ranges from 5.0 to 13g) (Falandysz 1987). However, canned cod-livers are consumed in larger amounts by the employees of the processing industries and others dealing with the production and marketing of these commodities. Similarly, relative preference is given to processed fishermen and coastal inhabitants due to cod-livers by The intake of persistent organochlorines from such contaminated seafood might be of toxic concern to these high-risk It was estimated that the 5% of Polish population consumes one can of processed cod-liver per annum (ca. 100 g) (Falandysz 1987). Table 2 while 1% ingests five cans every year shows the estimated annual intakes of organochlorines from canned cod-livers using different theoretical consumption rates. Due to low average consumption of the product, the organochlorine intake is small. When the higher consumption rates such as 53 g of fish/day, as observed in Finland (Moilanen et al. 1986) is applied for the dietary intakes of organochlorines, potential health effects on humans is evident. This particular case is applicable in Poland for the high-risk groups as mentioned above. It has been estimated that the high-risk groups consuming more than five cans of cod-liver could exhibit (950-1,600 μ g/yr for PCBs; 475-800 μ g/yr for DDTs; 29-48 μ g/yr for HCB; 26-46 μ g/yr for HCHs; 12-19 μ g/yr for chlordanes; 2.0-3.4 μ g/yr for heptachlor epoxide and 31-51 μ g/yr for aldrin and dieldrin) greater degree of exposure to these toxic contaminants. Even with the smaller consumption rate of 10 g/year of cod-liver, annual PCB intake is For example, in Canada the higher than in developed nations. total annual consumption of PCBs is only 32 μ g when the ingestion from all the food groups are taken into account (Davies 1988). Intake of 20 μ g from cod-liver alone in Poland is found to be significantly high. Considering these informations, canned codlivers are likely to impose problems to human health when consumed at higher amounts.

In order to compare the concentrations of PCBs and DDTs observed in this study with those published from other parts of the world we have summarized the data in Table 3. It is clear from the table that the concentrations observed in this study are much higher than those reported elsewhere. Higher levels of PCBs in the Baltic deserves attention as most of the recent investigations also encountered a higher contamination of the Baltic biota.

Acknowledgments. This research was supported by the Japanese Society for the Promotion of Science (JSPS) under the long-term visiting professor fellowship awarded to Dr. J. Falandysz, and partly by the Polish State Committee for Scientific Research (KBN) under grant DS.

REFERENCES

- Ballschmiter K, Zell M (1980) Baseline studies of the global pollution. I. Occurrence of organohalogens in pristine European and Antarctic aquatic environments. Intern J Environ Anal Chem 8: 15-35.
- Boer J (1989) Organochlorine compounds and bromodiphenylethers in livers of Atlantic cod (*Gadus morhua*) from the North Sea, 1977-1987. Chemosphere 18: 2131-2140.
- Davies K (1988) Concentrations and dietary intake of selected organochlorines, including PCBs, PCDDs, PCDFs in fresh food composites grown in Ontario, Canada. Chemosphere 17: 263-276.
- Dybern BI, Jensen S (1978) DDT and PCB in fish and mussels in the Kattegat-Skagerrak area. Meddlande från Havsfiskelaboratoriet, Lysekil no: 232
- Falandysz J (1984) Organochlorine pesticides and polychlorinated biphenyls in livers of cod from the southern Baltic, 1981. Z Lebensm Unters Forsch 179: 311-314.
- Falandysz J (1986) Organochlorine pesticides and polychlorinated biphenyls in livers of cod from the southern Baltic, 1983. Z Lebensm Unters Forsch 182: 224-227.
- Falandysz J (1987) Badanię wystepowania pozostałości polichlorowanych dwufenyli (PCB) w żywności pochodzenia morskiego oraz próba oszacowania dziennego spożycia tych związków w Polsce w latach 1970–1982. Stud Mat Mor Ins Ryb Ser D no:16.
- Falandysz J, Yamashita N, Tanabe S, Tatsukawa R (1992) Isomerspecific analysis of PCBs including toxic coplanar isomers in canned cod livers commercially processed in Poland. Z Lebensm Unters Forsch 194: 120-123.
- Freeman HC, Uthe JF, Silk PJ (1984) Polychlorinated biphenyls, organochlorine pesticides and chlorobenzenes content in livers from Atlantic cod (*Gadus morhua*) caught off Halifax, Nova Scotia. Environ Monitor Assess 4: 389-394.
- Haahti H, Perttilä M (1988) Levels and trends of organochlorines in

- cod and herring in the northern Baltic. Mar Pollut Bull 19: 29-32.
- Kannan K, Falandysz J, Yamashita N, Tanabe S, Tatsukawa R (1992a) Temporal trends of persistent organochlorine concentrations in cod-liver oil from the southern Baltic proper, 1971-1989. Mar Pollut Bull 24: 358-363.
- Kannan K, Tanabe S, Ramesh A, Subramanian AN, Tatsukawa R (1992b) Persistent organochlorine residues in foodstuffs from India and their implications on human dietary exposure. J Agric Food Chem 40: 518-524.
- Moilanen R, Pyysalo H, Kumpulainen J (1986) Average total dietary intakes of organochlorine compounds from the Finnish diet. Z Lebensm Unters Forsch 182: 484-488.
- NPRLF (1990) National Pesticide Residue Limits in Foods. Chemical Evaluation Division, Bureau of Chemical Safety, Food Directorate, Health and Welfare Canada.
- SFR (1983) Swedish Food Regulations Foreign substances in food, The National Swedish Food Administration, SLVFSV.
- Skåre JU, Stenersen J, Kveseth N, Polder A (1985) Time trends of organochlorine chemical residues in seven sedentary marine fish species from a Norwegian Fjord during the period 1972-1982. Arch Environ Contam Toxicol 14: 33-41.
- Westöö G, Norén K (1970) Klorpesticid- och polyklorbifenylhalter i fisk fångag i svenska vatten eller saluförd i Sverige 1967-1970. Vår Föda 22: 93-146.

Received March 20, 1992; accepted December 10, 1992.