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Contamination of Native Fish Stock by Hexachlorobenzene and Polychlorinated Biphenyl Residues

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Polychlorinated biphenyls (PCB) were first identified as an environmental contaminant in 1966. Their danger to human health became evident in 1968 through the so-called "Yusho incident" when more than 1600 people became ill after consuming rice oil which was contaminated with PCB (KURATSUNE 1980).

In addition to its acute toxity, PCB have been shown to be carcinogenic. SCHÄFFER et al. (1981) observed preneoplastic changes, neoplastic nodules and carcinoma in the livers of rats which had been given peroral doses of highly and less-highly chlorinated biphenyls.

Due to their great chemical stability, PCB are practically indestructible, even at high temperatures. From waste and garbage disposal plants they contaminate ground, water and atmosphere and reach, by way of raw materials, the food-chain. Particularly the higher chlorinated PCB, which are resistant to biotransformation, accumulate in the food-chain and are assimilated. Practically all foodstuffs of animal origin available at the present time contain residues of PCB. The compounds have been detected, for example, in pork and beef (BOISELLE and LANGNER 1981), in fish from the north Atlantic (BALLSCHMITER and ZELL 1980) and in seafood from the Mediterranean (KILIKIDIS et al. 1981, BRUNN et al. 1981).

Hexachlorobenzene (HCB) is incorporated in human food in the same way as PCB. It is of similar stability and is apparently also carcinogenic (SMITH and CABRAL 1980). Although its use as a seed preservative has been prohibited in West Germany since 1977, HCB enters the environment as a by-product of the industrial production of other chlorinated hydrocarbons.

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The contamination of salt-water fish with chlorinated hydrocarbons is particularly dangerous in coastal fishing areas (Ernährungsbericht 1980). Inland waters are also a pool for these compounds, as is proven, for example, through studies on fresh-water fish in France (KECK and RAFFENOT 1978) and Norway (BREVIK 1981).

The goal of our study was to determine whether and to what extent fish in inland waters of West Germany are contaminated with HCB and PCB residues.

MATERIAL AND METHODS

72 samples of native fish of varying origins, which were sent to the Staatliche Veterinäruntersuchungsamt Gießen for disection in 1980 and 1981, were tested to determine their concentration of HCB and PCB. Chlophen A-60, a commercial product of Beyer AG with an average grade of chlorination of 60 % was used as a standard. A large majority of the fish were trout, most of which came from commercial trout farms, but a number of other species were also tested. All of the fish lived in rivers, streams or ponds in West Germany, whereby a distinction was made between ponds which are in connection with flowing water (ponds F) and thosewithout such a connection (ponds Q).

Fish muscle was homogenized and further treated according to the procedure of STEINWANDTER and BUSS (1975). The fraction containing chlorinated hydrocarbons was further purified on a polystyrol gel to remove any remaining fats (Chromatography on Bio-Beads S-X 3, Bio-Rad Laboratories, Munich, W. Germany). Separation of the chlorinated hydrocarbons was achieved through two gas chromatographs (Hewlett-Packard, Model 5710 with ^{63}Ni-electron capture detector) with a packed column and a capillary column.

Packed column: 1,5 % OV 17 and 1,95 % OV 210 on Gaschrom Q 80 - 100 mesh, length 4 m, internal diameter 2 mm; column temperatur 220°C, detector 250°C, injection port 250°C; gas flow 27 ml/min Argon/Methan (90/10) (OV 17, OV 210 and Gaschrom Q were from Applied Science Laboratories Inc., P.O.Box 440, State College, Penna.).

Capillary column: Fused Silica Capillary Column 12 meter, SP 2100, Carbowax desactivated (Hewlett-Packard). Carrier-gas: Helium pressure 0,7 bar, spitless-mode, start delay 30 sec, split ratio 1:10, Make-up-gas Argon/Methan (90/100), 40 ml/min. A linear temperature program was used from 140 - 220°C, 4°/min. The temperature of detector and injection port was 250°C.

All samples were analysed twice. The packed column was used for qualitative analysis, the quantitative analysis was done on the capillary column and evaluated as previously described (BRUNN et al. 1981).

Hexachlorobenzene and Chlophen A-60, for comparison, were obtained from S. and J. Ehrenstorfer, Augsburg, W. Germany. All other chemicals were from Merck, Darmstadt, W. Germany, in the quality: "zur Rückstandsanalyse".

RESULTS AND DISKUSSION

As shown in Table 1, almost 92 % of the fish analysed contained HCB.

Origin	Number of samples	Free of HCB	Contaminated with HCB
Rivers	10	4	6
Streams	29	2	27
Ponds F	20	0	20
Ponds Q	13	0	13
Total	72	6	66

Table 1: Frequency of occurence of hexachlorobenzene in fish from inland German waters
(Ponds F: ponds connected to flowing water)
(Ponds Q: ponds without connection to flowing water)

The average concentration of HCB in fat of the specimens tested (Table 2) is narrowly below 0,5 mg/kg, the legal allowance in West Germany, and is highest in fat of fish caught in rivers.

Origin	Fat	total weight
Rivers	0,463	0,013
Streams	0,275	0,006
Ponds F	0,391	0,002
Ponds Q	0,265	$<$ 0,001
Total	0,349	0,005

Table 2: Average concentration (mg/kg) of HCB in fat and based on total weight of the analysed fish

Comparison of the values of HCB contamination in fish from rivers, streams and ponds gives an impression of the contamination of the waterways. The majority of our samples was obtained from relatively small waterways. The surprisingly high contamination of small streams could be due to unfiltered sewage let into the streams by small communities.

The analysis of polychlorinated biphenyl residues of the same type as Chlophen A-60 gives light to a similar but more distinct picture.

PCB residues were found in all fish which were analysed. Table 3 shows the extent of contamination. Fish caught in rivers and streams contained PCB in concentrations higher than 0,5 mg per kilogram total weight.

Origin	Fat	total weight
Rivers	40,283	0,825
Streams	35,261	0,657
Ponds F	27,083	0,204
Ponds Q	7,148	0,130
Total	27,444	0,454

Table 3: Average concentration (mg/kg) of polychlorinated biphenyls (of the same type as Chlophen A-60) based on fat and on total weight

The distribution of contamination with PCB is demonstrated in Table 4. As already demonstrated in Table 3, it is evident that contamination is highest in fish living in rivers and streams, where almost all specimens contained more than 0,1 mg PCB per kilogram total weight.

Origin	>0,1	0,01 - 0,1	<0,01
Rivers	10	0	0
Streams	26	3	0
Ponds F	6	14	0
Ponds Q	3	8	2

Table 4: Distribution of PCB contamination in mg/kg total weight

In conclusion it may be said that the analysis of HCB and PCB residues in native fish demonstrates the degree of contamination in various bodies of water. These results should be reaffirmed through further tests including river fish which remain in a particular location. Further examinations should also be extended to include less highly chlorinated PCB of the same type as Chlophen C, which has replaced Chlophen A-60 in its usage in West Germany.

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