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Pesticides and Polychlorinated Biphenyls in Fish from the Lahn River

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In a previous paper we reported on the presence of chlorinated hydrocarbons in fish from local rivers, streams and ponds (Brunn and Manz 1982). Contamination levels of hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB) were determined and the PCB levels in fish from the various habitats were compared. In that report we concluded that analysis of such compounds in fish might provide a useful indicator for the degree of pollution of inland waters.

To reaffirm this conclusion as well as to establish whether contamination levels in fish populations could be used to locate sources of contaminants, we have now measured levels of a number of chlorinated hydrocarbons in fish from the Lahn, a river described as "moderately polluted" by local water authorities (Hessischer Minister für Landesentwicklung Umwelt Landwirtschaft und Forsten 1980). Two species of fish were chosen for their typical territorial behavior, that is, individual fish of these species remain in given domains along the river. We have added low-chlorinated biphenyls to the list of compounds analyzed since mixtures of these substances have been chosen to replace high-chlorinated biphenyls for various technical applications in Western Germany.

MATERIALS AND METHODS

The Lahn river, located in central Western Germany is 245 km long, flowing from north east to south west. For this study we chose a section of the river 106 km long beginning at the source, just north of Marburg. To obtain a relevant sampling of fish, 20 concecutively numbered points were chosen along

§ This paper is an essential part of the thesis of W. Schüler.
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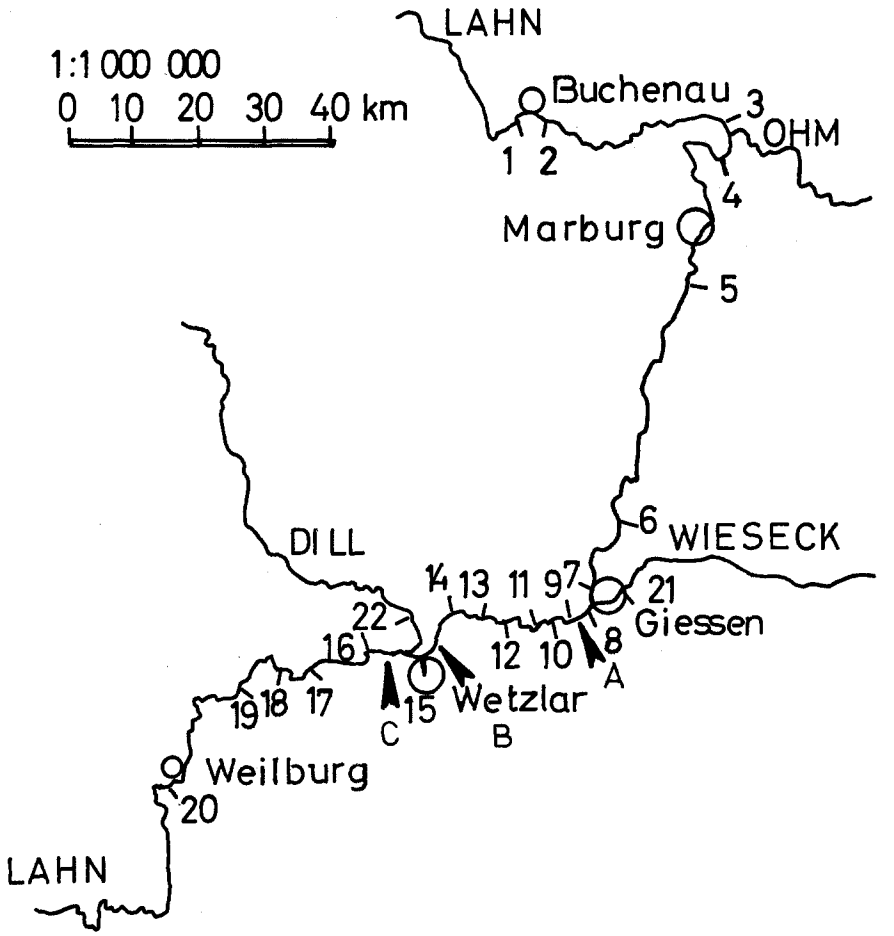

Fig. 1 Map of the Lahn with numbered collection points

The serially numbered points along the Lahn river were selected for collection of roach and perch. Points of possible contamination of the waterway are marked with an arrow-head.

the river. Two additional points, numbered 21 and 22, were selected at the mouths of two streams which flow into the Lahn (see Fig. 1).

Fish (roach and perch) were caught at the serially-numbered points along the Lahn. From the source to point 5 the river

flows through a rural agricultural area. South of point 5 the region becomes increasingly industrial. Two streams, the Ohm and the Wieseck and a river, the Dill flow into the Lahn along this stretch. The arrowheads denote potential sources of contamination; A and C, effluents of two municipal sewage plants and B, an influx of industrial waste water. Two species of fish, the roach (Rutilus rutilus L.) and the perch (Perca fluviatilis L.) were chosen for analysis since these species have been reported to show a pronounced territorial behavior (Ladiges and Vogt 1965; Muus and Dahlström 1981). In the fall of 1980 and spring of 1981, a total of 300 fish, 227 roach and 73 perch were caught at the various stations by means of electric shock. Fillets were cleaned and homogenized immediately or were frozen and stored at -20°C for further processing and qualitative gas chromatography as described elsewhere (Brunn and Manz 1982). For quantitative analysis, a fused silica capillary column (Hewlett Packard SP 2100, 25 M, Carbowax deactivated) was used. PCB peaks were positively identified by gas chromatography / mass spectrometry. Conditions for gas chromatography were as follows:

Splitless injection; start delay, 30 sec; split ratio, 1/10; linear temperature program, 140-220°C, 4°/min, 220°C isotherm; temperature of detector and injection port, 250°C; carrier gas, helium at 1.0 bar pressure; make-up gas, Argon/Methane (90/10) at 40 ml/min.

Samples were analyzed twice each for the following compounds: Hexachlorobenzene (HCB), pentachlorobenzene (PChB), α-, β- and γ-hexachlorocyclohexane (HCH), DDT and polychlorinated biphenyls (PCB). Since DDT cochromatographs with PCB on the columns used, DDT values were calculated from the breakdown product DDE which could be separated from other substances. Low-chlorinated biphenyls, marketed as Clophen C® by Bayer AG and referred to here as PCB-C and high-chlorinated biphenyls (Clophen A-60®) referred to as PCB-A-60 were analyzed separately. Pesticide values were evaluated as published previously (Brunn et al. 1981). For all values, scattering was reduced dependent upon absolute concentration as recommended by the German health authorities (Bundesgesundheitsblatt 1974).

Reference standards for chlorinated pesticides and Clophen A-60® were obtained from S. and E. Ehrenstorfer, Augsburg. Clophen C® was a gift of Bayer AG, Leverkusen. All other chemicals were from Merck, Darmstadt, of the grade, "for trace analysis" or from Riedel de Haën, Seelze, of the grade "pestanal".

Table 1 Occurence of pesticides and polychlorinated biphenyls in a total of 300 fish from the Lahn

	Frequency	
	Number of fish	Percentage
HCB	127	42
PChB	79	26
α-HCH	34	11
β-HCH	18	6
γ-HCH	92	31
DDT (as DDE)	273	91
PCB-C	300	100
PCB A-60	300	100

RESULTS AND DISCUSSION

The frequency of occurence of various chlorinated hydrocarbons in 300 fish analyzed, is shown in Table 1. All specimens were found to contain both low- and high-chlorinated biphenyls. The ubiquity of low-chlorinated compounds was unexpected since these substances were predicted to undergo environmental degradation and rapid excretion by animals (Schulte and Acker 1974). From the data obtained in the present study it must be assumed that this assumption is inaccurate and that inland waters can act as a pool for low-chlorinated biphenyls, providing an entry of these substances into the natural food chain. Recent routine investigations have also shown the presence of these compounds in nearly all game animals (see following report), poultry feed, chickens and eggs (Brunn unpublished observations).

DDE, an environmentally persistant decomposition product of DDT was detected in 91 % of all fish examined although use of DDT has been prohibited in Western Germany since 1972. HCB was found in 42 % and the HCB metabolite, PChB (Ingebrigtsen et al. 1981) in 26 % of all fish. HCB was banned as a pesticide in 1977, however, the compound continues to enter the environment as an industrial waste product (Courtney 1979). "Technical HCH", a mixture of α-, β-, γ- and δ-HCH was also banned from use as a pesticide in 1977; however, application of γ-HCH (Lindan®) is still permitted with certain restrictions. As a consequence of this disparate regulation, 31 % of all fish were contaminated with γ-HCH but only 11 % with α- and 6 % with the β-isomer.

Table 2 Contamination levels of various pesticides and polychlorinated biphenyls in fish

Substance	Average concentration Mean values [mg/kg body weight]	Spread of absolute values	Maximum permissable level
HCB	0.001	0.0 -0.233	0.050
PChB	trace levels	-	0.010
α-HCH	trace levels	-	0.050
β-HCH	trace levels	-	
γ-HCH	0.001	0.0 -0.002	0.200
DDT	0.023	0.0 -0.179	2.000
PCB-C	0.463	0.102-1.120	unspecified
PCB A-60	1.677	0.134-4.610	unspecified

Average concentrations were calculated from 2 measurements each of 300 fish specimens (roach and perch) combined from all 22 collection points along the Lahn. Trace levels are concentrations <0.001 mg/kg. Permissable levels refer to present regulations in Western Germany. No significant differences in residue concentrations were detected between the two species of fish.

Average concentrations and spreads of the absolute values for the various chlorinated hydrocarbons in all specimens are presented in Table 2. Maximum permissable levels, where specified, are also given.

Contamination with HCB, PChB, α-, β- and γ-HCH was insignificant. Only in the case of HCB was a maximum permissable level exceeded and then only in 4 samples. DDT concentrations were far below tolerance levels.

Special consideration must be given to the high levels of polychlorinated biphenyls in fish (Table 2). Concentrations of these technical substances were one-hundred times greater than those of regulated pesticides, reflecting the situation in various animal products which we reported recently (Brunn 1982). The concentrations of PCB A-60 reported here double those we reported previously for other fish, predominantly trout, from various inland waters (Brunn and Manz 1982). Maximum permissable tolerance levels for PCB have not yet been established for Western Germany, however, these recent observations clearly demonstrate the need for such regulative

Table 3 Mean PCB concentrations in all fish, based on fat and on body weight

Weight group [body weight]	Number of fish investigated	Average fat content [g/100 g body weight]	PCB-C		PCB A-60	
			[mg/kg fat]	[mg/kg body weight]	[mg/kg fat]	[mg/kg body weight]
20-50 g ($\bar{x}$=35.6)	110	1.09	54.450	0.341	182.994	1.635
50-100 g ($\bar{x}$=74.9)	141	1.74	33.807	0.469	119.138	1.755
>100 g ($\bar{x}$=135.8)	49	2.30	25.57	0.508	89.014	1.821

Animals were assigned to three groups according to weight;
$\bar{x}$ are the mean values of weights of the different groups.

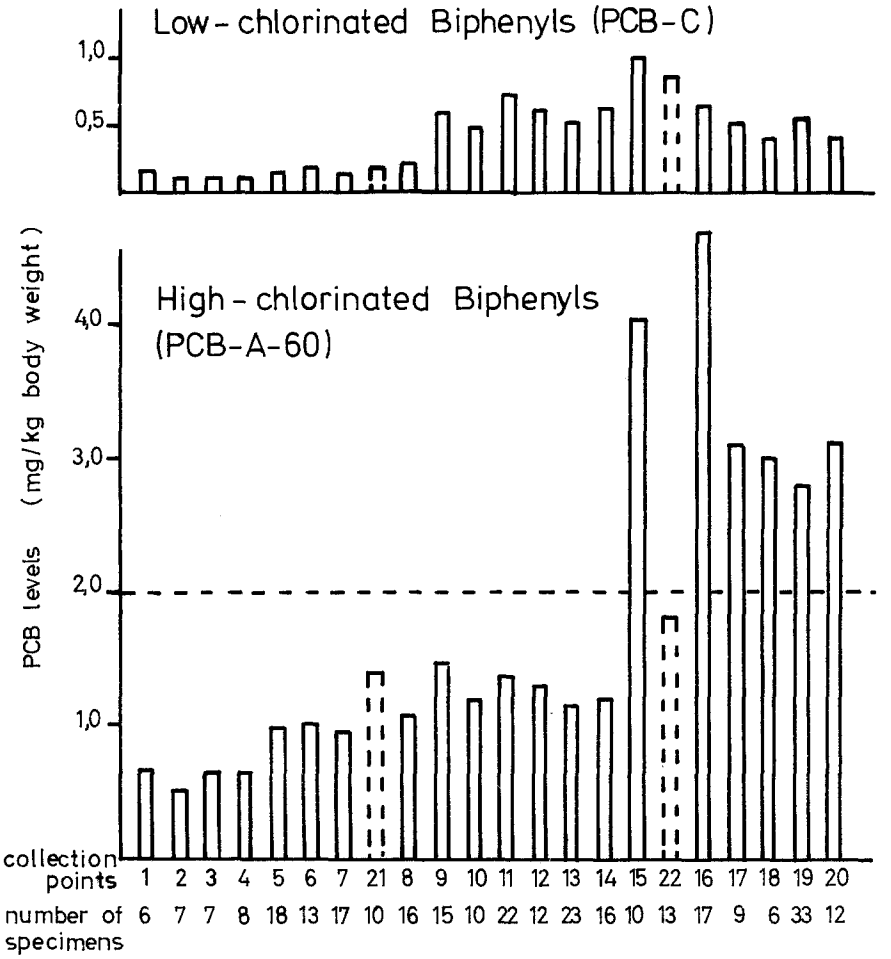

Fig. 2 PCB levels in fish caught at individual points along the Lahn

Progression of DDT and γ-HCH levels were also plotted (not shown). Levels of other insecticide residues were too low for this purpose.

measures. If PCB tolerance levels of 2 mg/kg body weight were specified, 26 % (78 fish) of the samples analyzed would have exceeded this limit.

We have chosen to present residue concentrations based on body weight rather than on fat weight for reasons depicted in Table 3. Values based on fat appear misleading because young fish have little body fat and concentrations of residues in fat are disproportionally high compared to values obtained from adult animals. Based on body weight, concentrations of contaminants are approximately equal in fish of all sizes.

A principle goal of this investigation was to determine whether a population of fish which demonstrate a distinct territorial behavior can be used as an indicator of local environmental pollution with chlorinated hydrocarbons as proposed for various wildlife forms by Drescher-Kaden et al. (1978). We therefore plotted the progression of PCB levels in fish from individual collection points along the Lahn (Fig. 2).

In the rural area from point 1 to point 4, PCB levels were constant and relatively low. Just upstream from point 4, water from a stream, the Ohm, enters the Lahn. The Ohm flows through a predominantly agricultural region so that at point 4 a slight increase was observed in levels of the pesticide, γ-HCH (not shown), however, no noticeable increase in PCB levels were detected. From point 5 the Lahn flows through an increasingly industrial area and PCB levels rise accordingly, clearly noticeable downstream of the Wieseck. There is a dramatic increase in PCB-A-60 levels at point 15, just downstream from an influx of industrial waste water, and again at point 16, downstream from the mouth of the Dill river and entry of effluents from a municipal sewage treatment plant. Downstream from point 15 all fish were found to be contaminated with PCB-A-60 in excess of 2 mg/kg.

From the observations presented above we conclude that measurements of chlorinated hydrocarbons in territorial fish such as roach and perch provide a useful indication of the degree to which the local environment is polluted with these substances. The method is sensitive enough to allow accurate localization of contamination sources such as sewage and industrial waste.

Of additional importance are the results showing high levels of PCB residues including low-chlorinated biphenyls present in fish from a river considered to be "only" moderately contaminated. These findings together with those in the following paper in which PCB was analyzed in non-aquatic game animals

serve to underline the increasing need for environmental monitoring of these substances. Analysis of tissue from aquatic and terrestrial wildlife as described here may provide a useful means to this end.

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