Chlorinated Insecticide Residues in the Eggs of Some Freshwater Fish

by

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Routine monitoring of the pesticide concentrations in a number of Iowa rivers over a period of years indicated that chlorinated hydrocarbon insecticides, used in row crop agriculture, were being carried into the rivers by soil erosion (JOHNSON and MORRIS, 1970).

Although the primary source of pesticides in Iowa rivers is believed to be surface runoff from agricultural applications, industrial waste and urban use will certainly add to this burden.

Irrespective of their source, these pesticides enter the stream mostly by being bound to sediment particles. A large percent of these particles will settle to the river bottom and provide a reservoir of these chemicals for aquatic life.

The concentrations of insecticides found were not uniform over the state, but were highest in areas where extensive row crop farming, with its accompanying erosion, was practiced. Because of these findings, a study was made of the pesticide levels in the edible flesh of fish from many of the rivers in Iowa (MORRIS and JOHNSON, 1971).

The levels of dieldrin found in the flesh of channel catfish (Ictalurus punctatus Rafinesque) from rivers draining areas under extensive agricultural cultivation were two to five times greater than the actionable level of 0.3 parts per million, which is the maximum concentration allowed by the U. S. Food and Drug Administration in fish for commercial sale. The dieldrin concentration in catfish from rivers which did not drain significant areas of row crop farm land were below the FDA limit. Pan and game fish were below the FDA limit for dieldrin in the edible portion in all areas sampled.

Fish are excellent biological compositors. Measurement of trace elements such as pesticides, that are present in their various tissues may give a much better picture of the relative pollution of a river

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than analysis of a single grab water sample.

Because of the significant aggregation of dieldrin in the flesh of catfish found in some rivers and the wide variation between species in pesticide content, a study of the pesticide levels in the eggs of some fish from five locations in Iowa was undertaken in the spring of 1971.

The locations were selected because of either high dieldrin levels in previous studies or the importance of commercial and sport fishing in the area.

Water from the Nishnabotna river system has consistently produced the highest pesticide content (dieldrin) of the Iowa rivers monitored. Also the fish from the Nishnabotna river system showed the highest dieldrin levels of any measured in 1970. The Coralville Reservoir of the Iowa River was selected because of elevated dieldrin levels in fish and water and also the large amount of sport fishing. Pools 11 and 19 on the Mississippi River were selected due to extensive commercial fishing and the significant increase in pesticide levels in fish flesh progressing from Pool 11 near the northern border of Iowa to Pool 19 near the southern border.

Materials and Methods

The fish eggs analyzed in this study were collected by the Iowa State Conservation Commission at the sites previously listed.

The roe were removed from the fish, wrapped in aluminum foil, frozen and sent to the State Hygienic Laboratory for analysis. Fifteen grams of eggs from each fish were analyzed by the Porter et al. procedure (1970).

The egg samples from Pools 11 and 19 of the Mississippi River contained measurable amounts of polychlorinated biphenyls (PCB's). The PCB's appeared in the 6% ethyl ether elute from the florisil column. They were separated from the pesticides in this fraction on a silicic acid column as described by ARMOUR and BURKE (1970). The amounts of PCB's present were calculated using aroclor 1254 as a standard.

The gamma and alpha isomers of chlordane in one of the samples (East Nishnabotna catfish, 12.8 inches) were separated from the majority of the other pesticides in the 6% florisil fraction by using a silica gel column and successive elutions with hexane for further confirmation of their identity. They were then converted to their dehydrochlorination products by the procedure of CHAU and COCHRANE (1969). The gas chromatograph retention times of these two products matched the retention times of the dehydrochlorination products of standard samples of gamma and alpha chlordane. Samples of pure gamma and alpha chlordane were supplied by Velsicol Chemical Corporation.

The cleaned up extracts were chromatographed on an F & M Model 400 gas chromatograph equipped with an electron capture detector. The temperatures of the injector, oven and detector respectively were 200°C, 175°C and 200°C. The carrier gas flow rate was 50 cc per minute. A 3% OV-1 on 100-120 mesh Gas-Chrom Q column was used for all quantitation and a 6%:4% QF-1:OV-1 column was used for confirmation.

The concentrations listed in tables I and II are on a wet weight basis.

Discussion and Results

The pesticide concentrations and extractable fat contents found are listed in table I.

The insecticides listed in table I are the identical ones detected in fish flesh in these Iowa rivers. Aldrin, heptachlor and DDT have all been used for insect control in Iowa agriculture, and it is not surprising to find their residues in the aquatic environment.

The presence of gamma and alpha chlordane is a little unexpected since chlordane has been used to a lesser extent in agriculture and other applications, such as termite and lawn insect control. A possible explanation for their detection is that they are present in technical heptachlor, (especially the gamma isomer) which as noted, has been used extensively in Iowa. As mentioned above in the Materials and Methods section, these two isomers of chlordane were confirmed by the procedure of CHAU and COCHRANE (1969).

Dieldrin is the major insecticide residue detected in the eggs. The highest levels of dieldrin were found at those locations where the highest concentrations were determined in fish flesh and water samples (MORRIS and JOHNSON, 1971). Channel catfish eggs, the one species analyzed at each sampling site, have dieldrin levels highest in the Nishnabotna River system and decreasing in order in the Iowa River and Pool 19 and Pool 11 of the Mississippi River.

Table I shows that in both Pool 11 and Pool 19 of the Mississippi River, the walleye (Stizostedion vitreum Mitchell) eggs have the highest lipid and dieldrin content, while the largemouth bass (Micropterus salmoides Lacepede) eggs are in between the walleye and channel catfish in both lipid and dieldrin content.

The levels of dieldrin found in the flesh of catfish were much higher than in the flesh of any pan or game fish, including walleye and largemouth bass, at all locations where they were sampled. Figure I graphically presents concentrations of dieldrin versus percent lipids. It also shows regression-equations plots determined by the least-squares method and correlation coefficients for the Iowa and Mississippi River samples. Even though, only three points on the graph are available for each of these locations, the correlation between percent lipid and dieldrin concentration appears quite good.

HENDERSON et al. (1971) state in their report on organochlorine insecticides residues in fish, that to date, samples collected at the same station are too few in number to establish definite size, species or lipid correlations with insecticides residues. However, REINERT (1970) indicates that in the great lakes' fish there is a definite relationship between oil content and whole fish pesticide concentrations.

The report on dieldrin in fish flesh from Iowa streams by MORRIS and JOHNSON (1971) showed a definite species difference in dieldrin concentration in the flesh of fish from the same location. Walleye and largemouth bass from the Mississippi and Iowa Rivers all had less than 100 parts per billion dieldrin in their flesh, while channel catfish from these same locations had 5 to 15 times the concentration of dieldrin in their flesh as did these game fish. Also there was a significant relationship between dieldrin concentration and size for channel catfish. One plausible explanation suggested for these relationships was the lipid content of the flesh, although it was not measured for that project.

No walleye eggs were collected from the Iowa River, but the concentrations of dieldrin in the eggs of walleye from this river can be calculated using the regression equation for the Iowa River, $Y=-26.2+193X$, where Y is the dieldrin concentration in ppb and X is the lipid content in percent. Assuming an average lipid level of 11.45% (average for the Mississippi walleye eggs), the calculated dieldrin value is 2,200 ppb.

TABLE I

Chlorinated Insecticides and Lipids in Fish Eggs

River	Species	Date Collected	Length Inches	Insecticides in Parts Per Billion: Diel-drin	DDE	TDE	DDT	H.E.[a]	Aldrin	Chlordane[b]	Per Cent Lipids
E.N.[c]	CCF[g]	6-24-71	12.8	930	240	150	84	57	175	350	2.5
E.N.	CCF	6-24-71	16.2	910	181	128	92	51	168	154	2.4
W.N.[d]	CCF	6-28-71	13.7	950	280	155	122	66	170	150	4.4
W.N.	CCF	6-28-71	14.9	910	360	180	175	76	162	161	4.2
M.19[e]	CCF	4-16-71	24.0	145	64	36	16	28			2.3
M.19	LMB[h]	4-15-71	17.5	455	190	107	46	69			6.3
M.19	Wall.[i]	4-13-71	24.3	690	250	170	72	93			11.3
M.11[f]	CCF	6-4-71	23.4	37	70	32	15	5			3.5
M.11	LMB	5-20-71	16.4	79	110	76	48	10			4.9
M.11	Wall.	4-16-71	27.5	142	190	98	69	13			11.6
Iowa	CCF	5-21-71	22.0	640	139	67	49	51		93	3.4
Iowa	CCF	5-23-71	19.4	420	110	56	28	37		72	2.4
Iowa	NP[j]	5-17-71	24.2	115	57	30	16	13		24	0.7

a Heptachlor Epoxide; b Alpha plus Gamma Chlordane; c East Nishnabotna;
d West Nishnabotna; e Mississippi Pool 19; f Mississippi Pool 11;
g Channel Catfish; h Largemouth Bass; i Walleye; j Northern Pike

Very little information is available on the effect on reproduction of dieldrin in fish eggs. However, based on work by BURDICK et al. (1964), which showed that concentrations of 4.75 ppm DDT in trout eggs produced at least 15% mortality in fry and on the greater toxicity of dieldrin, it is reasonable to postulate that 2.2 ppm (2,200 ppb) dieldrin in fish eggs would have some adverse affect on reproduction. Walleye are stocked in the Iowa River by the Iowa State Conservation Commission but their reproductive success there is not known.

TABLE II

Polychlorinated Biphenyls in Fish Eggs from the Mississippi River.

Location	Species	Date Collected	Length of Fish	PCB's[a]
Pool 19	CCF[b]	4-16-71	24.0	0.9
Pool 19	LMB[c]	4-15-71	17.5	2.9
Pool 19	Wall.[d]	4-13-71	24.3	5.5
Pool 11	CCF	6-4-71	23.4	1.5
Pool 11	LMB	5-20-71	16.4	3.2
Pool 11	Wall.	4-16-71	27.5	4.2

As Arochlor 1254; b Channel Catfish; c Largemouth Bass; d Walleye

Polychlorinated biphenyls (PCB's) were detected in samples from the Mississippi River. Their gas chromatographic recording matched that of arochlor 1254 very closely in both retention times and peak height ratios on both columns used.

The concentrations of PCB's found are listed in table II, while Figure II graphically presents the PCB content versus percent lipids, plus the linear regression equations and correlation coefficients for Pools 11 and 19.

The levels of PCB's found in the same species from Pools 11 and 19 are roughly the same thus, indicating that the major source of these industrial chemicals is upstream from Pool 11.

This is diametrically opposed to the dieldrin situation where its levels in both the eggs and flesh of fish are significantly higher in Pool 19 and Pool 11, indicating a significant addition of dieldrin into the river between these two pools.

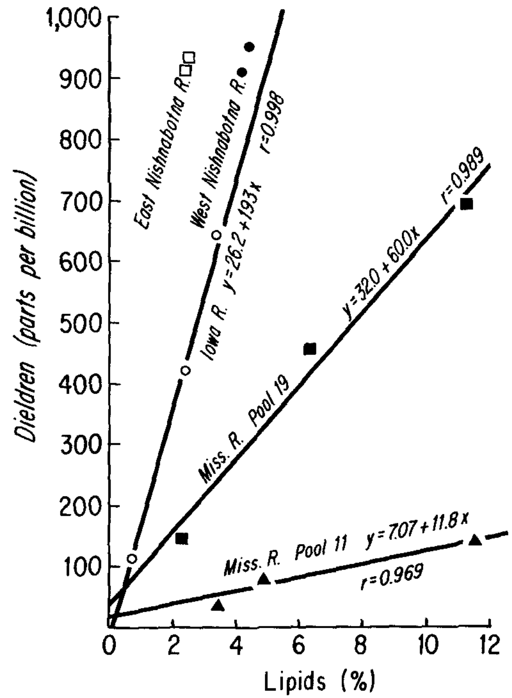

FIGURE I. Linear regression equations and correlation coefficients for dieldrin vs. lipids in fish eggs.

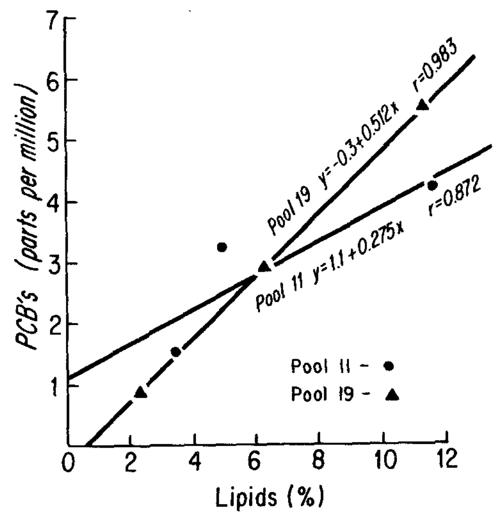

FIGURE II. Linear regression equations and correlation doefficients for PCB's vs. lipids in fish eggs.

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