Chlorohydrocarbons in Lake Superior Lake Trout (*Salvelinus namaycush*)

RONALD PAREJKO, RAYMOND JOHNSTON, and ROBERT KELLER
Department of Biology, Northern Michigan University
Marquette, Mich. 49855

Polychlorinated hydrocarbons used as pesticides and as industrial chemicals have been recognized as being ecologically significant compounds since they are metabolically quite recalcitrant and thus tend to accumulate in various global ecosystems (ABBOTT et al. 1966; JENSEN et al. 1969; RISEBROUGH et al. 1968). Generally the higher trophic level organisms, such as birds, fish, and some marine and terrestrial animals, contain increased concentrations of chlorinated hydrocarbons. Studies have indicated that some fish taken from the Great Lakes possess chlorohydrocarbon pesticide residue concentrations in excess of 5.0 ppm--the interim administrative limit for DDT in food set by the United States Food and Drug Administration (FDA) (HENDERSON et al. 1969; POFF and DEGURSE 1970; REINERT 1970). Recently, polychlorinated biphenyls (PCBs) usually identified as Aroclor[1] and the pesticide mirex[2] have been identified in Lake Ontario fish (KAISER 1974).

Fish taken from Lake Erie have also been found to be contaminated with PCBs, DDT and dieldrin (KELSO and FRANK 1974). Lake Michigan and Lake Superior salmonoid fish have likewise been reported to contain DDT and dieldrin (KLEINERT et al. 1968).

Since Lake Superior is North America's largest oligotrophic lake containing a sizable fishery of lake trout (Salvelinus namaycush), the present study was made to determine the extent of chlorohydrocarbon contamination in these fish taken from this relatively isolated lake. Data accumulated should offer an insight as to the present status of the chlorinated hydrocarbon concentrations in lake trout fished commercially and as part of a sports fishery.

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[1] Aroclor--Registered trademark, Monsanto Co., St. Louis, Mo.

[2] Mirex--Dodecachlorooctahydro-1, 3, 4-metheno-2H-cyclobuta (c, d) pentalene.

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Materials and Methods

Material: Lake trout used were netted in Lake Superior during the summer of 1971. Netting locations were: 1) about 2 miles E of Rock Harbor Light, Isle Royale and 2) about 15 miles SSW of Caribou Island. The locations are approximately 140 miles apart. Fish were wrapped in aluminum foil and frozen (-10°C) until used for analysis.

Ventral abdominal tissue, 15-20 g (muscle and adipose) taken from an area located between the pelvic and pectoral fins, was macerated with excess sodium sulfate and extracted three times with petroleum ether, in glass centrifuge tubes. The petroleum ether was decanted into a flask and was evaporated at room temperature under a hood. The fish-oil extracted was weighed and the chlorohydrocarbon residues were removed, from 3-5 g, by extraction into 200 ml. acetonitrile. The acetonitrile was suction filtered and the residues partitioned into 100 ml. petroleum ether, following shaking with 600 ml. distilled water and 10 ml. sat. NaCl in a separatory funnel. The petroleum ether layer was washed twice with 100 ml. portions of dist. water (UNITED STATES DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE 1971).

Florisil column chromatography was used to clean the petroleum ether extract. The petroleum ether extract was passed through a 125-175 X 22 mm activated Florisil column using 200 ml. of a 6% ethyl ether --94% petroleum ether eluant (UNITED STATES DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE 1971). The eluate was concentrated to approximately 5 mls, using a Kuderna-Danish concentrator and the PCBs were separated from the chlorohydrocarbon pesticides by column chromatography on a 3% water deactivated silicic acid-Celite 545 column (ARMOUR and BURKE 1970).

The silicic acid-Celite 545 column was first eluted with 225 ml. of petroleum ether (this eluate contains PCBs) and then with 200 ml. of acetonitrile-hexane-methylene chloride (1:19:80) (this eluate contains chlorohydrocarbon pesticides). Both eluates were concentrated with a Kuderna-Danish concentrator and with flowing N_2 to less than 1 ml. and diluted to volume, in a 10 ml. volumetric flask, in benzene. The samples were then stored in amber, glass stoppered bottles at 4°C until analyzed for residues by gas-liquid chromatography.

A F&M Model 402 High-efficiency gas chromatograph containing a 6' x 1/4" glass U column of (1:1) 15% QF-1 and 10% DC-200 on 80-100 mesh Chromosorb W-HP and a H^3 electron capture detector was used for analysis. Instrumental parameters were: injection port, 210; column, 190; and detector, 200 C with a 95% argon-5% methane flow rate of 60 ml/min. A Honeywell Model 16 recorder was used at a chart speed of 1/4" per min.

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Reagents: Pesticide and Aroclor standards were obtained from the Pesticides & Toxic Substances Effects Laboratory, National Environmental Research Center, Research Triangle Park, NC, USA. Organic solvents used were Fisher pesticide grade petroleum ether, methylene chloride, acetonitrile, hexanes and benzene. Fisher reagent (AR) grade sodium sulfate, Celite 545 and ethyl ether were used. Silicic acid was 100 mesh, Mallinckrodt, AR. Florisil was 60/100 PR, Floridin Co., Berkeley Springs, W. Va.

Recoveries of p, p'-DDT and Aroclor 1254 from salted fish tissue samples were 99% and 85% respectively. Reagent blanks passed through the entire analytical procedure produced no detectable peaks identified as chlorinated hydrocarbons upon analysis by gas chromatography.

Results and Discussion

The physical characteristics of the lake trout used for analysis are listed in Table 1. Sexually immature fish could not be easily sexed. The fish used were grouped into two age classes for statistical comparisons even though more accurate age determinations were made.

TABLE 1

Physical Characteristics of
20 Lake Superior Lake Trout Analyzed

Characteristic		Measurement
Sex		6 male; 9 female; 5 sexually immature
Age		13 less than 8 years old; 7 greater than or equal to 8 years old
Length	Range:	16.5" (42.0 cm) to 31.1" (78.5 cm)
	Mean:	22.9" (58.0 cm)
Weight	Range:	1.25 lb (569 g) to 22.02 lb (10,000 g)
	Mean:	5.71 lb (2597 g)
Per cent fish-oil extracted	Range:	10.6 to 51.7
	Mean:	30.9

All fish tissue extracts produced gas chromatographic peaks corresponding to some chlorohydrocarbon pesticide and/or polychlorinated biphenyl (PCBs as Aroclor) standard. The gas chromatograph was standardized for a number of chlorohydrocarbon pesticides and the Aroclors 1242, 1248, 1254, 1260 and 1262.

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Tables 2 and 3 present the chlorohydrocarbon pesticide concentrations detected in lake trout taken from Lake Superior during the summer of 1971. Concentrations of chlorohydrocarbon pesticides detected are expressed in ppm based on wet tissue weight in Table 2 and in ppm based on extracted fish-oil weight in Table 3. Lindane was detected in only 1 fish (5% of total number of fish analyzed), heptachlor was found in 2 fish (10%) and aldrin was found in 12 (60%) of the fish analyzed. The concentration of aldrin detected was always less than the Food and Drug Administration (FDA) action level of 0.3 ppm. The concentrations of heptachlor detected always exceeded this level; however, heptachlor was detected in only 10% of the fish analyzed.

TABLE 2

Chlorinated Hydrocarbon Pesticides Detected in Lake Superior Lake Trout Based on Wet Tissue Weight

Pesticide	No. of fish having Pesticides	% having Pesticides	Concentration Range Detected (ppm)	Mean Concen. Detec. (ppm)	Standard Deviation (ppm)
Lindane	1	5	-----	0.19	--
Heptachlor	2	10	0.49-2.77	1.63	1.14
Aldrin	12	60	0.08-0.22	0.12	0.05
p,p'-DDD[1]	10	50	0.48-1.86	0.99	0.40
p,p'-DDE[2]	17	85	0.95-6.39	2.39	1.58
p,p'-DDE[3]	3	15	0.07-0.38	0.24	0.16
p,p'-DDT[4]	3	15	0.58-4.05	1.77	1.97
o,p'-DDT[5]	2	10	0.72-1.29	1.01	0.40
Total DDT & Analogs	18	90	0.68-9.78	3.25	2.58

[1] p,p'-DDD (1,1-dichloro-2,2bis (p-chlorophenyl) ethane)

[2] p,p'-DDE (1,1-dichloro-2,2 bis (p-chlorophenyl) ethylene)

[3] p,p'-DDE (1,1-dichloro-2-(p-chlorophenyl)-2-(o-chlorophenyl) ethylene)

[4] p,p'-DDT (1,1,1-trichloro-2,2 bis (p-chlorophenyl) ethane)

[5] o,p'-DDT (1,1,1-trichloro-2-(p-chlorophenyl)-2-(o-chlorophenyl) ethane)

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TABLE 3

Chlorinated Hydrocarbon Pesticides Detected in Lake Superior Lake Trout Based on Extracted Fish-oil Weight

Pesticide	No. of fish having Pesticides	% having Pesticides	Concentration Range Detected (ppm)	Mean Concen. Detec. (ppm)	Standard Deviation (ppm)
Lindane	1	5	-----	0.59	--
Heptachlor	2	10	3.16-8.71	5.93	2.77
Aldrin	12	60	0.19-0.79	0.45	0.20
p,p'-DDD	10	50	1.69-4.59	2.83	0.99
p,p'-DDE	17	85	2.10-16.29	7.95	4.34
o,p'-DDE	3	15	0.42-1.50	0.82	0.57
p,p'-DDT	3	15	1.29-16.25	7.07	8.03
o,p'-DDT	2	10	4.52-5.16	4.84	0.45
Total DDT & Analogs	18	90	2.13-39.20	10.94	8.97

Dieldrin, a decomposition product of aldrin and 1-hydroxychlordene and heptachlor epoxide, decomposition products of heptachlor were not detected. The apparent absence of these products in the fish analyzed is difficult to explain as they might be expected to be found if the parental pesticide would be detected.

The o,p' and p,p' isomers of DDT were detected in 2 (10%) and 3 (15%) fish respectively. The DDE isomers, o,p' and p,p', were detected in 3 (15%) and 17 (85%) fish respectively and p,p'-DDD was detected in 10 (50%) fish. DDT and/or its analogs were detected in 18 or 90% of the fish analyzed. Mean concentrations of DDT and its decomposition products DDE and DDD detected in Lake Superior lake trout were significant but below the FDA action level of 5.0 ppm. The p,p'-DDE isomer was detected in 85% of the fish analyzed in concentrations varying from 0.95 to 6.39 ppm based on wet tissue weight. Some fish analyzed contained total DDT and analog concentrations in excess of the FDA action level for that pesticide.

As can be noted in Table 3 the concentrations of chlorohydrocarbon pesticides detected in lake trout and expressed in ppm based on extracted fish-oil weight are some 3-4 times that of the concentrations expressed

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on wet tissue weight. This may be expected as the mean extracted fish-oil concentration in the tissue used was approximately 30%.

Concentrations of DDT and its analogs detected in Lake Superior lake trout were generally less than those detected in Lake Michigan lake trout (REINERT 1970) and Cayuga Lake, NY lake trout (YOUNGS et al. 1972). This may be expected since the waters of Lake Superior receive relatively little run-off from agricultural land. The Lake Superior watershed area has not been completely exempt from the use of DDT however, as this pesticide has been used in the past to control the spruce budworm (Choristoneura fumiferana) and to a lesser extent in spraying orchards and residential gardens.

Chlorohydrocarbon pesticides not detected in Lake Superior lake trout include: hexachlorocyclohexane (BHC); p,p'-DDA; o,p'-DDD; m,p'-DDD; α and γ-chlordane; perthane; endrin; endosulfan; prolan and methoxychlor. Mirex, which may be present in the PCB fraction (KAISER 1974), was not identified in the fish used in this study.

The concentrations of PCBs, as Aroclors, detected in Lake Superior lake trout are reported in Tables 4 and 5. Aroclor concentrations detected in lake trout tissue are expressed in ppm based on wet tissue weight in Table 4 and in ppm based on extracted fish-oil weight in Table 5. Gas chromatographic peaks in the Aroclor (PCBs) fractions from extracted lake trout tissue were identified as corresponding to the Aroclor standards 1242, 1248, 1254 and 1262. Every fish analyzed had some chromatographic peaks which could not be identified as they did not correspond to Aroclor standards. It is assumed that these peaks may represent degradation products of some Aroclor isomers. Every lake trout analyzed contained compounds identified as Aroclor PCBs. Total Aroclor concentrations detected in these fish ranged from 2.7 to 13.8 ppm, with a mean of 7.0 ppm based on wet tissue weight.

TABLE 4

Aroclor Polychlorinated Biphenyls (PCBs)
Detected in Lake Superior Lake Trout
Based on Wet Tissue Weight

Aroclor	No. of fish having Aroclor	% having Aroclor	Concentration Range Detected (ppm)	Mean Concen. Detec. (ppm)	Standard Deviation (ppm)
1242	18	90	1.4-3.4	2.2	0.5
1248	17	85	1.1-4.1	2.2	1.0
1254	15	75	1.3-7.7	3.4	2.0
1262	8	40	0.9-3.0	1.5	0.7
Total Aroclors	20	100	2.7-13.8	7.0	3.5

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TABLE 5

Aroclor Polychlorinated Biphenyls (PCBs)
Detected in Lake Superior Lake Trout
Based on Extracted Fish-oil Weight

Aroclor	No. of fish having Aroclor	% having Aroclor	Concentration Range Detected (ppm)	Mean Concen. Detec. (ppm)	Standard Deviation (ppm)
1242	18	90	4.5-28.1	9.0	5.5
1248	17	85	2.8-15.0	7.6	3.5
1254	15	75	3.9-36.1	12.8	9.6
1262	8	40	1.9-6.2	3.8	1.5
Total Aroclors	20	100	7.6-62.8	25.6	15.3

Aroclor 1242 was detected in 18 (90%), Aroclor 1248 was detected in 17 (85%), Aroclor 1254 was detected in 15 (75%) and Aroclor 1262 was detected in 8 (40%) of the fish analyzed. The lower percent chlorinated Aroclors were detected in more fish than the more highly chlorinated Aroclors. This may result from a selective accumulation of lower chlorine containing PCB isomers or from a selective degradation of higher chlorine containing PCB isomers within the food chain associated with lake trout or a selective accumulation/elimination and/or degradation of PCB isomers within lake trout.

The peaks detected on gas chromatograms of PCB fractions of lake trout tissue extracts did not correspond to the Aroclor 1260 standard. Aroclor 1260 is an industrial mixture of PCB isomers that has been used quite extensively and therefore the absence of peaks corresponding to this standard is somewhat unexpected.

As in the case of chlorinated hydrocarbon pesticides, the concentrations of Aroclor PCBs detected in lake trout expressed in ppm based on extracted fish-oil are some 3-4 times that of the concentrations detected and expressed in ppm based on wet tissue weight.

Lake trout taken from Lake Superior and analyzed in this study contained PCBs generally in somewhat lower concentrations than northern long-nose gar (Lepistosteus osseus) or nothern pike (Esox lucius) taken from Lake Ontario (KAISER 1974) but contained PCB concentrations generally higher than yellow perch (Perca flavescens), white bass (Morone chrysops) and smallmouth bass (Micropterus dolomieui) taken from Lake Erie (KELSO and FRANK 1974). These higher concentrations detected in Lake Superior lake trout, as compared to Lake Erie fish, may be accounted for by the trophic level occupied and by the significantly higher concentrations of fish-oil in lake trout. The lake trout used for analyses in this

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study had fish-oil concentrations that were some 10 times the fish-oil concentrations found in the fish used in the Lake Erie study. Chlorohydrocarbons such as PCBs are fat soluble.

Table 6 shows the ratios of DDT analogs to DDT and ratios of total PCBs to DDE and to total DDT and analogs detected in Lake Superior lake trout. The mean DDE/DDT ratio is 1.66 and the mean DDD/DDE ratio is 0.48. Therefore, in the fish used in this study there is nearly twice as much DDE as DDT and about one-half as much DDD as DDE.

TABLE 6

Ratios of Chlorohydrocarbons Detected in Lake Superior Lake Trout

Ratio	N	Range	Mean	Standard Deviation
DDE/DDT	3	0.83-2.54	1.66	0.70
DDD/DDE	9	0.22-1.34	0.48	0.33
Total PCB/DDE	17	1.0-10.55	3.74	2.76
Total PCB/Total DDT and Analogs	18	0.79-19.71	3.65	4.25

These fish also have a mean total PCB/DDE ratio of 3.74 and a mean total PCB/DDT and analogs ratio of 3.65. There is nearly four times as much PCB in these lake trout as there is DDT or its analogs.

Because statistical correlations between lake trout age and DDT concentrations of lake trout taken from Cayuga Lake, NY indicated that increasing concentrations of DDT were correlated with increasing lake trout age (YOUNGS et al. 1972), similar correlations were attempted for the Lake Superior lake trout used here. Standard t tests at the 95% confidence interval were made in an attempt to correlate Lake Superior lake trout age, location of capture, sex or fat content with total PCB or total DDT and analogs concentrations. For each attempted correlation no statistically significant difference in comparative parameter could be determined. Caution should be taken in the interpretation of these statistical studies because the small sample size may be a limiting factor contributing to potential error.

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References

ABBOTT, D.C., R.B. HARRISON, J.O.G. TATTON and J. THOMSON: Nature 211, 259 (1966).

ARMOUR, J.A. and J.A. BURKE: J. Assoc. Off. Anal. Chem. 53, 761 (1970).

HENDERSON, C., W.L. JOHNSON and A. INGLIS: Pesticides Monitoring J. 3, 145 (1969).

JENSEN, S., A.G. JOHNELS, S. OLSSON and G. OTTERLIND: Nature 224, 247 (1969).

KAISER, K.L.E.: Science 185, 523 (1974).

KELSO, J.R.M. and R. FRANK: Trans. Amer. Fish. Soc. 103, 577 (1974).

KLEINERT, S.J., P.E. DEGURSE and T.L. WIRTH: Wis. Dept. Nat. Res. Tech. Bull. 41, p. 43 (1968).

POFF, R.J. and P.E. DEGURSE: Wis. Dept. Nat. Res. Man. Rep. 34, p. 17 (1970).

REINERT, R.E.: Pesticides Monitoring J. 3, 233 (1970).

RISEBROUGH, R.W., P. REICHE, D.B. PEAKALL, S.G. HERMAN and M.N. KIRVEN: Nature 220, 1098 (1968).

UNITED STATES DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE. Pesticide Analytical Manual, Vol. I. Methods which detect multiple residues. Washington, D.C.: U. S. Gov't. Prtg. Office. Reprint (1971).

YOUNGS, W.D., W.H. BUTENMANN and D.J. LISK: Environ. Sci. Technol. 6, 451 (1972).

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