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Pesticides in the Illinois Waters of Lake Michigan



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PESTICIDES IN THE ILLINOIS WATERS
OF LAKE MICHIGAN

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ABSTRACT

This study was initiated to determine present levels of pesticides in Lake Michigan fish, sediments, and water. Data was collected on six species of Lake Michigan fish (yellow perch, chubs, carp, coho salmon, alewife, and brown trout); open lake and tributary stream and ravine sediments; and open water, tributary stream, and sewage treatment plant effluents. Samples analyzed for pesticides were selected from the following list: Heptachlor, heptachlor epoxide, dieldrin, methoxychlor, lindane, aldrin, endrin, DDT and its analogs. Additional analyses were accomplished for polychlorinated biphenyls (PCB's), di-n-butyl phthalate: (DBP), and di(2-ethylhexyl) phthalate: (DOP).

The data indicate that PCB's were found at levels as high or higher than DDT in Lake Michigan water, sediment, and fish. PCB's have been found to complicate the routine analysis of DDT which may have caused earlier DDT data in the literature to be reported at levels higher than actual. Both DDT and the polychlorinated biphenyls were found at levels which cause concern for aquatic life and warrants the controlled use of these compounds.

This report was submitted in fulfillment of Grant No. 16050 ESP between the Office of Research and Development of the U.S. Environmental Protection Agency and the Illinois Environmental Protection Agency. This project was proposed and performed by the Illinois Environmental Protection Agency, Chicago, Illinois. The survey was made in the Illinois waters of Lake Michigan.

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SECTION I

CONCLUSIONS

1. The polychlorinated biphenyls (PCB's) were found in Lake Michigan fish and sediments at levels which cause concern for aquatic life. Aroclor 1254 was consistently found in fish flesh ranging from 0.1 to 3.3 ppm. Levels of Aroclor 1254 found in Lake Michigan sediments ranged between 2.48 and 46.92 ppb while tributary stream sediments ranged between 1.54 and 232.00 ppb. While not consistently found, Aroclor 1242 was detected in fish flesh at levels ranging from N.D. to 2.2 ppm. Aroclor 1242 found in Lake Michigan sediments ranged from N.D. to 106.07 ppb while tributary stream sediment levels ranged from N.D. to 553.00 ppb. The controlled use of these compounds appears warranted.

2. Levels of DDT, PCB's, and dieldrin in edible portions of six species of Lake Michigan fish were generally below interim guidelines for maximum concentration in fish flesh. These guidelines are 5.0 ppm for both DDT and PCB's and 0.3 ppm for dieldrin. Other chlorinated hydrocarbon insecticides were not consistently found in the edible portions of fish flesh. Fish analyzed included yellow perch, coho salmon, chubs, brown trout, carp and alewife.

3. Both offshore and tributary sediments showed highest levels for PCB's and DDT followed by methoxychlor and dieldrin. Tributary sediments showed levels higher than open lake sediments. Highest concentrations for PCB's were found in industrial areas in Waukegan and North Chicago. Highest concentrations of DDT were found in residential areas in Highland Park, while highest levels of both dieldrin and methoxychlor were found in Lake Forest. Concentrations of total DDT, methoxychlor, and dieldrin in Lake Michigan sediments ranged from 1.02 to 29.13, 0.13 to 6.60, and 0.03 to 1.25 ppb for each parameter respectively. Concentrations of total DDT, methoxychlor and dieldrin in the tributary and ravine sediments ranged from 0.42 to 942.00, 0.19 to 175.00, and 0.01 to 30.80 ppb for each parameter respectively.

4. PCB's and phthalates showed highest maximum concentrations in the sediments. Maximum levels of Aroclor 1242 and Aroclor 1254 were 553.00 ppb and 232.00 ppb respectively. Maximum levels of di(2-ethylhexyl) phthalate and di-n-butyl phthalate were 218.00 ppb and 120.00 ppb respectively. Methoxychlor was the only pesticide found at concentrations greater than 100.00 ppb. The maximum concentrations of this pesticide found was 175.00 ppb. Maximum concentrations for the majority of the isomers of DDT were below 50.00 ppb. Maximum levels for p,p'-DDD and p,p'-DDT were 66.50 ppb and 72.80 ppb respectively.

5. Sediment sampling has been shown to be useful in determining areas of high pesticide, PCB, or phthalate concentration and can be useful in indicating areas of future sampling.

6. In most cases sewage treatment plant effluents were shown to discharge higher concentrations of the pesticides, PCB's and phthalates than the tributary streams. Offshore water showed consistently low concentrations for all parameters. In the tributary streams Aroclor 1242 ranged from N.D. to 1810.0 ppt while Aroclor 1254 ranged from 61.0 to 841.0 ppt. Di-n-butyl phthalate was found in concentrations ranging from a trace to 147.0 ppt in 1972 and was not detected in 1971. Di(2-ethylhexyl) phthalate was not detected in the tributary streams. In sewage treatment plant effluents Aroclor 1242 ranged from N.D. to 4020.0 ppt. Levels of Aroclor 1254 ranged from 97.0 to 568.0 ppt. Di-n-butyl phthalate was detected at levels from 55.0 to 250.0 ppt. Di-(2-ethylhexyl) phthalate was found only in 1971 at levels from N.D. to 760.0 ppt.

7. The North Shore Sanitary District plant at Waukegan showed highest levels for total DDT, methoxychlor, phthalates, and PCB's. The North Shore Sanitary District plant at North Chicago showed highest levels for heptachlor epoxide and dieldrin. Maximum concentrations of DDT and methoxychlor were 259.0 and 106.0 ppt respectively. Maximum concentrations of heptachlor epoxide and dieldrin were 17.2 and 64.3 ppt respectively.

8. In sewage treatment plant effluents methoxychlor was the only pesticide found at concentrations greater than 100.00 ppt. Maximum concentrations of the majority of the isomers of DDT were below 50.0 ppt. This level was exceeded by o,p'-DDT and p,p'-DDT with maximum concentrations of 74.6 ppt and 132.6 ppt respectively.

SECTION II

RECOMMENDATIONS

1. Future research on Lake Michigan should be directed to determine the effects of various pesticides and exotic chemicals on aquatic life. Polychlorinated biphenyls (PCB's) and phthalates require further study.
2. Data from this study indicates that possible sources of DDT, polychlorinated biphenyls (PCB's), heptachlor epoxide, dieldrin, methoxychlor, and phthalates should be included in future water sampling programs. Industrial and municipal effluents should be monitored.
3. Monitoring of fish samples should continue and be directed toward determining trends. Data on DDT, PCB's, dieldrin, and phthalate concentrations should be collected. A continuous monitoring program should be conducted on the entire lake by a single Agency of the Federal government. Bordering Lake states should provide additional data as budgetary restraints permit.
4. Federal support of state monitoring programs, including sediment sampling, should be directed toward determining inputs of pesticides, heavy metals, and other exotic chemicals, results of which can be used in enforcing regulations adopted as a result of monitoring programs.

SECTION III

INTRODUCTION

The States of Illinois, Indiana, Michigan and Wisconsin were provided grants to conduct a monitoring program on Lake Michigan to determine levels of DDT and to develop an analytical capability for pesticide analysis. The pesticide monitoring program was coordinated by a technical committee established under the Lake Michigan Enforcement Conference. An initial report with recommendations was submitted to the conference in 1968 (The Lake Michigan Interstate Pesticide Committee of the Lake Michigan Enforcement Conference, 1968).

On September 23, 1969 the Sanitary Water Board of the Illinois Department of Public Health accepted an EPA Research and Development grant (16050 ESP) of \$40,000 or 66.4% of eligible grant period costs, whichever is less. On July 1, 1970 the Illinois Environmental Protection Agency replaced the Sanitary Water Board and assumed the responsibilities of the grant. Analytical capabilities for pesticides were being developed by the State throughout the grant period. Data reflected in this report was analyzed by Anderson Physics Laboratories, Inc. of Urbana, Illinois, with quality control being accomplished by the Illinois Environmental Protection Agency covering the period beginning in the fall of 1970 through July 1, 1972. Data collected by the Illinois Environmental Protection Agency in 1970 appears in the four-state report, "An Evaluation of DDT and Dieldrin in Lake Michigan", (The Lake Michigan Interstate Pesticide Committee, 1970). This report is made to include additional data collected and analyzed to fulfill requirements of Project 16050 ESP.

Information on present levels of DDT in Lake Michigan was sought in water, sediment, and fish tissue. As the project progressed, more parameters were analyzed. Polychlorinated biphenyls (PCB's), phthalates, heptachlor, heptachlor epoxide, dieldrin, methoxychlor, lindane, aldrin, and endrin levels were examined. Later in the project, a reduced number of stations were sampled with emphasis being placed on sewage treatment plant and tributary inputs. The total number of species of fish analyzed was reduced to allow an increased number of samples of yellow perch and chubs. Sediment samples were collected in the open lake and in tributary streams and ravines to determine present levels.

Data from this monitoring program provided information on present levels of various pesticides in Lake Michigan and indicated that PCB's and other environmental contaminants should receive further study.

While PCB's were not separated during routine analyses for the pesticides in 1970, this procedure was accomplished during 1971 and 1972. Both Vieth and Lee (1970) and WARF Institute, Inc. (1970) reported that PCB's may introduce serious errors or extreme difficulty in interpre-

ting results in pesticide analyses. While PCB's were found in Lake Michigan, their biological significance was not known. Studies were initiated by the National Water Quality Laboratory in Duluth, Minnesota (Nebeker, et al., 1972) to determine the toxicity of PCB's to fish and aquatic life. This study indicated that PCB's were cumulative and did exhibit a chronic toxicity at very low levels. Further monitoring will be needed to determine sources of PCB's.

SECTION IV
PESTICIDE MONITORING
LAKE MICHIGAN FISH

In 1969 concern over DDT contamination in Lake Michigan increased when it was found that hatchery mortality of coho salmon could have been caused by DDT (Willford, et al., 1969). Although PCB's were not reported, this compound could have been involved.

The Illinois Environmental Protection Agency initiated a program in 1970 to obtain pesticide residue levels in several species of Lake Michigan fish. In 1971 and 1972, analyses were expanded from testing for total DDT, heptachlor epoxide, and dieldrin to include polychlorinated biphenyls (PCB's), phthalates, methoxychlor, lindane (BHC), aldrin, endrin and heptachlor.

A total of 255 fish were analyzed over the three year period including samples of yellow perch, chubs, carp, coho salmon, alewife and brown trout. Difficulties in obtaining all species in 1972 limited collections to yellow perch and chubs. Fish were collected from commercial fishermen and the Illinois Conservation Department in the Chicago and Waukegan regions of Lake Michigan. Fish were separated by species and sex and composited into samples of five fish whenever possible according to recommendations of the technical pesticides committee (Lake Michigan Interstate Pesticide Committee, 1968).

In most species, levels of polychlorinated biphenyls (PCB's) were as high or higher than DDT. Levels of PCB and DDT were all below the interim guidelines of 5.0 ppm and 0.3 ppm for dieldrin established by the Food and Drug Administration (Tables 1, 2, and 3). Aroclor 1254 was identified in all samples analyzed, including yellow perch, chub, carp, coho, and alewife. Aroclor 1242 was found in several samples of yellow perch, chubs, carp, and coho salmon.

Chubs most often had the highest levels of PCB's and DDT while perch had the lowest. Alewives showed PCB levels comparable to chubs. Male yellow perch, chubs, and alewife had higher concentrations of PCB and DDT than females.

In this study heptachlor, heptachlor epoxide, methoxychlor, lindane, aldrin, endrin and phthalates were not found in concentrations which would indicate a present problem in fish flesh. Levels of DDT were lower than those found by Reinert (1970) in several species of Lake Michigan fish. Reinert based his work on whole fish while data in this study is based on the edible portions only. From the public health standpoint, the edible portions of fish flesh are considered to indicate a better picture of pesticide contamination since some

pesticides may be concentrated in various organs or fatty tissues which would be lost in cleaning or cooking and therefore would not be ingested. Earlier studies indicated total DDT concentrations without the separation of PCB's. Since PCB's were separated in this study, more meaningful data had been produced.

TABLE 1

PESTICIDES FOUND IN EDIBLE PORTIONS OF FOUR SPECIES OF LAKE MICHIGAN FISH (1970).
Values are expressed in parts per million (ppm) on a weight basis.

SPECIES	NUMBER AND SEX ANALYZED	SIZE IN INCHES	SAMPLE LOCATION	DATE COLLECTED	HEPTACHLOR EPOXIDE	DIELDRIN	<u>o, p' isomers</u>		<u>p, p' isomers</u>		DDD	TOTAL DDT
							DDE	DDT	DDE	DDT		
Yellow Perch	5 Female	9.0 - 10.0	Chicago	11/19/70	0.1	0.1	0.1	0.1	0.5	0.3	0.2	1.2
Yellow Perch	5 Female	9.0 - 9.5	Chicago	11/19/70	0.1	0.1	<0.1	0.1	0.4	0.3	0.1	0.9
Yellow Perch	5 Male	9.0 - 9.5	Chicago	11/19/70	0.1	0.1	0.1	0.1	0.6	0.6	0.2	1.6
Yellow Perch	5 Male	8.5 - 10.0	Chicago	11/19/70	0.1	0.1	0.1	0.1	0.6	0.5	0.2	1.5
Coho Salmon	4 Male	24.5 - 31.0	Waukegan	11/23/70	<0.1	<0.1	0.1	0.2	1.0	0.6	0.3	2.2
Coho Salmon	4 Male	28.0 - 29.0	Waukegan	11/13/70	<0.1	<0.1	0.1	0.2	0.9	0.4	0.2	1.8
Coho Salmon	3 Female	26.0 - 27.5	Waukegan	11/13-23/70	<0.1	<0.1	0.1	0.1	0.8	0.3	0.2	1.5
Coho Salmon	2 Female	25.0 - 27.5	Chicago	11/13/70	<0.1	<0.1	0.1	0.1	0.9	0.5	0.2	1.8
Chubs	5 Mixed	10.5 - 11.5	Waukegan	12/22/70	0.1	0.1	0.3	0.4	1.3	1.1	0.4	3.5
Chubs	5 Mixed	10.5 - 11.5	Waukegan	12/22/70	0.1	0.1	0.3	0.3	1.2	1.0	0.3	3.1
Brown Trout	3 Female	17.5 - 20.5	Chicago	11/13/70	<0.1	<0.1	0.2	0.3	1.3	0.8	0.5	3.1

TABLE 2

PESTICIDES, PCB'S AND PHTHALATES FOUND IN EDIBLE PORTIONS OF FIVE SPECIES OF LAKE MICHIGAN FISH (1971). Values are expressed in parts per million (ppm) on a wet weight basis.

SPECIES	NUMBER AND SEX ANALYZED	SIZE IN INCHES	SAMPLE LOCATION	DATE COLLECTED	HEPTACHLOR EPOXIDE	DIELDRIN	METHOXYCHLOR	LINDANE	DOP	DBP
Yellow Perch	4 Male	7.0 - 10.5	Chicago	10/6/71	<0.1	<0.1	ND	ND	0.3	<0.1
Yellow Perch	5 Male	8.0 - 11.0	Chicago	10/6/71	<0.1	<0.1	ND	ND	0.3	<0.1
Yellow Perch	5 Female	8.0 - 12.0	Chicago	10/6/71	<0.1	<0.1	ND	<0.1	0.2	<0.1
Yellow Perch	5 Female	8.0 - 10.0	Chicago	10/6/71	<0.1	<0.1	ND	ND	0.4	<0.1
Chub	5 Female	9.0 - 10.0	Waukegan	7/13/71	<0.1	0.1	ND	<0.1	1.3	0.1
Chub	5 Female	10.0 - 10.5	Waukegan	7/13/71	<0.1	0.1	ND	<0.1	1.1	0.1
Chub	5 Male	9.5 - 12.0	Waukegan	7/13/71	<0.1	0.2	ND	<0.1	1.2	0.1
Chub	5 Male	10.0 - 12.0	Waukegan	7/13/71	<0.1	0.2	ND	<0.1	1.3	0.1
Carp	5 Male	17.5 - 27.5	Chicago	4/13 - 4/20/71	<0.1	0.1	0.1	ND	ND	0.1
Carp	4 Male	17.0 - 23.5	Chicago	4/20/71	<0.1	<0.1	<0.1	ND	T	<0.1
Carp	4 Female	18.0 - 25.0	Chicago	4/13 - 4/20/71	<0.1	0.1	<0.1	ND	ND	<0.1
Carp	5 Female	22.5 - 25.5	North Chicago	5/25/71	<0.1	<0.1	ND	ND	ND	ND
Carp	5 Female	23.5 - 30.0	North Chicago	5/25/71	T	<0.1	ND	ND	ND	ND
Carp	5 Male	18.0 - 23.0	Chicago	4/13 - 4/20/71	<0.1	0.1	ND	ND	ND	ND
Coho Salmon	5 Male	18.5 - 21.5	Chicago	4/13 - 4/20/71	<0.1	<0.1	ND	ND	ND	<0.1
Coho Salmon	4 Male	18.0 - 20.0	Chicago	4/13 - 4/20/71	<0.1	<0.1	0.1	ND	ND	0.1
Coho Salmon	5 Female	18.5 - 21.0	Chicago	4/13 - 4/20/71	<0.1	0.5	ND	ND	ND	<0.1
Coho Salmon	5 Female	18.5 - 22.0	Waukegan	5/26/71	<0.1	0.1	ND	ND	ND	ND
Coho Salmon	5 Female	19.5 - 22.5	Waukegan	5/26/71	<0.1	0.1	ND	ND	ND	ND
Coho Salmon	5 Male	20.0 - 23.5	North Chicago	5/26/71	<0.1	0.1	ND	ND	ND	ND
Coho Salmon	4 Male	18.5 - 21.5	North Chicago	4/13 - 5/26/71	<0.1	0.1	ND	ND	ND	<0.1
Alewife	5 Male	6.0 - 7.0	Chicago	5/11/71	<0.1	0.1	ND	<0.1	ND	ND
Alewife	5 Male	6.0 - 7.0	Chicago	5/11/71	<0.1	0.1	ND	<0.1	ND	ND
Alewife	5 Female	6.0 - 7.0	Chicago	5/11/71	<0.1	0.1	ND	T	ND	ND
Alewife	5 Female	6.0 - 7.0	Chicago	5/11/71	<0.1	0.1	ND	<0.1	ND	ND
Alewife	5 Female	6.0 - 7.0	North Chicago	4/28/71	<0.1	0.1	ND	<0.1	ND	ND
Alewife	5 Female	6.0 - 7.0	North Chicago	4/28/71	<0.1	0.1	ND	<0.1	ND	ND
Alewife	5 Male	6.0 - 7.0	North Chicago	4/28/71	<0.1	0.1	ND	ND	ND	ND
Alewife	5 Male	6.0 - 7.0	North Chicago	4/28/71	<0.1	0.1	ND	ND	ND	ND

DOP = di (2-ethylhexyl) phthalate

DBP = di-n-butyl phthalate

T = Trace

ND = Not Detected

TABLE 2
(Continued)

PESTICIDES, PCB'S AND PHTHALATES FOUND IN EDIBLE PORTIONS OF FIVE SPECIES OF LAKE MICHIGAN FISH (1971). Values are expressed in parts per million (ppm) on a wet weight basis.

SPECIES	NUMBER AND SEX ANALYZED	SIZE IN INCHES	SAMPLE LOCATION	DATE COLLECTED	o, p' isomers			p, p' isomers			TOTAL DDT	Aroclor	
					DDE	DDD	DDT	DDE	DDD	DDT		1242	1254
Yellow Perch	4 Male	7.0 - 10.5	Chicago	10/6/71	0.1	<0.1	0.1	0.5	0.1	0.4	1.2	.1	.3
Yellow Perch	5 Male	8.0 - 11.0	Chicago	10/6/71	<0.1	<0.1	0.1	0.2	0.1	0.2	0.6	.1	.2
Yellow Perch	5 Female	8.0 - 12.0	Chicago	10/6/71	<0.1	<0.1	<0.1	0.1	<0.1	0.1	0.3	--	.1
Yellow Perch	5 Female	8.0 - 10.0	Chicago	10/6/71	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	0.3	--	.1
Chub	5 Female	9.0 - 10.0	Waukegan	7/13/71	<0.1	<0.1	0.3	1.8	0.1	1.2	3.5	.2	2.5
Chub	5 Female	10.0 - 10.5	Waukegan	7/13/71	<0.1	<0.1	0.3	1.6	0.1	0.9	2.9	.2	1.9
Chub	5 Male	9.5 - 12.0	Waukegan	7/13/71	0.1	0.1	0.4	1.9	0.3	1.4	4.2	.3	3.1
Chub	5 Male	10.0 - 12.0	Waukegan	7/13/71	<0.1	<0.1	0.3	1.9	0.3	1.5	4.0	.4	2.8
Carp	5 Male	17.5 - 27.5	Chicago	4/13 - 4/20/71	<0.1	0.1	0.1	0.5	0.3	<0.1	1.0	1.3	1.0
Carp	4 Male	17.0 - 23.5	Chicago	4/20/71	<0.1	0.1	<0.1	0.3	0.2	<0.1	0.7	1.1	1.5
Carp	4 Female	18.0 - 25.0	Chicago	4/13 - 4/20/71	<0.1	0.1	<0.1	0.5	0.3	<0.1	0.9	1.0	0.9
Carp	5 Female	22.5 - 25.5	North Chicago	5/25/71	0.1	0.1	<0.1	0.3	0.5	<0.1	1.0	--	1.7
Carp	5 Female	23.5 - 30.0	North Chicago	5/25/71	0.1	0.1	<0.1	0.5	0.5	<0.1	1.3	--	1.9
Carp	5 Male	18.0 - 23.0	Chicago	4/13 - 4/20/71	--	0.2	<0.1	0.6	1.1	<0.1	2.0	--	1.9
Coho Salmon	5 Male	18.5 - 21.5	Chicago	4/13 - 4/20/71	<0.1	<0.1	<0.1	0.3	0.1	0.1	0.6	1.0	0.9
Coho Salmon	4 Male	18.0 - 20.0	Chicago	4/13 - 4/20/71	<0.1	<0.1	<0.1	0.2	<0.1	0.1	0.4	0.8	0.9
Coho Salmon	5 Female	18.5 - 21.0	Chicago	4/13 - 4/20/71	<0.1	<0.1	<0.1	0.3	<0.1	0.1	0.5	0.7	0.7
Coho Salmon	5 Female	18.5 - 22.0	Waukegan	5/26/71	<0.1	<0.1	0.1	0.2	0.1	<0.1	0.5	--	0.8
Coho Salmon	5 Female	19.5 - 22.5	Waukegan	5/26/71	0.1	--	<0.1	0.4	0.1	<0.1	0.6	--	1.3
Coho Salmon	5 Male	20.0 - 23.5	Waukegan	5/26/71	0.1	--	<0.1	0.3	0.1	<0.1	0.5	--	1.1
Coho Salmon	4 Male	18.5 - 21.5	North Chicago	4/13 - 5/26/71	<0.1	<0.1	<0.1	0.5	0.1	0.1	0.7	2.2	1.8
Alewife	5 Male	6.0 - 7.0	Chicago	5/11/71	0.1	<0.1	<0.1	1.0	0.2	0.3	1.8	--	3.0
Alewife	5 Male	6.0 - 7.0	Chicago	5/11/71	0.1	T	0.1	1.1	0.2	0.3	1.9	--	3.3
Alewife	5 Female	6.0 - 7.0	Chicago	5/11/71	--	--	0.1	1.0	0.1	0.1	1.3	--	2.5
Alewife	5 Female	6.0 - 7.0	Chicago	5/11/71	--	T	<0.1	0.5	0.1	0.1	0.8	--	2.4
Alewife	5 Female	6.0 - 7.0	North Chicago	4/28/71	--	T	0.1	1.1	0.1	0.1	1.4	--	2.8
Alewife	5 Female	6.0 - 7.0	North Chicago	4/28/71	0.1	<0.1	0.1	1.2	0.2	0.1	1.7	--	2.8
Alewife	5 Male	6.0 - 7.0	North Chicago	4/28/71	0.1	<0.1	<0.1	1.1	0.2	0.2	1.6	--	2.7
Alewife	5 Male	6.0 - 7.0	North Chicago	4/28/71	0.1	--	0.1	1.0	0.1	0.2	1.5	--	3.2

T = Trace

TABLE 3

PESTICIDES, PCB'S AND PHTHALATES FOUND IN THE EDIBLE PORTIONS OF TWO SPECIES OF LAKE MICHIGAN FISH (1972). Values are expressed in parts per million (ppm) on a wet weight basis.

SPECIES	NUMBER AND SEX ANALYZED	SIZE IN INCHES	SAMPLE LOCATION	DATE COLLECTED	HEPTACHLOR EPOXIDE	DIELDRIN	DBP	<u>O, p' Isomers</u>			<u>p, p' Isomers</u>			TOTAL DDT	AROCOLOR 1254
								DDE	DDD	DDT	DDE	DDD	DDT		
Chubs	5 Male	8.5 - 10.0	Waukegan	5/25/72	<0.1	0.1	<0.1	0.1	<0.1	0.6	2.0	0.2	1.7	4.6	2.8
Chubs	5 Female	8.5 - 10.0	Waukegan	5/25/72	<0.1	0.1	<0.1	0.1	<0.1	0.3	1.2	0.1	0.9	2.6	2.5
Chubs	5 Female	9.0 - 9.5	Waukegan	5/25/72	<0.1	0.1	<0.1	0.2	<0.1	0.2	1.0	0.1	0.7	2.2	2.5
Chubs	5 Female	8.5 - 9.0	Waukegan	5/25/72	<0.1	0.1	<0.1	0.1	<0.1	0.2	1.0	0.1	0.6	2.0	2.8
Chubs	5 Female	8.0 - 8.5	Waukegan	5/25/72	<0.1	0.1	0.1	0.1	<0.1	0.3	1.3	0.1	0.9	2.7	2.9
Chubs	5 Female	8.5 - 10.0	Waukegan	5/25/72	<0.1	0.2	0.1	0.1	<0.1	0.3	1.2	0.1	1.1	3.0	2.9
Chubs	5 Female	8.5 - 10.0	Waukegan	5/25/72	<0.1	0.2	0.1	0.1	<0.1	0.3	1.2	0.2	1.2	3.0	3.1
Chubs	5 Female	8.0 - 8.5	Waukegan	5/25/72	<0.1	0.1	<0.1	0.1	<0.1	0.2	1.1	0.1	1.0	2.5	3.1
Yellow Perch	5 Female	8.0 - 9.5	Waukegan	6/28/72	<0.1	<0.1	ND	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	0.2	0.3
Yellow Perch	4 Female	8.5 - 9.0	Waukegan	6/28/72	<0.1	<0.1	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.3
Yellow Perch	5 Male	8.0 - 9.5	Waukegan	6/28/72	<0.1	<0.1	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.3
Yellow Perch	5 Female	8.5 - 9.5	Waukegan	6/28/72	<0.1	<0.1	ND	<0.1	ND	<0.1	<0.1	<0.1	0.1	0.1	0.2
Yellow Perch	5 Male	9.0 - 9.5	Waukegan	6/28/72	<0.1	<0.1	ND	<0.1	ND	<0.1	0.1	<0.1	0.1	0.2	0.3
Yellow Perch	5 Male	8.0 - 9.0	Waukegan	6/28/72	<0.1	<0.1	ND	<0.1	ND	<0.1	0.1	<0.1	<0.1	0.2	0.3

DBP = di-n-butyl phthalate
 ND = Not Detected

SECTION V
PESTICIDE MONITORING
LAKE MICHIGAN SEDIMENTS

In 1970 and 1971, fifty sediment samples were collected in tributary streams and ravines in Lake County and at stations offshore from Lake and Cook Counties in Illinois (Tables 4 and 5). Stream and ravine sediment samples were collected approximately 50 yards upstream from Lake Michigan. Lake samples were collected 40 to 80 yards offshore from seven North Shore Sanitary District (NSSD) sewage treatment plants and at stations approximately one to three miles offshore using a Ponar dredge (Figure 1). As could be expected offshore stations contained low levels of pesticides, PCB's, and phthalates. Tributary stream and ravine sediments reflected possible contamination from residential spraying programs. Some of the exotic chemicals were found in greater concentrations in industrial areas and off sewage treatment plants in Lake County. Analysis of sediments was found to be useful in locating areas in which additional sampling could possibly determine sources.

At the offshore stations, PCB's were usually found in highest concentrations followed by DDT, methoxychlor, dieldrin, and heptachlor epoxide. Concentrations averaged less than 7.0 ppb for total DDT, 1.24 ppb for methoxychlor, <0.5 ppb for dieldrin, and <0.6 ppb for heptachlor epoxide. Aldrin, endrin, lindane, heptachlor, and di-n-butyl phthalate were not detected in sediments of the open lake. Di(2-ethylhexyl) phthalate was rarely found in the open water sediments.

Tributary stream and ravine sediments reflected highest concentrations of PCB's and total DDT followed by methoxychlor, heptachlor epoxide, dieldrin, and heptachlor. Lindane and the phthalates were not consistently found in the tributary sediments. Aldrin and endrin were not detected.

Concentrations of total DDT, dieldrin, and lindane found in stream sediments compared favorably with results found by the Wisconsin Alumni Research Foundation (WARF Institute, Inc., 1970) in its survey of 73 sediments samples collected in streams tributary to Lake Michigan.

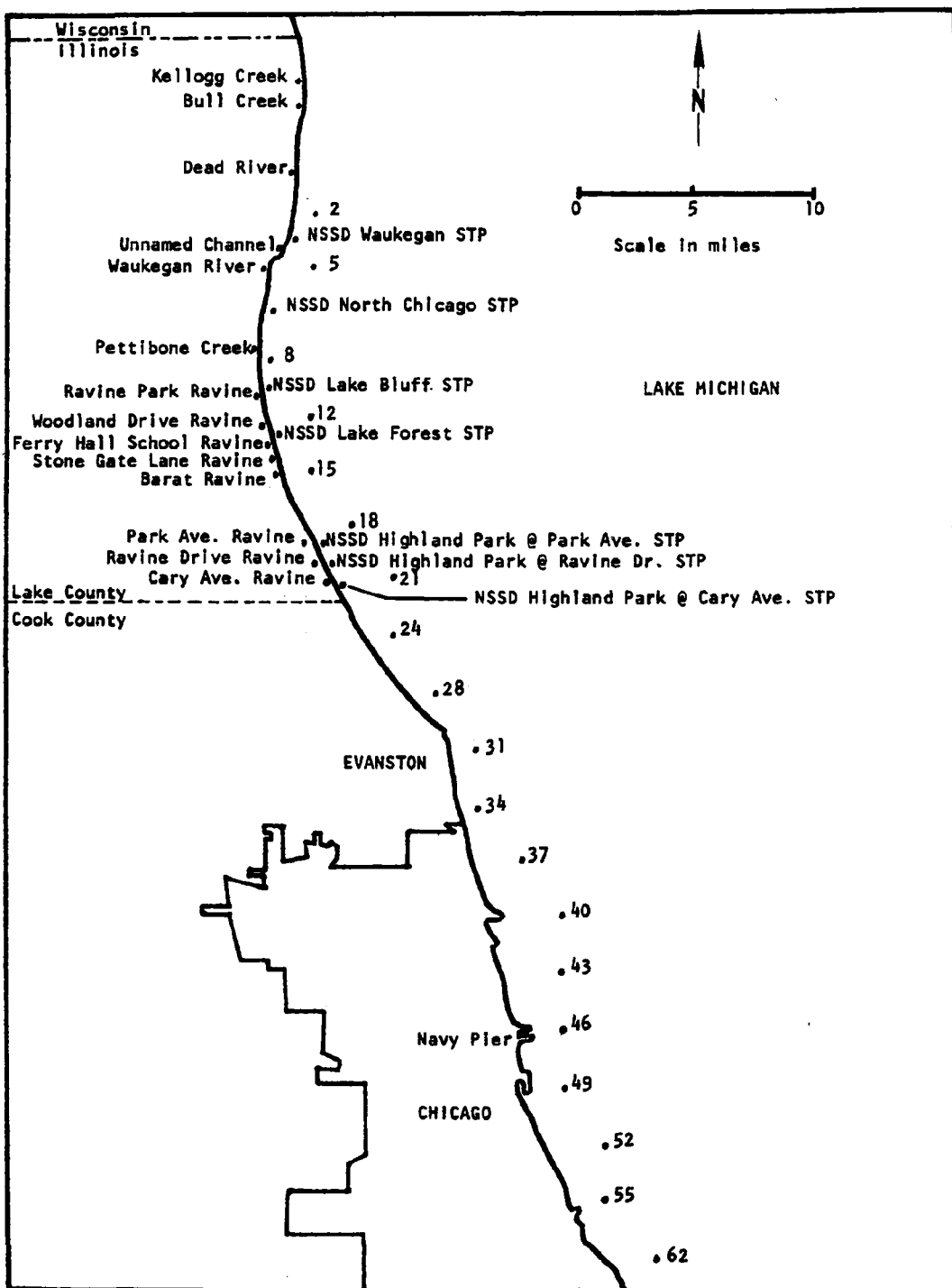


FIGURE 1. LOCATIONS OF SEDIMENT SAMPLING STATIONS

OPEN WATER SEDIMENTS

Heptachlor epoxide

Heptachlor epoxide levels averaged below 0.6 ppb and ranged from ND - 1.35 ppb at a point 40 - 80 yards offshore from the North Shore Sanitary District sewage treatment plant in Lake Bluff.

Dieldrin

Concentrations of dieldrin averaged less than 0.5 ppb and ranged from 0.03 - 1.25 ppb. The highest level was found at lake bed station number 43 offshore from Chicago.

Methoxychlor

Concentrations of methoxychlor averaged 1.24 ppb and ranged from 0.13 - 6.60 ppb. The highest level was found at station number 37 offshore from Chicago.

Di (2-ethylhexyl) phthalate: (DOP)

Di (2-ethylhexyl) phthalate was rarely found in the open water sediments. This chemical was found in three out of 24 samples at values ranging from ND - 7.18 ppb.

o,p'-DDE

Concentrations of o,p'-DDE ranged from <0.1 - 0.97 ppb. The highest level (0.97 ppb) was found 40 - 80 yards offshore from the North Shore Sanitary District plant at Park Avenue in Highland Park. Twenty samples collected in 1971 averaged 0.07 ppb.

o,p'-DDD

Concentrations of o,p'-DDD ranged from 0.02 - 5.47 ppb. The highest level (5.47 ppb) was found at lake bed station number 46 offshore from Chicago. Twenty-four samples collected in 1971 averaged 1.01 ppb.

o,p'-DDT

Concentrations of o,p'-DDT ranged from 0.02 - 4.00 ppb. The highest level (4.00 ppb) was found 40 - 80 yards offshore from the North Shore Sanitary District plant at Park Avenue in Highland Park. Twenty-two samples collected in 1971 averaged 0.24 ppb.

p,p'-DDE

Concentrations of p,p'-DDE ranged from 0.06 - 4.82 ppb. The highest level (4.82 ppb) was found at lake bed station number 43 offshore from Chicago. Twenty-four samples collected in 1971 averaged 1.21 ppb.

TABLE 4

PESTICIDES FOUND IN SEDIMENTS FROM LAKE MICHIGAN AND TRIBUTARY STREAMS AND RAVINES IN ILLINOIS (1970). Values are expressed in parts per billion (ppb) on a dry weight basis.

SAMPLE LOCATION	HEPTACHLOR EPOXIDE	DIELDRIN	o, p' Isomers			p, p' Isomers			TOTAL DDT
			DDE	DDD	DDT	DDE	DDD	DDT	
Tributary Streams and Ravines ¹									
Waukegan River	9.80	4.09	---	---	0.50	6.40	30.60	18.00	55.50
Pettibone Creek	9.30	21.40	1.02	35.00	27.50	67.30	258.00	340.00	728.82
Lake Bluff-Ravine	2.60	1.37	0.61	---	6.50	4.60	58.80	24.00	94.51
Lake Forest-Woodland Drive Ravine	57.00	30.80	17.00	62.00	83.00	52.00	353.00	375.00	942.00
Lake Forest-Barat Creek	3.10	3.40	1.10	2.73	7.50	8.57	27.50	50.10	97.50
Highland Park-Ravine Drive Ravine	2.40	2.64	0.91	53.00	17.50	27.20	120.20	81.60	300.21
	(14.03)	(10.62)	(4.13)	(30.55)	(23.15)	(27.68)	(141.32)	(148.12)	(369.76)
Lake Sediments ²									
Waukegan	0.38	0.29	0.39	0.75	---	0.06	1.41	1.14	3.75
North Chicago	0.98	0.64	---	0.65	0.02	1.15	4.23	1.73	7.78
Lake Bluff	1.35	0.80	0.03	---	0.50	3.00	12.60	13.00	29.13
Lake Forest	0.58	0.28	0.05	---	0.25	0.77	2.88	1.20	5.15
Highland Park (Park Avenue)	0.26	0.55	0.97	3.60	4.00	0.48	0.02	1.90	10.97
Highland Park (Ravine Drive)	0.17	0.08	0.01	1.87	---	0.45	0.01	0.89	3.23
Highland Park (Cary Avenue)	0.15	0.28	0.04	0.02	0.50	0.75	3.12	1.97	6.40
	(0.55)	(0.42)	(0.25)	(1.38)	(1.05)	(0.95)	(3.47)	(3.12)	(9.49)

1 50 yards upstream from Lake Michigan.

2 40-80 yards offshore of the indicated sewage treatment plant.

p,p'-DDD

Concentrations of p,p'-DDD ranged from 0.01 - 12.60 ppb. The highest level (12.60 ppb) was found 40 - 80 yards offshore from the North Shore Sanitary District Lake Bluff plant. Twenty-four samples collected in 1971 averaged 3.04 ppb.

p,p'-DDT

Concentrations of p,p'-DDT ranged from 0.11 - 13.00 ppb. The highest level (13.00 ppb) was found 40 - 80 yards offshore from the North Shore Sanitary District sewage treatment plant at Lake Bluff. Twenty-four samples collected in 1971 averaged 1.21 ppb.

Aroclor 1242

Concentrations of Aroclor 1242 ranged from ND - 106.07 ppb. The highest level was found 40 - 80 yards offshore from the North Shore Sanitary District sewage treatment plant at North Chicago. Twenty-four samples collected in 1971 averaged 23.66 ppb.

Aroclor 1254

Concentrations of Aroclor 1254 ranged from 2.48 - 46.92 ppb. The highest level (46.92 ppb) was found at lake bed station number 43 off of Chicago. Twenty-four samples collected in 1971 averaged 14.66 ppb.

TRIBUTARY SEDIMENTS

Heptachlor Epoxide

Concentrations of heptachlor epoxide ranged from 0.02 - 57.00 ppb. The highest level (57.00 ppb) was found in the Woodland Drive ravine in Lake Forest approximately 50 yards upstream from Lake Michigan.

Dieldrin

Concentrations of dieldrin ranged from 0.01 - 30.80 ppb. The highest level was found (30.80 ppb) approximately 50 yards upstream from Lake Michigan in the Woodland Drive ravine in Lake Forest.

Methoxychlor

Concentrations of methoxychlor ranged from 0.19 - 175.00 ppb. The highest level (175.00 ppb) was found in Barat Ravine in Lake Forest approximately 50 yards upstream from Lake Michigan.

Lindane

Concentrations of lindane were detected in 4 of 13 samples. Levels ranged from ND - 0.15 ppb.

TABLE 5

PESTICIDES, PCB'S AND PHTHALATES FOUND IN LAKE MICHIGAN SEDIMENTS AND IN TRIBUTARY
STREAM AND RAVINE SEDIMENTS IN ILLINOIS (1971). Values are expressed in parts per
billion (ppb) on a dry weight basis.

SAMPLE LOCATION	HEPTACHLOR EPOXIDE	DIELDRIN	METHOXYCHLOR	LINDANE	HEPTACHLOR	DOP	DBP
<u><1 to 3 MILES OFFSHORE</u>							
NSSD Park Ave. STP (Highland Park)	0.02	0.14	0.31	ND	ND	4.13	ND
NSSD Lake Forest STP (Lake Forest)	0.01	0.11	0.55	ND	ND	ND	ND
NSSD Lake Bluff STP (Lake Bluff)	0.01	0.06	0.91	ND	ND	ND	ND
NSSD North Chicago STP (North Chicago)	0.02	0.13	0.80	ND	ND	ND	ND
NSSD Waukegan STP (Waukegan)	ND	0.03	0.30	ND	ND	7.18	ND
Lake Bed Station 60	0.06	0.29	0.70	ND	ND	ND	ND
Lake Bed Station 55	0.07	0.48	1.11	ND	ND	ND	ND
Lake Bed Station 52	0.02	0.19	0.87	ND	ND	ND	ND
Lake Bed Station 49	0.15	0.67	1.94	ND	ND	ND	ND
Lake Bed Station 46	0.11	0.52	1.73	ND	ND	ND	ND
Lake Bed Station 43	0.08	1.25	2.18	ND	ND	ND	ND
Lake Bed Station 40	0.17	1.22	1.15	ND	ND	ND	ND
Lake Bed Station 37	0.12	0.86	6.60	ND	ND	ND	ND
Lake Bed Station 34	0.01	0.09	0.71	ND	ND	ND	ND
Lake Bed Station 31	0.01	0.05	0.71	ND	ND	ND	ND
Lake Bed Station 28	0.01	0.23	0.92	ND	ND	ND	ND
Lake Bed Station 24	0.01	0.14	4.68	ND	ND	ND	ND
Lake Bed Station 21	ND	0.04	0.68	ND	ND	ND	ND
Lake Bed Station 18	ND	0.03	0.67	ND	ND	ND	ND
Lake Bed Station 15	0.01	0.04	0.60	ND	ND	ND	ND
Lake Bed Station 12	0.02	0.07	0.52	ND	ND	ND	ND
Lake Bed Station 8	0.02	0.11	0.59	ND	ND	ND	ND
Lake Bed Station 5	0.02	0.23	0.13	ND	ND	ND	ND
Lake Bed Station 2	0.02	0.05	0.41	ND	ND	1.05	ND
	(0.04)	(0.29)	(1.24)	(ND)	(ND)	(0.52)	(ND)
<u>-10 to YARDS UPSTREAM FROM LAKE</u>							
Bull Creek (Zion)	0.03	0.08	0.50	ND	0.06	ND	ND
Dead River (Zion)	0.02	0.17	0.44	ND	0.05	ND	ND
Unnamed channel (Waukegan)	0.07	1.04	9.40	ND	ND	218.00	ND
Waukegan River (Waukegan)	3.75	0.44	2.98	ND	0.24	ND	ND
Pettibone Creek (North Chicago)	2.08	0.57	2.44	ND	0.01	51.30	ND
Stone Gate Lane Ravine (Lake Forest)	2.04	0.43	11.80	ND	0.05	42.90	ND
Berry Hall School Ravine (Lake Forest)	3.50	0.95	41.00	0.01	0.08	ND	ND
Cary Avenue Ravine (Highland Park)	3.81	1.60	13.10	0.01	0.07	ND	ND
Ravine Drive Ravine (Highland Park)	2.83	2.54	9.10	ND	0.09	28.50	25.00
Park Ave. Ravine (Highland Park)	3.27	9.50	6.90	0.03	0.12	57.00	120.00
Barat Ravine (Lake Forest)	0.15	1.04	175.00	ND	0.01	ND	ND
Ravine Park Ravine (Lake Bluff)	1.64	4.25	1.80	0.15	0.03	ND	ND
Kellogg Creek (Zion)	0.03	0.01	0.19	ND	ND	ND	ND
	(1.79)	(1.78)	(21.10)	(0.02)	(0.06)	(30.60)	(11.20)

DOP = di (2-ethylhexyl) phthalate

DBP = di-n-butyl phthalate

ND = Not Detected

TABLE 5
(CONTINUED)

PESTICIDES, PCB'S AND PHTHALATES FOUND IN LAKE MICHIGAN SEDIMENTS AND IN TRIBUTARY
STREAM AND RAVINE SEDIMENTS IN ILLINOIS (1971). Values are expressed in parts per
billion (ppb) on a dry weight basis.

SAMPLE LOCATION	o, p' Isomers			p, p' Isomers			TOTAL DDT	Aroclor	
	DDE	DDD	DDT	DDE	DDD	DDT		1242	1254
<u><1 to 3 MILES OFFSHORE</u>									
NSSD Park Ave. STP (Highland Park)	0.01	0.68	0.14	0.67	2.81	0.62	4.93	11.11	12.42
NSSD Lake Forest STP (Lake Forest)	---	0.22	0.12	0.43	1.10	0.38	2.25	10.51	7.02
NSSD Lake Bluff STP (Lake Bluff)	0.01	0.30	0.13	0.40	1.55	0.60	2.99	44.36	14.45
NSSD North Chicago STP (North Chicago)	---	0.31	0.06	0.44	1.43	0.31	2.55	106.07	26.54
NSSD Waukegan STP (Waukegan)	---	0.08	---	0.94	0.23	0.12	1.37	17.32	11.97
Lake Bed Station 60	0.10	3.32	0.22	2.37	9.14	0.93	16.08	4.46	8.63
Lake Bed Station 55	0.06	1.75	0.38	1.21	5.42	1.93	10.75	3.58	3.15
Lake Bed Station 52	0.04	1.58	0.36	1.11	2.96	0.97	7.02	8.48	3.33
Lake Bed Station 49	0.04	0.93	0.16	1.40	6.18	1.30	10.01	13.65	12.42
Lake Bed Station 46	0.25	5.47	1.42	4.52	8.88	4.66	25.20	49.33	38.65
Lake Bed Station 43	0.26	3.64	0.75	4.82	9.74	7.25	26.46	83.35	46.92
Lake Bed Station 40	0.09	0.99	0.60	2.17	4.24	1.76	9.85	17.23	9.38
Lake Bed Station 37	0.14	0.93	0.13	2.88	3.28	2.82	10.18	30.82	33.50
Lake Bed Station 34	0.02	0.63	0.08	0.52	2.15	0.59	3.99	1.24	2.48
Lake Bed Station 31	0.02	0.52	0.06	0.48	1.74	0.73	3.55	ND	3.87
Lake Bed Station 28	0.04	1.05	0.10	1.32	3.38	0.87	6.76	18.55	17.25
Lake Bed Station 24	0.04	0.61	0.09	0.88	2.02	1.39	5.03	2.48	5.83
Lake Bed Station 21	0.02	0.51	0.11	0.46	1.72	0.34	3.16	8.60	6.64
Lake Bed Station 18	0.01	0.15	---	0.29	0.80	0.11	1.36	10.53	5.56
Lake Bed Station 15	0.02	0.10	0.07	0.39	0.76	0.29	1.63	7.43	5.26
Lake Bed Station 12	0.03	0.16	0.05	0.32	0.62	0.16	1.34	19.25	17.45
Lake Bed Station 8	0.04	0.12	0.07	0.49	0.98	0.20	1.90	24.76	16.30
Lake Bed Station 5	---	0.07	0.07	0.14	1.19	0.49	2.23	46.11	34.52
Lake Bed Station 2	<0.01	0.07	0.02	0.22	0.43	0.28	1.02	4.98	8.36
	(0.07)	(1.01)	(0.24)	(1.21)	(3.04)	-(1.21)	(6.73)	(23.66)	(14.66)
<u>10 to 50 YARDS UPSTREAM FROM LAKE</u>									
Bull Creek (Zion)	0.02	0.04	ND	0.17	0.08	0.11	0.42	13.00	9.10
Dead River (Zion)	0.02	ND	0.07	0.19	0.14	0.37	0.79	12.30	6.29
Unnamed channel (Waukegan)	0.24	2.75	0.50	0.66	5.56	4.08	13.79	553.00	83.04
Waukegan River (Waukegan)	0.85	1.68	0.39	1.47	4.80	0.98	10.17	374.00	131.00
Pettibone Creek (North Chicago)	0.06	11.00	21.00	7.60	41.00	54.30	134.96	173.40	232.00
Stone Gate Lane Ravine (Lake Forest)	ND	9.50	2.75	6.70	49.00	11.40	79.35	2.48	8.74
Berry Hall School Ravine (Lake Forest)	0.73	1.63	9.00	5.82	20.70	15.10	52.98	6.34	12.34
Gary Avenue Ravine (Highland Park)	0.10	20.50	6.95	7.46	66.50	21.90	123.41	3.00	17.90
Ravine Drive Ravine (Highland Park)	1.60	8.00	4.54	6.72	44.20	19.64	84.70	ND	6.38
Park Ave. Ravine (Highland Park)	0.29	16.00	27.00	22.90	62.20	72.80	201.19	4.32	1.54
Barat Ravine (Lake Forest)	ND	0.35	0.53	0.89	1.70	1.82	5.29	4.37	2.91
Ravine Park Ravine (Lake Bluff)	0.91	8.13	1.98	3.44	18.90	7.10	40.46	1.31	2.54
Kellogg Creek (Zion)	0.05	0.03	0.22	0.34	0.16	0.68	1.48	1.77	2.56
	(0.44)	(6.63)	(6.24)	(4.95)	(24.23)	(16.16)	(57.61)	(95.77)	(32.27)

ND = Not Detected

Heptachlor

Concentrations of heptachlor ranged from ND - 0.24 ppb. The highest level (0.24 ppb) was found in the Waukegan River approximately 50 yards upstream from Lake Michigan.

Di (2-ethylhexyl) phthalate: (DOP)

DOP was detected in 5 of 13 samples collected in 1971. Concentrations ranged from ND - 218.00 ppb. The highest concentration (218.00 ppb) was obtained from an unnamed channel in Waukegan.

Di-n-butyl phthalate: (DBP)

DBP was detected in 2 of 13 samples collected in 1971. Concentrations ranged from ND - 120.00 ppb. The highest concentration (120.00 ppb) was obtained approximately 50 yards upstream from Lake Michigan in the Park Avenue Ravine in Highland Park.

o, p'-DDE

Concentrations of o, p'-DDE ranged from ND - 17.00 ppb. The maximum level of 17.00 ppb was found in the Woodland Drive ravine in Lake Forest.

o, p'-DDD

Concentrations of o, p'-DDD ranged from ND - 62.00 ppb. The maximum level was found in the Woodland Drive ravine in Lake Forest.

o, p'-DDT

Concentrations of o, p'-DDT ranged from ND - 83.00 ppb. The maximum level was found in the Woodland Drive ravine in Lake Forest.

p, p'-DDE

Concentrations of p, p'-DDE ranged from 0.17 - 67.30 ppb. The highest level was found in Pettibone Creek in North Chicago.

p, p'-DDD

Concentrations of p, p'-DDD ranged from 0.08 - 353.00 ppb. The highest level was found in Woodland Drive ravine in Lake Forest.

p, p'-DDT

Concentrations of p, p'-DDT ranged from 0.11 - 375.00 ppb. The highest level was found in Woodland Drive ravine in Lake Forest.

Aroclor 1242

Concentrations of Aroclor 1242 ranged from ND - 553.00 ppb. The maximum level (553.00 ppb) was found in an unnamed channel in Waukegan.

Aroclor 1254

Concentrations of Aroclor 1254 ranged from 1.54 - 232.00 ppb. The maximum level (232.00 ppb) was found in Pettibone Creek in North Chicago.

SECTION VI
PESTICIDE MONITORING
LAKE MICHIGAN WATER

Forty-five samples were collected at open water stations, water treatment plants (raw water), tributary streams, and sewage treatment plant final effluents over the three year study. In 1971 and 1972, water sampling was expanded at the tributary streams and sewage treatment plants to determine inputs after it has been established that total DDT levels in Lake Michigan were in the range of one to ten parts per trillion (Lake Michigan Interstate Pesticide Committee, 1972). There are only two counties in Illinois which border Lake Michigan. These are Lake and Cook counties. All sewage treatment plant effluents and tributary stream sources enter Lake Michigan from Lake County (Figure 2).

In 1971 and 1972, analyses were performed on total DDT and its analogs, polychlorinated biphenyls (PCB's), phthalates, heptachlor, heptachlor epoxide, dieldrin, methoxychlor, lindane, aldrin, and endrin. In 1970, water samples were analyzed for DDT, dieldrin, and heptachlor epoxide only (Tables 6, 7, and 8).

In 1970, six crib samples from water treatment plants and 3 open water samples showed concentrations of DDT, heptachlor epoxide and dieldrin all below 1 ppt.

A total of 23 sewage treatment plant samples were collected in the three year period. North Shore Sanitary District plants at North Chicago and Waukegan were sampled each year. Sewage treatment plants at Lake Bluff, Lake Forest, and three at Highland Park were sampled in 1970 only. Sewage treatment plant effluents generally showed higher concentrations of both PCB's and DDT than did the tributary streams. Concentrations of PCB's greatly exceeded concentrations of other pesticides in 1971 sampling but showed reduced values in 1972. Dieldrin showed a decrease from 1971 while DDT showed increased concentrations. While di (2-ethylhexyl) phthalate was found in sewage treatment effluents at concentrations up to 760 ppt in 1971, it was not found in 1972. In 1972, di-n-butyl phthalate was found in both sewage treatment plant effluents and tributary streams. Lindane, aldrin, endrin and heptachlor were not detected in sewage treatment plant effluents or the tributary streams.

Over the three year period, thirteen tributary samples were collected at two locations in Lake County, Illinois. Samples were collected at the Waukegan River in Waukegan and Pettibone Creek in North Chicago.

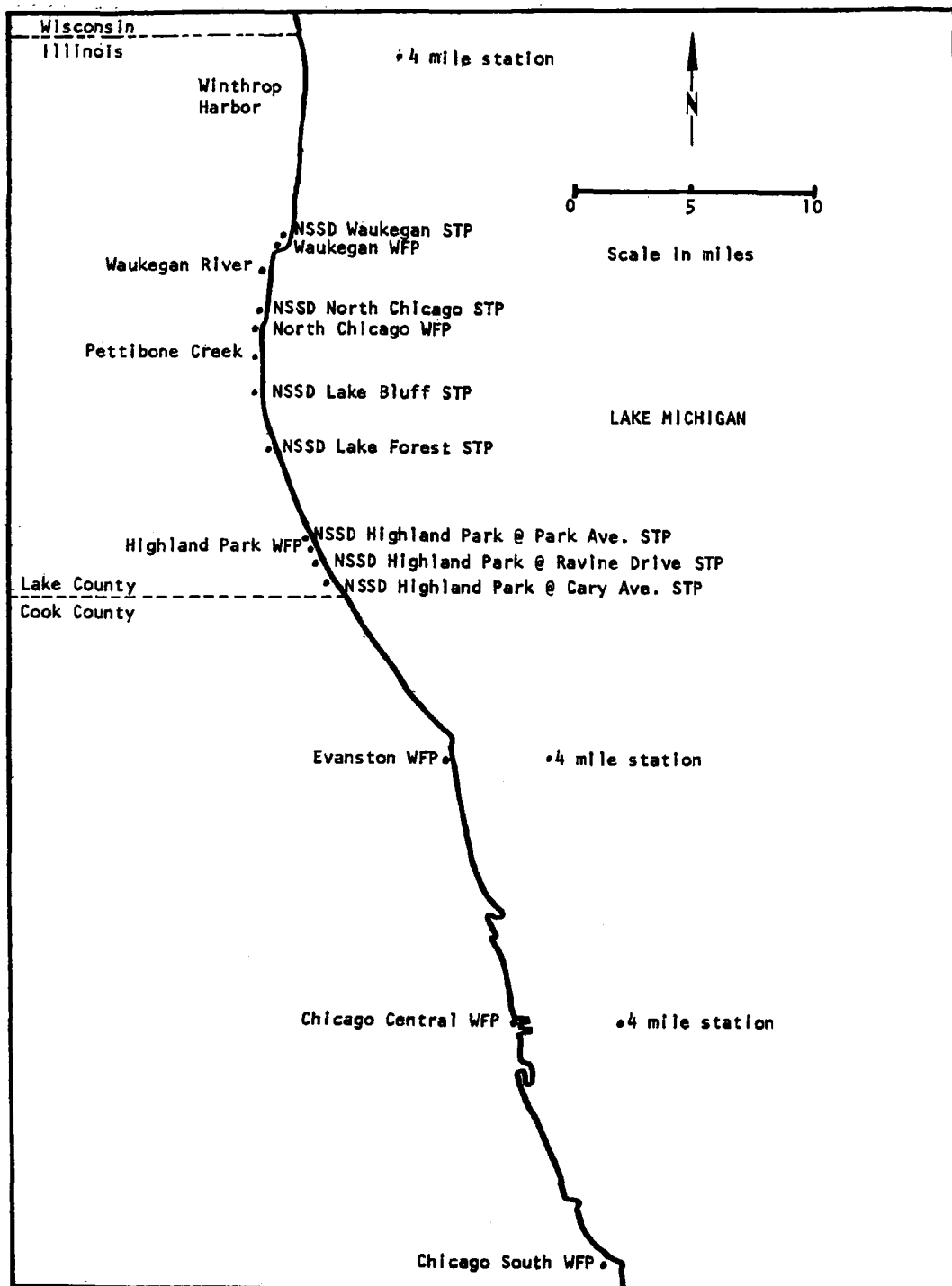


FIGURE 2. LOCATIONS OF WATER SAMPLING STATIONS

STREAMS

Heptachlor epoxide

Heptachlor epoxide levels averaged <0.6, 2.1 and 2.9 ppt for 1970, 1971, and 1972 respectively. Annual ranges were <0.2 - 1.0, ND - 5.4, and 1.2 - 4.5 ppt during the respective period.

Dieldrin

Dieldrin levels averaged 1.2, 10.4, and 2.5 ppt for 1970, 1971, and 1972 respectively. Annual ranges were 0.9 - 1.4, 2.1 - 22.5, and 1.7 - 3.7 ppt during the respective period. The highest concentration of dieldrin (22.5 ppt) was obtained at the Waukegan River on 8/18/71.

Methoxychlor

Concentrations of methoxychlor averaged 15.5 ppt in 1971 and 48.0 ppt in 1972. The range in concentrations during 1971 was 2.9 - 30.7 ppt and 22.6 - 89.1 ppt in 1972. Highest levels were obtained from Pettibone Creek in North Chicago.

Di-n-butyl phthalate: (DBP)

Concentrations of di-n-butyl phthalate were not detected in 1971. In 1972, levels averaged 93.6 ppt and ranged from a trace to 147.0 ppt. Similar concentrations were found at both stream stations.

o, p'-DDE

This isomer was not detected in 1971 and 1972.

o, p'-DDD

o, p'-DDD averaged 1.0 ppt in 1971 and 0.2 ppt in 1972. This isomer was consistently found in low concentrations at both stream stations.

o, p'-DDT

o, p'-DDT averaged <0.6, 1.4 and 8.4 ppt in 1970, 1971 and 1972. Levels found during this period were <0.3 - 0.9, ND - 2.7, 2.3 - 12.5 ppt respectively.

p, p'-DDE

This isomer averaged 1.1, 2.5, and 9.2 ppt in 1970, 1971, and 1972. Ranges of concentrations were 0.6 - 1.6, 1.7 - 2.9, 3.9 - 20.3 ppt during this period. There was a continued increase in the concentration of this isomer over the 3 year period.

p, p'-DDD

This isomer averaged 4.5, 3.6 and 3.3 ppt in 1970, 1971 and 1972 respectively. Ranges of concentrations were 1.8 - 7.2, 2.2 - 5.0, 1.7 - 6.7 ppt during this period.

TABLE 6

PESTICIDES IN WATER SAMPLES FROM LAKE MICHIGAN AND TRIBUTARY SOURCES IN ILLINOIS (1970). Values are expressed in parts per trillion (ppt).

SAMPLE LOCATION	DATE COLLECTED	HEPTACHLOR EPOXIDE	DIELDRIN	O, p' Isomers	p, p' Isomers			TOTAL DDT
				DDT	DDE	DDD	DDT	
<u>Tributary Streams¹</u>								
Waukegan River	11/2/70	1.0	1.4	<0.3	1.6	1.8	2.8	6.3
Pettibone Creek	11/2/70	<u><0.2</u>	<u>0.9</u>	<u>0.9</u>	<u>0.6</u>	<u>7.2</u>	<u>6.2</u>	<u>14.9</u>
		(<0.6)	(1.2)	(<0.6)	(1.1)	(4.5)	(4.5)	(10.6)
<u>Sewage Treatment Plants²</u>								
NSSD Waukegan	10/23/70	0.7	2.4	0.8	5.1	0.4	4.9	11.2
NSSD North Chicago	10/23/70	0.6	2.5	1.8	1.7	0.3	3.7	7.5
NSSD Lake Bluff	11/2/70	<0.2	1.5	<0.3	0.3	0.9	1.2	2.5
NSSD Lake Forest	11/2/70	<0.2	2.2	0.4	1.5	0.4	1.2	3.5
NSSD Highland Park - Park Avenue	11/2/70	<0.2	1.6	0.4	0.9	0.8	1.1	3.2
NSSD Highland Park - Ravine Drive	11/2/70	<0.2	2.3	0.3	3.4	1.5	3.9	9.1
NSSD Highland Park - Cary Avenue	11/2/70	<u><0.2</u>	<u>0.6</u>	<u>0.5</u>	<u>0.7</u>	<u>0.3</u>	<u>1.1</u>	<u>2.6</u>
		(<0.3)	(1.9)	(0.6)	(1.9)	(0.7)	(2.4)	(5.7)
<u>Open Water Samples³</u>								
Winthrop Harbor	10/20/70	<0.2	<0.2	<0.3	<0.3	<0.3	<1.0	0.4
Evanston	10/20/70	<0.2	<0.2	<0.3	<0.3	<0.3	<1.0	<0.3
Chicago ⁴	10/20/70	<u><0.2</u>	<u><0.2</u>	<u><0.3</u>	<u><0.3</u>	<u><0.3</u>	<u><1.0</u>	<u>0.3</u>
		(<0.2)	(<0.2)	(<0.3)	(<0.3)	(<0.3)	(<1.0)	(<0.3)
<u>Water Plant Intake Samples⁵</u>								
Waukegan	10/23/70	<0.2	<0.2	0.3	<0.3	<0.3	<1.0	0.9
North Chicago	10/23/70	<0.2	<0.2	<0.3	<0.3	<0.3	<1.0	0.5
Highland Park	10/23/70	<0.2	<0.2	<0.3	<0.3	<0.3	<1.0	0.4
Evanston	10/23/70	<0.2	<0.2	<0.3	<0.3	<0.3	<1.0	0.5
Chicago Central	10/23/70	<0.2	<0.2	<0.3	<0.3	<0.3	<1.0	0.3
Chicago South	10/23/70	<u><0.2</u>	<u><0.2</u>	<u><0.3</u>	<u><0.3</u>	<u><0.3</u>	<u><1.0</u>	<u>0.3</u>
		(<0.2)	(<0.2)	(<0.3)	(<0.3)	(<0.3)	(<1.0)	(0.5)

- 1 50 yards upstream from Lake Michigan
- 2 Final effluent to Lake Michigan
- 3 4 miles offshore
- 4 4 miles offshore from Chicago Central water plant
- 5 Crib water samples ranging from 1/3 to 2 1/4 miles offshore.

p, p'-DDT

This isomer averaged 4.5, 11.0 and 29.6 ppt in 1970, 1971, and 1972. Ranges of concentrations were 2.8 - 6.2, 9.3 - 13.0, and 22.2 - 38.4 ppt during the respective time periods. There was a continued increase in the concentration of this isomer over the 3 year period.

Aroclor 1242

This polychlorinated biphenyl was sampled only in 1971 and 1972 and averaged 712.0 and 139.0 ppt during this period respectively. Ranges of concentrations were 140.0 - 1810.0 ppt in 1971 and ND - 653.0 in 1972. The highest level (1810.0 ppt) was found at the Waukegan River.

Aroclor 1254

Aroclor 1254 was sampled in 1971 and 1972 and averaged 258.0 and 213.0 ppt during this period respectively. Ranges of concentrations were 192.0 to 388.0 ppt in 1971 and 61.0 - 841.0 ppt in 1972. The highest level (841.0 ppt) was found at Pettibone Creek.

SEWAGE TREATMENT PLANTS

Heptachlor epoxide

Average concentrations were <0.3, 5.4, and 2.8 ppt for 1970, 1971 and 1972 respectively. Annual ranges were 0.2 - 0.7, 0.3 - 17.2, and 1.2 - 7.8 ppt during the respective time period. Concentrations of heptachlor epoxide were comparable between plants except for a high level of 17.2 ppt obtained at the North Shore Sanitary District sewage treatment plant at North Chicago on 8/4/71.

Dieldrin

Average concentrations were 1.9, 36.0, and 16.2 ppt for 1970, 1971, and 1972 respectively. Annual ranges were 0.6 - 2.5, 13.7 - 64.3, and 6.3 - 29.2 ppt during the respective time period. Highest levels were obtained from the North Shore Sanitary District sewage treatment plant at North Chicago.

Methoxychlor

Concentrations of methoxychlor averaged 36.0 ppt in 1971 and ranged between ND and 106.0 ppt. In 1972, levels ranged from 20.7 - 59.8 ppt and averaged 34.6 ppt. Highest levels were most often found at the North Shore Sanitary District sewage treatment plant at Waukegan.

Di(2-ethylhexyl) phthalate: (DOP)

Di(2-ethylhexyl phthalate) was detected in sewage treatment plant effluents only in 1971 sampling. Highest levels were obtained at the

TABLE 7

PESTICIDES FOUND IN WATER SAMPLES FROM SEVERAL ILLINOIS STREAMS AND SEWAGE PLANTS
 TRIBUTARY TO LAKE MICHIGAN (1971). Values are expressed in parts per trillion (ppt).

SAMPLE LOCATION	DATE COLLECTED	Heptachlor Epoxide	Dieldrin	Methoxychlor	DOP	o, p' Isomers			p, p' Isomers			TOTAL DDT	Aroclor	
						DDE	DDD	DDT	DDE	DDD	DDT		1242	1254
Waukegan River	8/18/71	5.4	22.5	5.9	ND	ND	2.5	0.8	2.4	5.0	13.0	23.7	1810.0	388.0
Waukegan River	7/29/71	ND	14.5	2.9	ND	ND	ND	ND	1.7	4.0	9.3	15.0	---	---
Pettibone Creek	8/26/71	1.4	2.5	22.4	ND	ND	0.7	2.1	2.9	3.0	10.0	18.7	187.0	194.0
Pettibone Creek	7/29/71	1.6	2.1	30.7	ND	ND	0.8	2.7	2.9	2.2	11.8	20.4	140.0	192.0
		(2.1)	(10.4)	(15.5)	(ND)	(ND)	(1.0)	(1.4)	(2.5)	(3.6)	(11.0)	(19.5)	(712.0)	(258.0)
NSSD Waukegan STP	9/17/71	3.2	13.7	106.0	760.0	3.3	5.8	3.5	6.1	6.0	13.0	37.7	601.0	139.0
NSSD Waukegan STP	8/4/71	4.1	23.8	26.5	650.0	7.5	ND	3.1	4.9	3.6	8.2	27.3	2105.0	472.0
NSSD Waukegan STP	7/22/71	4.1	38.8	21.8	90.0	ND	5.0	ND	5.8	6.2	3.0	20.0	4020.0	568.0
NSSD North Chicago STP	7/23/71	0.3	64.3	17.7	160.0	ND	ND	ND	1.2	1.0	2.3	4.5	1070.0	250.0
NSSD North Chicago STP	8/4/71	17.2	31.8	44.2	ND	ND	ND	2.3	4.8	ND	13.5	20.6	268.0	153.0
NSSD North Chicago STP	8/25/71	3.3	43.5	ND	90.0	ND	ND	ND	2.9	5.5	6.5	14.9	534.0	217.0
		(5.4)	(36.0)	(36.0)	(292.0)	(1.3)	(1.8)	(1.5)	(4.3)	(3.7)	(7.8)	(20.8)	(1433.0)	(299.6)

DOP = di (2-ethylhexyl) phthalate

ND = Not Detected

North Shore Sanitary District plant at Waukegan with concentrations reaching 760.0 ppt.

Di-n-butyl phthalate: (DBP)

Di-n-butyl phthalate was not detected in six samples analyzed in 1971. In 1972, levels ranged between 55.0 - 250.0 ppt and averaged 110.0 ppt. Highest concentrations were most often found at the North Shore Sanitary District plant at Waukegan.

o, p'-DDE

o, p'-DDE was found in only 2 of 6 samples in 1971 and none of 10 samples in 1972. Both concentrations (3.3 and 7.5 ppt) were obtained from the North Shore Sanitary District plant at Waukegan.

o, p'-DDD

o, p'-DDD was detected in 2 of 6 samples in 1971 and none out of 10 samples in 1972. Both concentrations (5.0 and 5.8 ppt) were obtained from the North Shore Sanitary District plant at Waukegan.

o, p'-DDT

o, p'-DDT averaged 0.6, 1.5, and 29.3 ppt in 1970, 1971, and 1972 respectively. Concentrations ranged from <0.3 - 1.8, ND - 3.5, and 1.6 - 74.6 ppt during the respective time period. Levels increased markedly in 1972 at both the North Chicago and Waukegan North Shore Sanitary District plants.

p, p'-DDE

p, p'-DDE averaged 1.9, 4.3, and 17.7 ppt in 1970, 1971, and 1972 respectively. Concentrations ranged from 0.3 - 5.1, 1.2 - 6.1, 7.6 - 42.6 ppt during the respective time period. The maximum level of 42.6 ppt was obtained at the North Shore Sanitary District plant in Waukegan.

p, p'-DDD

p, p'-DDD averaged 0.7, 3.7, and 4.9 ppt in 1970, 1971, and 1972 respectively. Concentrations ranged from 0.3 - 1.5, ND - 6.2, 1.5 - 9.2 ppt during the respective time period. Similar levels were obtained at both the North Chicago and Waukegan plants of the North Shore Sanitary District.

p, p'-DDT

Higher levels of this isomer were found than any of the other isomers of the DDT complex. Concentrations averaged 2.4, 7.8 and 70.3 ppt for 1970, 1971, and 1972 respectively. Concentrations ranged from 1.1 - 4.9, 2.3 - 13.5, and 10.6 - 132.6 ppt during the respective time period. A marked increase was noted in 1972 at both the North Chicago and Waukegan North Shore Sanitary District plants.

TABLE 8

PESTICIDES FOUND IN WATER SAMPLES FROM ILLINOIS STREAMS AND SEWAGE PLANTS TRIBUTARY TO LAKE MICHIGAN (1972). Values are expressed in parts per trillion (ppt).

SAMPLE LOCATION	DATE COLLECTED	Heptachlor Epoxide	Dieldrin	Methoxychlor	DBP	o, p' Isomers			p, p' Isomers			TOTAL DDT	Aroclor	
						ODE	ODD	ODT	ODE	ODD	ODT		1242	1254
Waukegan River	5/24/72	3.1	2.6	27.2	107.0	ND	ND	11.7	7.1	2.8	36.5	58.1	62.0	114.0
Waukegan River	5/23/72	3.4	2.1	22.6	92.0	ND	ND	12.5	10.2	1.7	35.0	59.4	120.0	136.0
Waukegan River	5/25/72	4.5	2.0	29.4	77.0	ND	ND	9.8	5.4	1.9	22.7	39.8	57.0	61.0
Waukegan River	6/29/72	3.8	2.6	29.5	T	ND	0.7	2.3	12.9	6.7	22.2	44.8	84.0	119.0
Pettibone Creek	5/24/72	1.6	3.1	65.5	122.0	ND	ND	12.5	4.7	2.0	38.4	57.6	ND	111.0
Pettibone Creek	5/25/72	1.2	1.7	72.4	147.0	ND	ND	7.2	3.9	2.4	26.3	39.8	ND	107.0
Pettibone Creek	6/29/72	2.6	3.7	89.1	110.0	ND	0.6	3.1	20.3	5.9	26.4	56.3	653.0	841.0
		(2.9)	(2.5)	(48.0)	(93.6)	(ND)	(0.2)	(8.4)	(9.2)	(3.3)	(29.6)	(51.0)	(139.0)	(213.0)
NSSD Waukegan STP	5/16/72	2.2	14.5	45.7	120.0	ND	ND	14.3	7.6	1.7	70.5	94.1	ND	139.0
NSSD Waukegan STP	5/19/72	2.9	11.6	36.5	100.0	ND	ND	21.4	7.9	4.3	68.2	101.8	ND	105.0
NSSD Waukegan STP	5/23/72	7.8	8.3	40.8	87.0	ND	ND	16.1	9.9	7.1	49.1	82.2	ND	97.0
NSSD Waukegan STP	5/22/72	3.7	12.5	37.4	65.0	ND	ND	74.6	42.6	9.2	132.6	259.0	ND	118.0
NSSD Waukegan STP	6/17/72	1.4	6.7	59.8	250.0	ND	ND	1.9	10.4	2.1	16.3	30.7	17.0	111.0
NSSD North Chicago STP	5/22/72	1.6	29.2	20.7	55.0	ND	ND	53.5	37.4	6.5	110.9	208.3	ND	104.0
NSSD North Chicago STP	5/23/72	3.2	26.0	22.8	97.0	ND	ND	43.0	20.4	6.0	87.7	157.1	ND	100.0
NSSD North Chicago STP	5/16/72	2.3	25.5	28.3	58.0	ND	ND	32.2	18.2	5.2	77.5	133.1	ND	132.0
NSSD North Chicago STP	5/19/72	1.2	21.8	27.5	70.0	ND	ND	34.7	14.8	4.9	79.7	134.1	ND	161.0
NSSD North Chicago STP	6/17/72	1.2	6.3	26.6	206.0	ND	ND	1.6	7.7	1.5	10.6	21.4	21.0	178.0
		(2.8)	(16.2)	(34.6)	(110.0)	(ND)	(ND)	(29.3)	(17.7)	(4.9)	(70.3)	(122.0)	(3.8)	(124.0)

DBP = di-n-butyl phthalate
T = Trace
ND = Not Detected

Aroclor 1242

Concentrations averaged 1433.0 ppt in 1971 and 3.8 ppt in 1972. Ranges in concentrations in 1971 were 268.0 - 4020.0 ppt compared to ND to 21.0 ppt in 1972. The maximum level of 4020.0 ppt was obtained at the North Shore Sanitary District plant at Waukegan.

Aroclor 1254

Concentrations averaged 299.8 ppt in 1971 and 124.0 ppt in 1972. Concentrations ranged between 139.0 - 568.0 ppt in 1971 and 97.0 - 178.0 ppt in 1972. Highest levels were obtained from the North Shore Sanitary District plant in Waukegan in 1971. Lower levels were obtained at this and the North Chicago plant in 1972.

SECTION VII

RESULTS AND DISCUSSION

The monitoring program established by the Illinois Environmental Protection Agency was directed to determine levels of pesticides discharged as well as levels presently found in Lake Michigan water, sediment, and fish.

Monitoring results indicate that levels of DDT, polychlorinated biphenyls (PCB's), and dieldrin in edible portions of six species of Lake Michigan fish were generally below interim guidelines for maximum concentration in fish flesh which are 5.0 ppm for both DDT and PCB's and 0.3 ppm for dieldrin. Other chlorinated hydrocarbon insecticides were not consistently found in the edible portions of fish flesh. The species of fish with highest fat content also had highest PCB or DDT concentrations. Chubs most often had the highest levels of PCB's and DDT while yellow perch had the lowest. Alewives showed PCB concentrations comparable to chubs. Male yellow perch, chubs, and alewife had higher concentrations of PCB and DDT in the edible portions of their flesh than did the females of the species.

Highest concentrations of the pesticides, PCB's, and phthalates in sediments were obtained in the tributary streams and ravines indicating possible contamination by residential spraying and industrial discharge. Highest levels were obtained in industrial areas in North Chicago and Waukegan. Open water sediments were considerably lower for all parameters. In the sediments polychlorinated biphenyls were generally found at concentrations higher than the pesticides. Aroclor 1242 concentrations ranged from ND at the Ravine Drive Ravine in Highland Park to 553.00 ppb in an unnamed channel in Waukegan. Aroclor 1254 levels ranged from 1.54 ppb in the Park Avenue Ravine in Highland Park to 232.00 ppb in Pettibone Creek in North Chicago. Although not consistently found in the sediments one of the phthalates did reach a concentration in excess of 200 ppb. Di(2-ethylhexyl) phthalate was found in both industrial and residential areas but in only 5 of 13 samples with levels ranging from N.D. - 218.00 ppb. The maximum level was obtained in an industrial area in Waukegan in an unnamed channel. Di-n-butyl phthalate was found in only 2 of 13 samples both located in Highland Park. Concentrations obtained were 25.00 and 120.00 ppb.

Total DDT, methoxychlor, dieldrin, and heptachlor epoxide were found in highest concentrations in tributary sediments located in residential areas indicating the past history of localized spray programs. DDT concentrations ranged from 0.42 from Bull Creek in Zion to 942.00 ppb in the Woodland River Ravine in Lake Forest. Ranges in levels of methoxychlor, dieldrin, and heptachlor epoxide were 0.19 - 175.00, 0.01 - 30.80, 0.02 - 57.00 ppb respectively over the three year period. Areas of highest concentration were found in residential areas in Lake Forest.

Lindane and heptachlor concentrations were all less than 1 ppb. Aldrin and endrin were not detected.

Water samples collected at six water treatment plant intakes and at locations approximately 4 miles offshore of Winthrop Harbor, Evanston, and Chicago all showed levels of less than 1.0 ppt heptachlor epoxide, dieldrin, and total DDT. Water samples collected at tributary stream and sewage treatment plants showed somewhat higher levels. Lindane, aldrin, endrin, and heptachlor, were not detected in sewage treatment plant effluents or tributary streams.

In the tributary streams PCB's were found in highest concentrations followed by the phthalates, methoxychlor, DDT, dieldrin, and heptachlor epoxide.

Aroclor 1242 ranged from ND - 1810.0 ppt in 1971 and 1972. The highest concentration of Aroclor 1242 was obtained from the Waukegan River in Waukegan. Aroclor 1254 ranged from 61.0 - 841.0 ppt in 1971 and 1972. The highest concentration of Aroclor 1254 was obtained in Pettibone Creek in North Chicago.

Di(2-ethylhexyl) phthalate was not detected in the tributary streams during the three year study while di-n-butyl phthalate was found in concentrations ranging from a trace - 147.0 ppt in 1972. Similar levels were found at both stream stations. Di-n-butyl phthalate was not identified in the 1971 sampling.

Levels of methoxychlor increased considerably at both the Waukegan River and Pettibone Creek in 1972. Concentrations at these stream stations averaged 15.5 ppt in 1971 and 48.0 ppt in 1972. Highest concentrations were found on Pettibone Creek during the study period. Levels of total DDT ranged from 6.3 - 59.4 ppt at both stations during the three year period. Highest concentrations were obtained in 1972 at both Pettibone Creek and the Waukegan River. The cause of the increased 1972 levels is unexplained.

Over the study period levels of dieldrin found in Pettibone Creek were less than 4.0 ppt while the Waukegan River samples ranged from 1.4 - 22.5 ppt. Heptachlor epoxide concentrations from tributary streams ranged from below detectable levels to 5.4 ppt over the three year period. Sewage treatment plant effluents showed higher values for most pesticides. The North Shore Sanitary District plant at Waukegan most often had the highest levels for total DDT, methoxychlor, di-(2-ethylhexyl) phthalate, di-n-butyl phthalate, Aroclor 1242, and Aroclor 1254. Maximum concentrations obtained at this location were 259.0 ppt for total DDT, 106.0 ppt for methoxychlor, 760.0 ppt for di(2-ethylhexyl) phthalate, 250.0 ppt for di-n-butyl phthalate, 4020.0 ppt for Aroclor 1242 and 568.0 ppt for Aroclor 1254.

The North Shore Sanitary District Plant at North Chicago had highest

levels for heptachlor epoxide and dieldrin. Maximum concentrations for these parameters were 17.2 ppt for heptachlor epoxide and 64.3 ppt for dieldrin.

This study indicates that the polychlorinated biphenyls are present in Lake Michigan in concentrations equal to or in excess of DDT. It is known that PCB's exhibit a chronic toxicity to aquatic life at very low levels (Nebeker et. al., 1972). The fact that PCB's were not analytically separated from DDT in earlier studies indicates that DDT concentrations were reported at levels higher than actual. This study indicates that both DDT and the PCB's were found at levels which warrant concern for both aquatic life and wildlife. The other pesticides and the phthalates were found at lower levels which do not indicate the degree of concern that do DDT and the PCB's.

SECTION VIII

ACKNOWLEDGEMENTS

This project was initiated by the Sanitary Water Board of the Illinois Department of Public Health and transferred to the Illinois Environmental Protection Agency in July of 1970 when the Sanitary Water Board was abolished.

Laboratory analyses were accomplished by Anderson Physics Laboratories, Inc. of Urbana, Illinois with quality control being accomplished by the Illinois Environmental Protection Agency special test unit laboratory.

Cooperation in obtaining fish samples were offered by the Illinois Conservation Department, Hope Fisheries of Waukegan, and Rocky's Fisheries of Chicago and was greatly appreciated. Assistance offered by the North Shore Sanitary District in obtaining composite effluent samples is also appreciated.

Completion of the grant including sample collection and report preparation was accomplished by Lake Michigan/DesPlaines Biological Sub-Unit personnel in the Division of Water Pollution Control of the Illinois Environmental Protection Agency.

Support of the project by the U.S. Environmental Protection Agency Office of Research and Development, and the help provided by Mr. LeRoy E. Scarce, the Grant Project Officer, was greatly appreciated.

SECTION IX

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SECTION X
APPENDICES

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APPENDIX A

ANALYTICAL QUALITY

CONTROL DATA

APPENDIX A
ANALYTICAL QUALITY CONTROL DATA
PROCEDURE FOR LABORATORY ANALYSIS

ANALYTICAL CONDITIONS

All samples were analyzed according to the "FWPCA Method for Chlorinated Hydrocarbon Pesticides in Water and Wastewater" with the U.S. Environmental Protection Agency Lake Michigan Basin Office modification employing 1000 ml Erlenmeyer flasks fitted (24/40 ground glass connections) with Snyder distillation columns in place of the Kuderna-Danish concentration system for removal of solvents.

SEPARATION PROCEDURE - WATER

2000 ml of each gallon water sample was extracted three times with 250 ml of 15% ethyl ether in hexane. Extracts were then dried over anhydrous sodium sulphate, combined in a 1000 ml Erlenmeyer flask, a Snyder column attached, and all but 2 ml of the solvent removed by distillation (the Na_2SO_4 was decontaminated by heating overnight at 450°C). Nanograde methylene chloride has proven to be a superior solvent for extracting polar and non-polar pesticides from water and various substrates and may be substituted for the above mixture of ether and hexane.

The 2 ml concentrated extracts were transferred to the standardized florisil column as described in the following section.

Analysis of a fortified water sample indicated a high level of recovery (90 to 97%) for most materials tested except di(2-ethylhexyl) phthalate where there was approximately 85% of the chemical found in the third florisil fraction.

SEPARATION PROCEDURE - FISH

50 grams of the edible portion of fish was blended with 100 ml of redistilled alcohol in 100 ml of water and 100 ml of 50% diethyl ether in hexane (all solvents were nanograde). This mixture was filtered in a Buechner funnel with a suction flask using #1 Whatman paper and washed with hexane.

The solvent was removed in an Erlenmeyer flask with attached Snyder column on a steam bath. 100 ml of H_2O was added to the concentrate and then extracted with 100 ml hexane in a separatory funnel. The hexane layer was dried over sodium sulfate and then reduced to about 8 ml. This solution was placed in a centrifuge tube on a warm water bath and purified air was blown over it to remove all the hexane. The remaining oil was weighed to determine its percentage in the fish flesh. Next 100 mg of the fish oil was placed on the florisil column (later,

APPENDIX A TABLE I

ANALYTICAL QUALITY CONTROL DATA

percent recovery for parameters tested

PARAMETER TESTED	SAMPLE		
	FISH	SEDIMENTS	WATER
PESTICIDES			
Heptachlor Epoxide	90-98%	95-98%	95-98%
Dieldrin	90-98%	95-98%	95-98%
Methoxychlor	90-98%	95-98%	95-98%
Lindane	90-98%	95-98%	95-98%
Aldrin	90-98%	95-98%	95-98%
Endrin	90-98%	95-98%	95-98%
Heptachlor	90-98%	95-98%	95-98%
o,p' DDE	90-98%	95-98%	95-98%
o,p' DDD	90-98%	95-98%	95-98%
o,p' DDT	90-98%	95-98%	95-98%
p,p' DDE	90-98%	95-98%	95-98%
p,p' DDD	90-98%	95-98%	95-98%
p,p' DDT	90-98%	95-98%	95-98%
POLYCHLORINATED BIPHENYLS (PCB's)			
Aroclor 1232	--	--	--
Aroclor 1242	90-98%	90-98%	90-98%
Aroclor 1248	--	--	--
Aroclor 1254	90-98%	90-98%	90-98%
Aroclor 1260	--	--	--
PHTHALATES			
di-n-butyl phthalate (DBP)	85-95%	90%	90%
di(2-ethylhexyl) phthalate (DOP)	85-95%	90%	90%

APPENDIX A TABLE 2

ANALYTICAL QUALITY CONTROL DATA

limits of detectability for parameters tested

PARAMETER TESTED	SAMPLE		
	FISH	SEDIMENTS	WATER
PESTICIDES			
<u>Heptachlor Epoxide</u>	<25 PPT	<2.5 PPT	<.2 PPT
<u>Dieldrin</u>	<25 PPT	2.5 PPT	.2 PPT
<u>Methoxychlor</u>	100 PPT	10 PPT	1 PPT
<u>Lindane</u>	25 PPT	2.5 PPT	.25 PPT
<u>Aldrin</u>	25 PPT	2.5 PPT	.25 PPT
<u>Endrin</u>	25 PPT	2.5 PPT	.25 PPT
<u>Heptachlor</u>	25 PPT	2.5 PPT	.25 PPT
<u>o,p' DDE</u>	25 PPT	2.5 PPT	.25 PPT
<u>o,p' DDD</u>	25 PPT	2.5 PPT	.25 PPT
<u>o,p' DDT</u>	25 PPT	2.5 PPT	.25 PPT
<u>p,p' DDE</u>	25 PPT	2.5 PPT	.25 PPT
<u>p,p' DDD</u>	25 PPT	2.5 PPT	.25 PPT
<u>p,p' DDT</u>	100 PPT	10 PPT	1 PPT
POLYCHLORINATED BIPHENYLS (PCB's)			
<u>Aroclor 1232</u>	--	--	--
<u>Aroclor 1242</u>	4 PPB	400 PPT	40 PPT
<u>Aroclor 1248</u>	--	--	--
<u>Aroclor 1254</u>	2.5 PPB	250 PPT	25 PPT
<u>Aroclor 1260</u>	--	--	--
PHTHALATES			
<u>di-n-butyl phthalate (DBP)</u>	2 PPB	200 PPT	20 PPT
<u>di-(2-ethyl-hexyl) phthalate (DOP)</u>	10 PPB	1 PPB	100 PPT

APPENDIX A TABLE 3
ANALYTICAL QUALITY CONTROL DATA
Sample Fortification (in PPM)

	Fish	Sediment	Water
Chlorinated hydrocarbon pesticides	.01 .005 .002 .001 .0005	.001 .0005 .0002 .00005 .00002	.0001 .00005 .00002 .000005 .000002
PCB's	.10 .05 .02 .01 .005	.01 .005 .002 .001 .0005	.001 .0005 .0002 .0001 .00005
Phthalates	1.00 0.20 0.05 0.01 0.002	.10 .02 .005 .001 .0002	.01 .002 .0005 .0001 .00002
5 replicates			
Total number of Tests	25	25	25

fish samples were run as above except 10 grams of fish flesh was used and all the oil obtained was placed on the florisil column, except for chubs where 2 grams were used). The florisil separation procedure is listed in this appendix. Three fractions were obtained from this procedure. This first fraction F₁ was subjected to a silicic acid separation (procedure in this appendix), to separate the PCB's completely from the pesticides. The third fraction F₃ from the florisil procedure which was eluted with 200 ml of a 50-50 mixture of diethyl ether-hexane contained di(2-ethylhexyl) phthalate and di-n-butyl phthalate with some fish oil. This fraction was reduced to 0.5 ml. The phthalates were separated from the fish oil using Gelman's Instant Thin Layer Chromatograms. The entire oily residue was placed near the bottom of the sheet and the sheet was developed with acetonitrile. After the acetonitrile rose 1" above the oil residue the sheet was removed and dried. It was then placed in 90% methanol - 10% H₂O mixture and this was permitted to rise 3" above the acetonitrile front. This effectively removed the phthalate esters from the fish oil. The TLC sheet was cut at the acetonitrile and methanol fronts and the phthalate esters were extracted in 10 ml hexane containing 10 drops of H₂O. This was then reduced to 1 ml prior to injection into the gas chromatograph (fraction 4).

1 to 5 ml of the fractions were injected into the electron capture GLC unit. In these analyses two columns varying in length were used. Both were packed with 3% QF-1 and 1% OV-17 on Supelcoport. One was 3M X 1/8" and the other was 20" X 1/8". Fraction F₁ was run only on the 3M column but F₂ and F₄ were run on both. The shorter column facilitated the analysis of methoxychlor and di(2-ethylhexyl) phthalate.

SEPARATION PROCEDURE - SEDIMENT

100 grams of sediment was mixed with 100 ml ethyl alcohol + 100 ml H₂O in a 1000 ml Erlenmeyer flask. This mixture was extracted in the Erlenmeyer flask with 100 ml of a 50-50 mixture of diethyl ether-hexane.

The ether-hexane layer was separated and dried with anhydrous sodium sulfate. It was then concentrated to less than 5 ml and subjected to a florisil separation procedure.

The first fraction from this was further separated by means of a silica gel column. This separated the PCB's from the remaining pesticides. These procedures are listed in detail in a later portion of this appendix. The various fractions were concentrated to volumes which were appropriate for GLC analysis.

PREPARATION AND USE OF THE FLORISIL COLUMN

30 grams of florisil containing 3% water was prepared for chromatographic separations by pre-elution with 50 ml acetone, 50 ml anhydrous diethyl ether, and finally with 100 ml dry nanograde hexane.

The pesticide extract in 2 ml hexane was carefully transferred to the florisil column with 3-4 one ml portions of hexane. The elution pattern was as follows:

F₁ - 90 to 100 ml hexane eluted PCB's, o,p' and p,p' DDE, heptachlor, some (50%) alpha BHC, o,p' and p,p' DDT (20%).

F₂ - 250 ml 10% ether in hexane eluted the remaining chlorinated hydrocarbon insecticides including methoxychlor ethylene.

F₃ - 200 ml 50% ether in hexane eluted di(2-ethylhexyl) phthalate.

The second and third fraction (F₂ & F₃) were collected in 500 ml Erlenmeyer flasks, Snyder Columns attached, and volumes reduced on a steam bath to ca. 5 ml. The extracts were then transferred to a volumetric flask at a concentration suitable for G.L.C. determinations.

SILICA GEL SEPARATION OF PCB'S FROM DDT'S

The first florisil fraction (F₁) was reduced in volume to ca. 2 ml and the PCB's separated from DDE and DDT on a silicic acid-celite or silica gel column. Silica Gel 60 (Mereck) 70-325 mesh heated for 3 to 4 days at 22°C was found to be very effective in separating these compounds. The F₁ concentrate was transferred with three 1 ml portions of hexane to a column containing 30 grams of Silica Gel 60 (The florisil and silica gel were pretested to verify the elution pattern).

210 ml dry hexane eluted by gravity in 60 to 90 minutes contained the PCB's. The following elution with 150 ml 10% ether in hexane removed the DDE's and DDT's. Both fractions were concentrated by distillation through a Snyder column.

The concentrates were adjusted to a suitable volume for G.L.C. analysis.

INSTRUMENTATION

A Varian Aerograph 204 with 2 columns equipped with 63 Ni detector was operated under the following conditions:

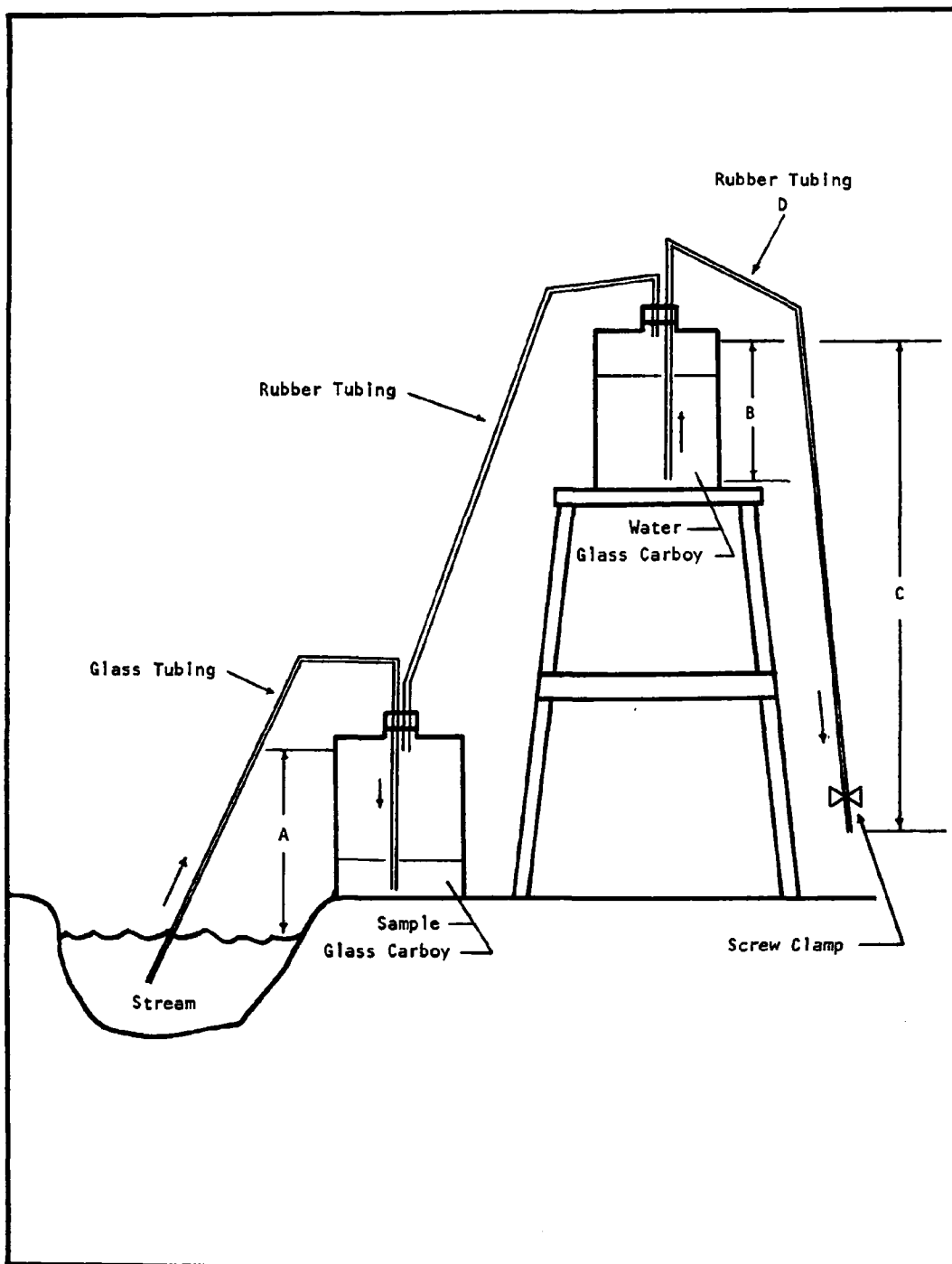
1. Port temperature of 225°C.
2. Column temperature of 200 to 210°C.
3. Detector temperature of 255°C.
4. High resolution column 1/8" X 8 meters packed with 100/200 mesh Supelcoport containing 2.0% QF1 and 1.25% OV-17.

5. Short one meter column containing 4.0% QF1 and 2.0% OV-17 on Supelcoport used for methoxychlor and di(2-ethylhexyl) phthalate. Other columns used for fish analysis are listed in the separation procedure for fish.
6. Two other columns of greater and less polarity than those mentioned are useful for some confirmation tests.

A portion of the extracts analyzed by Anderson Physics Laboratories were provided to the Environmental Protection Agency for varification on results.

Values obtained in analysis were not corrected in relation to percent recovery.

APPENDIX B
FIELD METHODS



APPENDIX B FIGURE 1. COMPOSITE WATER SAMPLER

APPENDIX B
FIELD METHODS
FIELD SAMPLING PROCEDURES

WATER SAMPLES

One gallon samples were collected in glass bottles with aluminum foil placed between the glass and the cover. Initially all samples collected were grab samples. During 1971 a composite sampler utilizing two 5 gallon carboys was employed at the tributary streams. A period of 24 hours was covered during compositing. The sample collected in the 5 gallon carboy was mixed and a one gallon portion was saved for analysis. The carboy was then rinsed with nanograde hexane before the sampler was again used. Figure one of this appendix illustrates the composite sampler. To obtain a sample the upper carboy is filled with water which is allowed to drain out slowly through the tubing indicated by the letter D. As the water drains from this carboy, the vacuum created siphons a sample into the lower carboy. The rate of flow may be regulated by a pinch clamp on tubing D. Samples were collected through glass tubing to avoid contamination with any plasticizer which could have been present in rubber tubing. Care had to be used so that the distance C on the figure was greater than A plus B. In 1972 composite samples from the North Chicago and Waukegan sewage treatment plant were provided by the North Shore Sanitary District.

FISH SAMPLES

Fish samples were collected either directly from a commercial fisherman or collected during netting operations by the Illinois Conservation Department. For fish over one pound a fillet was taken, while smaller fish were taken whole. The sample then was labeled by species, sex, length and weight and location, placed in aluminum foil, and put on ice prior to delivery to the laboratory. These samples were then frozen until analyzed.

SEDIMENT SAMPLES

Sediment samples from streams and ravines were collected directly in 6 ounce glass bottles with aluminum foil placed between the glass and the cover. Samples of Lake Michigan sediment were collected with a Ponar dredge. No preservatives were added to sediment samples. These samples were not refrigerated or frozen prior to analysis.

In general the lapse time between collection and analysis of all types of samples ranged from several weeks to more than one month.

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16. Abstract <p>This study was initiated to determine present levels of pesticides in Lake Michigan fish, sediments, and water. Data was collected on six species of Lake Michigan fish (yellow perch, chubs, carp, coho salmon, alewife, and brown trout); open lake and tributary stream and ravine sediments; and open water, tributary stream, and sewage treatment plant effluents. Samples analyzed for pesticides were selected from the following list: heptachlor, heptachlor epoxide, dieldrin, methoxychlor, lindane, aldrin, endrin, DDT and its analogs. Additional analyses were accomplished for polychlorinated biphenyls (PCB's), di-n-butyl phthalate (DBP), and di (2-ethylhexyl) phthalate (DOP).</p> <p>The data indicate that PCB's were found at levels as high or higher than DDT in Lake Michigan water, sediment, and fish. PCB's have been found to complicate the routine analysis of DDT which may have caused earlier DDT data in the literature to be reported at levels higher than actual. Both DDT and the polychlorinated biphenyls were found at levels which cause concern for aquatic life and warrants the controlled use of these compounds.</p> <p>This report is submitted in fulfillment of grant number 16050 ESP under the sponsorship of the U.S. Environmental Protection Agency.</p>					
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