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Ecological Research Series

An Evaluation of DDT and Dieldrin in Lake Michigan

Office of Research and Monitoring
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EPA-R3-72-003

August 1972

AN EVALUATION OF DDT AND DIELDRIN IN LAKE MICHIGAN

By

The Lake Michigan Interstate Pesticides Committee
of the
Lake Michigan Enforcement Conference

Project Nos. 16050 EYV,EYS,EPV,ESP

Prepared for

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ABSTRACT

The presence of pesticides and particularly the chlorinated hydrocarbon insecticides in Lake Michigan water is responsible for biological accumulations that affect a wide variety of legitimate uses. The data collected from waters, wastewaters, invertebrate organisms and fish all suggest that DDT plus analogs and dieldrin are observed consistently at levels that warrant concern from both a public health and wildlife preservation standpoint. The sources of these chlorinated hydrocarbon insecticides include not only industrial and wastewater effluents but also diffuse sources such as from agricultural activities and municipal pest control programs.

The evaluation of the chlorinated hydrocarbon insecticides in both wastewater and biological specimens is complicated by the presence of products such as polychlorinated biphenyls and phthalates. These products interfere with the analysis for the target insecticide and, indeed, have biological implications of their own.

This report is submitted in fulfillment of four cooperative grants to the Lake Michigan Enforcement Conference participating state under the sponsorship of the Environmental Protection Agency and include grant numbers 16050 EYV (Wisconsin), 16050 EYS (Indiana), 16050 EPV (Michigan) and 16050 ESP (Illinois) for an investigation of "Evaluation of Pesticide Sources and Levels Tributary to Lake Michigan".

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SECTION I

CONCLUSIONS

1. The analysis of water samples from the open waters of Lake Michigan strongly suggests a real and inherent variability that makes water sampling for the purpose of developing general residue levels impractical. The concentrations present challenge the limit of detectability of the analytical methods employed. Several laboratories recorded substantial analytical discrepancy when analyzing split samples, thereby further complicating interpretation of results.

2. After cautious interpretation of the data, the committee generally agreed that the most likely concentrations of DDT in open lake waters were between one and ten parts per trillion. Those analyses that revealed unusually high levels of pesticide were probably the result of artifacts such as surface scums of floating oils, suspended debris or in-laboratory contamination.

3. The data accumulated by municipal water intake sampling strongly suggest concentrations of chlorinated hydrocarbon pesticides in the inshore waters were higher than in open lake waters and much more variable. The biological accumulation potential is, therefore, greater in inshore waters since most of the important biological representatives spend an extended period of time within these inshore water areas.

4. Tributary streams to Lake Michigan discharge chlorinated hydrocarbon pesticides into the lake. Urban and fruit-growing areas are the more significant contributors of pesticides to the lake than are diversified agriculture areas.

5. Dieldrin levels in tributary streams and lake waters were generally at the limit of detectability, one part per trillion or less.

6. Most sewage treatment plant discharges contained less than ten parts per trillion DDT. For those plants with more than ten parts per trillion total DDT, there were likely point sources. However, in the City of Milwaukee, no point source was found. The Milwaukee system is so complex that it is virtually impossible to eliminate all potential sources by field investigation. Sewage treatment plants with dieldrin concentrations above the detectable levels also had identifiable point sources.

7. Lake Michigan waters contain many substances that are extractable and measureable by commonly used methods for pesticide analyses and are, therefore, potential interferences in typical pesticide analytical procedures. The polychlorinated biphenyls constitute a complex of such substances that are present in Lake Michigan. Phthalate esters more recently have been identified at detectable levels. These chemicals are present in greater concentrations in biological and wastewater samples than in open lake waters. The polychlorinated biphenyls are present in sufficient

quantity, with sufficient evidence of biological impact, to warrant an independent evaluation.

8. Biological sampling with sentinel organisms (clams) reflected unusually high pesticide concentrations and sources. Subtle concentration differences that might be brought about by a relatively small discharge relative to the stream could not be detected by clam analyses. Resident arthropods generally contained higher levels of DDT and its analogs than sentinel clams. Resident fish appeared to be the most reliable biological monitor.

9. The biological magnification of chlorinated hydrocarbon insecticides in sport and commercially valuable species of fish suggests that fish should be used to reflect concentration trends in the lake water. It is believed that the residue levels established during the last two years will be adequate to serve as a base line to establish the trend in future years. It seems unlikely these trends can be conveniently established by water sampling because of analytical and sampling complications.

10. The levels of DDT in sport and commercially valuable species of fish exceed the five parts per million action level established by the Food and Drug Administration, essentially preventing sale of Lake Michigan fish. Other chlorinated hydrocarbon pesticides do not exceed the established residue tolerances, although dieldrin levels approach the action limit. Exotic chemicals other than chlorinated hydrocarbons were not measured in this study.

11. The four states in the Lake Michigan Drainage Basin have adopted legislation authorizing various pesticide use control programs. Wisconsin, through basic legislation and subsequent rules, has essentially prohibited the use of chlorinated hydrocarbons that have been found in Lake Michigan. Michigan and Indiana have adopted adequate use control legislation but the rules have not yet been promulgated. Illinois has a legislative restriction on DDT but not on other chlorinated hydrocarbons. Michigan, Illinois, and Indiana have adopted legislation regulating commercial pesticide applicators. Wisconsin legislation regulating commercial applicators is still pending.

12. The effect of the pesticides in Lake Michigan on fish reproduction potential is not resolved as yet - this concern in part generated the establishment of a technical committee to review pesticide pollution in the lake. Both Wisconsin and Michigan are able to hatch and rear coho fry in adequate numbers to sustain the anadromous fish stocking program using Lake Michigan brood fish. The effect on natural reproduction in lake trout is not known.

13. The pesticides in Lake Michigan through biological magnification may have a potential effect on both domestic and wild animals that

eat fish or other organisms from the lake. Hazards to wild bird populations and mink ranching operations are being investigated. Preliminary data suggest that exotic chemicals including chlorinated hydrocarbon insecticides produce measurable changes on reproductive potentials.

SECTION II

RECOMMENDATIONS

1. Fish sampling for pesticide residues should be established in accordance with the Bureau of Sport Fisheries and Wildlife and Commercial Fisheries' recommendations. This monitoring should be conducted within the Federal structure or should be contracted to an agency with the ability both to collect and process the collections from the entire lake. Analyses and sampling must be performed in the same way in order to compare data or correlation data must be established if new collection or analytical techniques are used.

2. A water quality monitoring program should be initiated for inshore waters in order to determine whether the pesticide burden of fish is related to the pesticide concentration of inshore waters.

3. The conferees should insist on adequate legislation to record pesticide usage of other than the chlorinated hydrocarbons.

4. As with pesticides, the discharge of polychlorinated biphenyls, phthalates and other persistent chemicals should be abated to prevent accumulations of these persistent compounds in Lake Michigan. Particular attention should be devoted to possible replacements for chlorinated hydrocarbons such as toxaphene, methoxychlor, chlordane and benzene hexachloride.

5. The levels of metal contamination of Lake Michigan water and/or fish should be clearly established at this time so that residue trends can be assessed in the future.

6. Polychlorinated biphenyl concentrations should be ascertained for water and fish. Control programs for polychlorinated biphenyls and other exotic chemicals should be initiated.

SECTION III

INTRODUCTION

In the late 1940's, when the organic insecticides first became available for general distribution, an extensive scientific effort was extended toward evaluating the toxicity of these new products. Cottam and Higgins, 1946, evaluated the effects of DDT on fish and wildlife principally from forest land and aquatic habitats. The authors concluded that DDT should be used only where the need for specific control was carefully evaluated. Metcalf, 1948, summarized the mode of action of organic insecticides and evaluated the toxicity data available to that date. In the early 1950's, Rudd and Genelly reviewed the literature concerned with the toxicity of pesticides to both wild and domestic animals. Rudd and Genelly, 1956, summarized the toxicological data available to that time. In general, the chlorinated hydrocarbons and particularly DDT were recognized as only moderately toxic to mammals. The California Pesticide Information and Safety Manual, 1968, gives the acute oral toxicity of DDT to rats as approximately 120 mg/kg. The dermal toxicity of DDT is approximately 2,500 mg/kg. Both dieldrin and aldrin are somewhat more toxic to mammals than DDT. Both of these compounds have an oral toxicity of approximately 50 mg/kg and an acute dermal toxicity of perhaps 90 mg/kg. Endrin is the most toxic of the common persistent chlorinated hydrocarbons with an oral toxicity to rats of approximately 10 mg/kg, and a dermal toxicity of approximately 15 mg/kg. It is apparent that the aquatic organisms are substantially more sensitive than terrestrial organisms and in the early use of these products, efforts were made to avoid exceeding acceptable levels in water. In general, the acute toxicities of the chlorinated hydrocarbons were recognized as legitimate risk factors when weighed against the benefits accrued in both agriculture and public health.

By the mid 1950's, conservationists were convinced that the organochlorine insecticides were causing more damage than was generally recognized. Evidence of reproductive failures associated with organochlorine pesticides was noted in mid-1950 literature (Genelly and Rudd, 1956). The mortality of grebes associated with DDD applications on Clear Lake, California, demonstrated biological magnification. Many of the early investigations of organochlorine implications in the environment were seriously hampered by the inability to detect pesticides at levels that have since been shown to produce significant, sublethal effects.

Prior to 1960, the standard analytical technique for DDT was the Schechter-Haller method (Schechter <u>et al.</u>, 1945). This technique was adequate for residue analysis in higher organisms where accumulations were in the part per million range but it was not adequate to measure residue levels in water or lower organisms where accumulations were not that high.

By the early 1960's, there were many instances of wildlife mortality due to organochlorine insecticide applications and especially DDT applications. Rachel Carson (1962) highlighted actual and potential environmental damages of pesticides in a popular and controversial review which focused public attention on the problem. The Carson review precipitated a report by the President's Science Advisory Committee (May, 1963) that generally recognized concern for the environment. However, the report recommendations related mainly to developing data substantiating or refuting allegations of detrimental effects. The committee did recognize the persistence of some pesticides and recommended that there be an orderly reduction of these materials.

In 1960, Dale Coulson successfully applied the gas chromatograph technique to residue analysis, but his colorimetric detector lacked sensitivity desirable in residue analysis. Lovelock and Lipsky, 1960, first suggested the potential of the electron capture detector in residue analysis. The electron capture detector was radically different from conventional detectors and has extreme sensitivity but lacks qualitative certainty.

During the 1960's, literally hundreds of papers were published in which the investigators utilized the gas chromatograph separation and the electron capture detector for residue analysis. Hunt and Bischoff, 1960, clearly traced the effect of DDD applications on a resident grebe population and Burdick <u>et al</u>., (1964) found a correlation of lake trout hatchery mortalities with DDT residues in the eggs. These two studies clearly indicated that the acute toxicity was not the only cause for concern for natural fish and wildlife populations, but that residue accumulations had a far-reaching impact that could be attributed to a wide variety of sublethal mechanisms.

The former Wisconsin Conservation Department in a survey report issued in February, 1966, reported on pesticide residue analyses on 126 samples from Wisconsin rivers and lakes (Wisconsin Conservation Department Survey Report, February 14, 1966). Although most analyses were less than one part per million of DDT and analogs, the report noted that "every sample contained DDT and its analogs and about three-fourths of them contained dieldrin". Hickey, 1966, working in cooperation with the Wisconsin Conservation Department, developed residue data in herring gulls associated with the Lake Michigan ecosystem and showed relatively higher levels attributed to food chain magnification. Hickey <u>et al</u>., (1966) found higher residues at virtually all trophic levels in Lake Michigan than in organisms not associated with the lake.

The Bureau of Commercial Fisheries between 1965 and 1967 processed approximately 450 fish samples from Lake Michigan and observed both DDT, its analogs and dieldrin at levels substantially higher than observations from Wisconsin lake fish (Carr and Reinert, 1968).

In June, 1968, the Wisconsin Department of Natural Resources initiated a survey of pesticides in invertebrate organisms as a method of evaluating point sources and regional contamination. This approach was later revised, as a result of the Lake Michigan Enforcement Conference Pesticide Committee (November, 1968) to include mussel monitoring as proposed by Bedford et al., 1968.

In the early 1960's, several agencies initiated investigations on the Great Lakes, particularly Lake Michigan, to evaluate the effect of pesticides on various aspects of the lake ecology.

In January, 1968, the Federal Water Pollution Control Administration called a Four-State Enforcement Conference on Pollution of Lake Michigan. In March, 1968, the conferees concluded, "Pesticides are found in Lake Michigan and its tributary streams resulting from the application of these materials. The ever-increasing use of these materials threatens water uses for recreation, fish and wildlife and water supplies." The conferees took positive action toward a review and study of the pesticide problem in Lake Michigan in the following recommendation:

> "A technical committee on pesticides will be established to be chaired by a member of the Federal Water Pollution Control Administration with representatives from each State. The Committee shall evaluate the pesticide problem and recommend to the conferees a program of monitoring and control. The first report will be submitted in six months to the conferees. The States shall seek legislation to license commercial applicators."

The technical committee completed the "Report on Insecticides in Lake Michigan" in November, 1968. The report identified potential problems resulting from pesticide use in the Lake Michigan Basin and made recommendation for monitoring and control. The pesticide committee concluded early that only insecticides appeared to warrant consideration since there was no evidence suggesting significant amounts of other pesticides in the Lake Michigan ecosystem. This conclusion was a matter of priority and meant that there were immediate and pressing problems that warranted consideration first.

Probably, there was more information available on Lake Michigan than the other Great Lakes, but the only significant data available were on DDT and dieldrin residues in fish. Concentration estimates of these chemicals in the waters of Lake Michigan were essentially nonexistent and those that were recorded were open to question because of analytical and collection methods.

An immediate review of the hazards of pesticides to the Lake Michigan ecosystem was difficult since the quantity of pesticides in the water had not been established. The committee, through the Bureau of Commercial Fisheries, collected open water samples from both the southern and northern basins. Split sample analyses by three independent laboratories gave reasonable reproducibility with the following levels of insecticides reported:

DDT	2.0 nanograms/liter (parts per trillion)
DDD	1.0 nanograms/liter (parts per trillion)
DDE	0.5 nanograms/liter (parts per trillion)
Dieldrin	1.0 nanograms/liter (parts per trillion)

These levels of insecticides challenged the limits of detectability of the most sensitive quantitative techniques available and left the impression that the levels were essentially zero. However, one part per trillion is 1.67×10^{12} molecules per liter and the samples from open lake water, collected throughout the greater portion of the lake, when viewed in this respect, were contaminated. Furthermore, it was suspected that inshore areas had variable but higher concentrations. The committee subsequently reviewed the potential hazards these insecticides might produce in the Lake Michigan system.

The Lake Michigan Enforcement Conference Technical Committee on Pesticides in its report dated November, 1968, outlined an investigational program designed to elucidate information essential to evaluating the impact of pesticides on Lake Michigan. In February, 1969, the Lake Michigan Enforcement conferees accepted the pesticide committee report which called for monitoring of chlorinated hydrocarbon pesticides in Lake Michigan water, tributary streams, fish and other biological specimens.

SECTION IV

PESTICIDE MONITORING - LAKE MICHIGAN OPEN WATER

The pesticide committee recommended two sampling areas in the central portion of the lake, one in the northern basin and one in the southern basin, and three collections per year at these sites. It was further recommended that the Chicago water intake at the Central District Filtration Plant be sampled weekly for insecticides.

The original proposal planned for the City of Chicago was to provide the analytical support to this program as part of its routine water analysis. Unfortunately, that support did not materialize and in April, 1970, the Lake Michigan Basin Office of the Environmental Protection Agency began the analysis. Between April, 1970, and January, 1971, twenty-one samples were processed in accordance with the analytical procedure outlined in Appendix I, Procedure 1. The data are tabulated in Appendix I, Table 1.

The data revealed the common presence of ten chlorinated hydrocarbons. Total DDT plus analogs recorded during the summer ranged between 2 and 66 parts per trillion, principally as DDT. These values appear high when compared with the original lake data which suggested two parts per trillion in open lake water collected in the summer of 1968. The committee recognized this analytical discrepancy and subsequently initiated through the Lake Michigan Basin Office of the Environmental Protection Agency, a series of quality control samples so that the analytical procedures and data reliability could be evaluated among participating laboratories. These analytical comparisons are provided in Appendix I, Table 2.

These data were reviewed by the committee on April 13, 1971, and the following conclusions regarding the analytical reliability of pesticide analysis on lake water were drawn:

1. The levels of chlorinated hydrocarbon pesticides present in Lake Michigan water challenged the sensitivity of the techniques that were employed and available at the initiation of the program.

2. The presence of interfering compounds probably accounts for the interpretations suggesting the presence of all except DDT, DDE and dieldrin. Phthalates and polychlorinated biphenyls are at least two compounds known to be present in Lake Michigan waters that produce false pesticide readings.

3. The level of DDT plus analogs in Lake Michigan water (southern basin) is somewhere between one and ten parts per trillion. No judgment was made on actual variability of these pesticides in the water.

4. Laboratory or sampling contamination may account for unusually high recording since the analysis challenges the limits of detectability and yet is sensitive to one part per trillion.

The Lake Michigan Basin Office of the United States Environmental Protection Agency made 22 collections, all in the southern basin, on 11 dates during 1969 and 1970. Appendix I, Table 3 is a summary tabulation of those data with station locations identified in Appendix I, Figure 1. The data suggest similar concentrations in surface water and deep water for total DDT on six of ten occasions. On four occasions the difference between surface and bottom collections was apparent but the concentration of DDT appeared to be distributed vertically throughout the water mass. These data further permit comparison of the analyses from a single laboratory at the Chicago water intake and other Lake Michigan waters (southern basin). A nonpaired comparison of the concentration of total DDT in samples from the Chicago water intake (Appendix I, Table 1) and from the southern basin of Lake Michigan (Appendix I, Table 3) indicates a calculated student's "T" value of 2.46, indicating a significant difference. From these data one might conclude that even if the absolute levels recorded are in error, there is a high probability that there is more total DDT at the Chicago water intake than in open lake waters. Unfortunately, there are sufficient seasonal differences in the data from the Chicago intake to temper this conclusion.

The Wisconsin Department of Natural Resources also provided analyses of open water of Lake Michigan as part of its general sampling program. The data are tabulated in Appendix I, Table 4. The analytical procedures utilized by the Wisconsin Department of Natural Resources for water analysis are described in Appendix I, Procedure 2.

Thirteen samples were collected from Green Bay, two of which contained DDT plus analogs, at detectable levels. Typically the limit of detectability would be two parts per trillion, but several of the Green Bay samples had impaired the detectable concentration of twenty-five open lake water samples collected from Lake Michigan between Sturgeon Bay and Kenosha. One sample (#359) had 1,510 parts per trillion DDT (the collection was made five miles off Sturgeon Bay so it was probably without shoreline influence and it is possible that an oil slick from the vessel engine could have accounted for this residue level), 13 samples had less than two parts per trillion, four samples contained five parts per trillion or less, and three had ten parts per trillion or more. These residue levels are considerably less than those recorded by the Lake Michigan Basin Office and are consistent with the determination of July, 1968.

Two one liter open water samples were collected with a brass kemmerer water sampler at 100-foot intervals and composited into a single analysis to be compared with the surface collection. At one station, 25 miles off Milwaukee, both the surface sample and the profile sample contained approximately three parts per trillion. A second comparison five miles off Kewaunee revealed no pesticides in the surface water sample and 11 parts per trillion in the profile sample composite.

A second series of profile samples was collected off Two Rivers at different depths in April, 1971 and analyzed individually. The four profile samples taken between the surface and 325 feet have remarkably reproducible levels of total DDT as shown below:

Depth (feet)	Total DDT (parts per trillion)
3	4
100	3
200	5
325	3

Profile analyses were completed after an additional sample collected from Port Washington was processed to determine the extraction efficiency. The raw water sample contained eight parts per trillion total DDT and one part per trillion dieldrin. It was spiked and analyzed by the procedure in Appendix I, Procedure 2 and the results are tabulated below:

	Total DDT	% Efficiency	Dieldrin	% Efficiency
Raw Water	8	---	1	---
With 10 ppt dieldrin			8.8	78%
With 20 ppt dieldrin			20.0	95%
With 20 ppt DDT	33.5	128%		
With 40 ppt DDT	57.0	123%		

Slightly more DDT was recovered than was added, suggesting the extraction efficiency is acceptable. The Wisconsin Department of Natural Resources analyzed Lake Michigan waters from six municipal water intakes and there was <1 ng/l DDT in 10 of the 22 samples processed. Twelve samples with DDT >1 ng/l had unusual variability, with one sample from Milwaukee showing 221 ng/l. These data are presented in Appendix I, Table 5. An explanation for the apparent variability in these samples is that the water intakes are inshore and subject to wave action and lake currents.

The Michigan Water Resources Commission analyzed 20 samples from Lake Michigan municipal water intakes. Appendix I, Table 6 is a summary of that data, collected from November, 1970 to April, 1971. The results from inshore water are consistent with the Wisconsin data.

The Illinois Environmental Protection Agency analyzed six water samples from water intakes of Illinois communities. All were less than one part per trillion total DDT and 0.1 part per trillion dieldrin, substantially lower than those levels reported by Wisconsin, Michigan, and samples analyzed by the United States Environmental Protection Agency. Indiana did not analyze lake water for chlorinated hydrocarbon insecticides. WARF, Inc., sampled Lake Michigan in July, 1969, using private funds. This survey included water, sediment, fish and plankton from tributary streams as well as the lake. Sixty-six sites were sampled between July 8 and July 29, 1969. Open water collections were made at 34 of the 66 sample sites and processed in accordance with the procedures outlined in Appendix I, Procedure 3. The data on open water are tabulated in Appendix I, Table 8. Twenty-one of the 34 samples revealed less than five parts per trillion total DDT, thirteen samples exceeded five parts per trillion, and one sample exceeded 20 parts per trillion. These data are consistent with the Wisconsin open water data.

Dieldrin concentrations obtained by the WARF survey revealed much less variability than did total DDT, but residue levels were higher than anticipated. This absence of variability in dieldrin concentrations suggests that extraction efficiency is reasonably efficient or at least consistent and that the variability observed is indeed real and not merely analytical scatter. WARF found benzene hexachloride in open lake waters. It appeared as a gas chromatograph peak in virtually every sample and was confirmed by thin layer chromatography techniques. It seems most unlikely to be a result of pesticide application since relatively little benzene haxachloride has been used and furthermore, benzene hexachloride is more degradable than other chlorinated hydrocarbons. The WARF report (1970) calls particular attention to the presence of unknown hexane-soluble, electron-capturing compounds that may be part of peaks identified and quantified as pesticides by gas chromatography. In spite of this potential source of over-estimates of pesticides, the levels in water developed by WARF are relatively low with a most probable number of total DDT at less than five parts per trillion.

SECTION V

TOTAL PESTICIDE IN LAKE MICHIGAN

In view of the analytical difficulties associated with water analysis, it is not possible to offer confident poundage estimates of the pesticides in the lake. It seems feasible, however, to offer the range that the poundage might include. The volume of the lake is approximately 1,170 cubic miles or 108×10^{14} pounds of water. Assuming conservatively that the water has two parts per trillion of DDT plus analogs (suggested by the Wisconsin and WARF data), then the total DDT in Lake Michigan water is 21,600 pounds.

The Lake Michigan Basin Office data suggest approximately 20 parts per trillion of DDT plus analogs as 216,000 pounds of DDT in the lake water. Even the higher of these levels is reasonable if one considers the tonnage of DDT that was utilized in the Lake Michigan Drainage Basin. If the lower figure is accurate, the lake seems efficient in purging itself of DDT, presumably through precipitation to the bottom sediment where it may be biologically less active than when in the water. A second explanation, if the lower figure is accurate, is that pesticide contributions to the lake are really very small. It is more likely that the truth is in a combination of relatively substantial use in the basin over the years, relatively little contribution to the lake itself and a comparatively inefficient precipitation and/or degradation process.

SECTION VI

LAKE MICHIGAN TRIBUTARY WATERS

Water and biological monitoring on tributary streams was intended for two purposes:

1. To permit a material balance calculation of pesticide input and loss.

2. To identify unusual pesticide sources.

The monitoring of river water was completed by the states. The ten largest were selected for more intensive sampling because they had the majority of flow into the lake. Two stations were selected on the Milwaukee River to separate the urban and rural contribution. The rivers selected are tabulated in Appendix II, Table 1 and are geographically identified in Appendix II, Figure 1.

The Wisconsin Department of Natural Resources sampled four stations on three rivers: the Menominee River (boundary water between Wisconsin and Michigan), the Fox River, and two stations on the Milwaukee River. In addition to these major stream sampling sites, the Wisconsin Department of Natural Resources made pesticide analyses on other Wisconsin tributary waters with lesser flow.

Composite samples were recommended to minimize the hazards of grab sampling of stream waters but the method of composite collection was left to the states. The Wisconsin Department of Natural Resources used variable flow tube pumps for composite collections. Three-day composites were collected in 20-liter, hexane-washed carboys and the contents were sub-sampled for analysis. The results are tabulated in Appendix II, Table 2.

1. Fox River - Brown County.

    Five composite samples were collected from the Fox River, 0.1 mile above the mouth. One sample contained 16 parts per trillion DDT. The limit of detectability was two parts per trillion in only two samples. Three samples had interferences that masked a low level of DDT. In the sampling collected on May 7, 1970, there was a strong suggestion of polychlorinated biphenyl interference. Of four grab samples collected from the Fox River on August 27-29, 1969, two had a strong indication that DDT and analogs were present. The Fox River receives continual industrial and domestic wastewater but the most likely pesticide concentration was less than ten parts per trillion, suggesting that the sewage treatment plants and the paper-making discharges have, at worst, a minor effect on the DDT and dieldrin in the stream waters.

2. Menominee River - Marinette County

Four collections were made on the Menominee River, 0.2 miles above the mouth of the river. All were two to three day composites and two parts per trillion detectability was achieved on three of the four occasions. DDT and dieldrin were found. The collections were all made below the Menominee-Marinette industrial and domestic outfalls. The DDT levels are apparently less than two parts per trillion and dieldrin levels are apparently less than 1 part per trillion.

3. Milwaukee River - urban

Five urban collections were made at the Wells Street crossing in downtown Milwaukee. These samples revealed unusual variability. A sample in April had 460 parts per trillion DDT and 650 parts per trillion dieldrin. Two other samples had 2 parts per trillion DDT and three had 1 part per trillion dieldrin. This variability suggests that if the tributary streams are responsible for pesticides in the lake, water analysis cannot readily be used in calculating a material balance. Intensive sampling of discrete water strata or slug loadings would be essential to calculating a material balance.

4. Milwaukee - rural

The Milwaukee River rural sample was taken above the City of Grafton in Ozaukee County. Five composite collections (two days) were made during the summer of 1970. Interfering substances were not present and consequently the limit of detectability was at or near two parts per trillion. Four of the five rural Milwaukee River collections revealed less than two parts per trillion DDT. One sample revealed 16 parts per trillion dieldrin. These data suggest that, if the rural area is responsible for pesticide contributions, slug loadings that are unpredictable and virtually impossible to use in developing a material balance on the lake are responsible.

The Wisconsin Department of Natural Resources provided additional composite and grab sample analyses on other Wisconsin streams in an effort to find those streams that were discharging unusual pesticide loads. In essence, the Sturtevant tributary and the north branch of the Pike River (Racine County) were the only collections that revealed high levels of chlorinated hydrocarbon insecticides (Appendix II, Table 2).

Composite tributary sampling was requested of Michigan on the Grand, Kalamazoo, Manistee, Muskegon and St. Joseph Rivers. Three composite samples were collected on these rivers by the Michigan Water Resources Commission and one other sample was taken on each of five non-specified streams. The results of these analyses are tabulated in Appendix II, Table 3. Collection and analytical procedures for composite samples are described in Appendix II, Procedure 1. DDT and its metabolites and isomers were found in all samples at concentrations from <1 to 184 parts per trillion. The highest concentrations were found during the fall of 1970 in the lower peninsula streams, but there appeared to be considerable polychlorinated biphenyl interference in these samples. Relatively little difference in DDT concentrations was found between streams or dates in the 1971 samples.

Low levels (<1 to 3 parts per trillion) of dieldrin were found in 21 of 29 stream samples.

The Indiana State Board of Health processed river water samples from Burns Ditch, Trail Creek and the St. Joseph River. Collections of water samples were made with a DU-1 Brail's ford automatic sampler. The samples were set to fill a one gallon jug in 24 hours and were secured to the bank or a dock by a rope tie with enough of the coupling tube in the water to assure that any fluctuations in the water level would not interrupt the sampling. A total of 24 composite collections was made between June and November of 1970. The results of these analyses are tabulated in Appendix II, Table 4. In general, lindane, heptachlor, aldrin, DDE, dieldrin, endrin and DDD were not detected at a ten parts per trillion limit of detectability. On 10 occasions, DDT was observed at recordable levels between 11 and 47 parts per trillion. These data are similar to those from Wisconsin streams.

The Indiana data for Trail Creek are particularly significant since they attempted to quantify the pesticide usage in the basin at the time of sampling. The land usage in the drainage basin was as follows:

Michigan City residential	5,203	(14.7%)
Farmland	19,940	(56.0%)
Woodland and Swamp	9,972	(27.9%)
Orchards	499	(1.4%)

DDT usage was recorded only in the orchards amounting to 6 pounds, suggesting that the DDT entering the lake from Indiana is from applications made in past years.

The Illinois Environmental Protection Agency reported on only two grab samples from the Waukegan River and Pettibone Creek in November of 1970. The samples had 6.24 and 14.95 parts per trillion total DDT (Appendix II, Table 5).

The Wisconsin Alumni Research Foundation survey of July, 1969, included grab water samples from 62 tributary streams discharging to Lake Michigan. Samples were processed in accordance with procedures outlined in Appendix I, Procedure 3 and the data are tabulated in Appendix II, Table 6. Polychlorinated biphenyl concentrations were not included in this series and the limit of detectability for chlorinated hydrocarbons was ten parts per trillion.

Of the 62 samples, 38 were less than ten parts per trillion. The scatter in total DDT concentrations is similar to that observed in Wisconsin data (Appendix II, Table 2). Stream water pesticide level comparisons between Wisconsin data, Michigan data and WARF data confirm this scatter, as seen in the following table.

RIVER	Wisconsin Analysis Total DDT	WARF Analysis Total DDT	Michigan Analysis Total DDT
Fox	38, 183, 10, 10, 16	---	---
Pike	10, 10, 10, 2, 2 2	49.1	
Kewaunee	1	10	
Manitowoc	10, 10	10	
East Twin	1	10	
West Twin	1	27.6	
Menominee	2, 10, 2, 2	53.8	4, 19, 4
Peshtigo	2	10	
Milwaukee	65, 85, 5, 15		
Oconto	2	10	
Pensaukee	2	10	
No. Br. Pike	29, 60, 10, 30	49.1	
Sheboygan	5, 2	260	
Galien		56.9	96, 17
St. Joseph		10	113, 11, 5
Kalamazoo		10	84, 11, 2
Grand		11.4	119, 22, 12
Muskegon		10	152, 12, 1
Manistee		24.4	184, 7, 11
Boardman		10	159, 1, 65
Manistique		10	11, 8, 2

The apparent scatter between Wisconsin data and WARF data with results comparable in quantitation strongly suggests a real variability and not merely inconsistent extraction and analysis. The Michigan data reported in Appendix II, Table 2 has been corrected for an analytical error. The collections of May and July, 1971, are reasonably consistent with WARF, Inc., and Wisconsin data.

It appears from 100 or more analyses on tributary stream waters that it is virtually impossible to resolve the discharge levels of pesticide either because of unreliable analytical procedures or because of real variability that would require analytical support unwarranted from a cost-benefit standpoint.

SECTION VII

BIOLOGICAL MONITORING OF TRIBUTARIES

The Enforcement Conference Pesticide Committee recommended a seasonal biological monitoring program in most tributaries during the ice-free season to identify sources of pesticides. Living mussels were selected as the monitor organism because they siphon a large volume of water and have the potential ability to concentrate the chlorinated hydrocarbons in their flesh. Wisconsin and Indiana also sampled other resident invertebrates. The data from Michigan, Wisconsin, and Indiana are summarized in Appendix III, Tables 1 to 3.

Wisconsin Biological Monitoring

The Wisconsin program included biological monitoring on virtually all tributary streams in the Lake Michigan Drainage Basin. Most mussels were collected from Ox Creek in Douglas County. Their background level of chlorinated hydrocarbons was variable and generally low but the absolute level was not germane, because the organisms would be permitted to reach a new level of pesticide equilibrium that would represent the test environment. Collection and analytical procedures are outlined in Appendix III, Procedures 1 and 2.

In Wisconsin, more than 50% of the mussels analyzed for DDT and analogs were below ten parts per billion, a concentration considered as background. Forty-five percent had concentrations between 10 and 100 parts per billion and represented a significant contamination. Three percent of the samples exceeded 100 parts per billion. Those counties which revealed samples with significant levels of apparent DDT included: Door, Kenosha, Ozaukee, Racine and Sheboygan. The potential pesticide sources on streams where mussels had high residue levels have been evaluated and enforcement actions have been completed or are continuing. High residue levels in mussels of Door County may result from runoff from numerous orchards. Kenosha, Milwaukee, Ozaukee, Racine and Sheboygan counties are relatively populous and industrialized with numerous potential point sources that are now prohibited from using DDT and dieldrin.

Only 13 mussel samples (14%) contained a detectable concentration of dieldrin, six of which exceeded ten parts per billion. The higher levels of dieldrin were all from mussels in southeastern streams that are industrialized. Enforcement actions have been completed and surveys in 1971 will establish the success of the enforcement program.

Michigan Biological Monitoring

The Michigan Water Resources Commission processed 17 mussel samples from Michigan streams. The data are tabulated in Appendix III, Table 2.

Field and laboratory techniques are described in Appendix III, Procedure 3.

Concentrations of total DDT found in mussels ranged from 27 to 83 parts per billion with a mean of 51 parts per billion. Mussels held in north shore streams averaged 33.2 parts per billion with no individual collection greater than 40 parts per billion total DDT. Mussels in the lower peninsula tributaries usually had higher concentrations of DDT. Two other areas with relatively high concentrations of DDT in the mussels were the Grand Traverse Bay-Leland Peninsula region and the Lake Michigan shoreline from the Manistee River to the Black River in Van Buren County. Mussel collections from five streams in these regions averaged 67.6 parts per billion and four streams averaged 65.0 parts per billion. All other lower peninsula streams had concentrations in mussels ranging between 27 to 44 parts per billion.

All dieldrin concentrations were less than ten parts per billion and most were less than three.

Indiana Biological Monitoring

Ten mussel samples were analyzed from Indiana streams discharging into Lake Michigan (Appendix III, Figure 1). The data are tabulated in Appendix III, Table 3. Seven mussel samples had less than ten parts per billion DDT, and one had 48 parts per billion DDT when it was removed from Burns Ditch in July, 1970. Dieldrin was less than ten parts per billion.

The Indiana Board of Health collected resident invertebrates from the same streams as the mussel collections and noted little correlation between the two.

SECTION VIII

FISH MONITORING

The Enforcement Conference Pesticide Committee recommended that four species of fish be collected in April and October at four sampling stations on Lake Michigan. Two samples of ten fish (five of each sex) were to be examined in accordance with the following schedule:

Station	Species	Number of Samples	Composition of the Samples
Green Bay	Alewives	2	5 males, whole body
		2	5 females, whole body
	Yellow Perch	2	5 males, whole body
		2	5 females, whole body
Waukegan,			
Saugatuck,			
Charlevoix	Alewives	2	5 males, whole body
		2	5 females, whole body
	Yellow Perch	2	5 males, muscle only
		2	5 females, muscle only
	Chubs	2	5 males, muscle only
		2	5 males, whole body
		2	5 females, muscle only
		2	5 females, whole body
	Coho Salmon	2	5 females, muscle only
		2	5 males, muscle only

The collection and analyses were done by the Bureau of Commercial Fisheries. Data gathered by the Bureau between 1965 and 1968 were essentially the only data available to the committee when the 1968 report was prepared. Unfortunately, the Bureau of Commerical Fisheries was unable to complete the schedule but did continue the monitoring that had been initiated in the mid-1960's and developed residue levels over the investigational period.

Appendix IV, Table 1 is a summary of data accumulated by the Bureau of Commercial Fisheries between 1965 and 1969. The commercially important species including lake herring, lake trout and coho salmon all exceed five parts per million total DDT, an action level established by the United States Food and Drug Administration. Apparently, the 0.3 parts per million dieldrin tolerance is not exceeded in these commercially important species.

During the summers of 1969 and 1970, the Bureau of Commercial Fisheries processed chub, coho salmon, and lake trout samples for total DDT and dieldrin. Appendix IV, Table 2 is a summary of analyses from these collections (Reinert, 1970). Twenty-three lake trout were collected from the South Haven-Saugatuck area of Lake Michigan in May, June and July, 1970. DDT concentrations (DDT, DDD, DDE) in nineteen of these fish between 558 and 660 millimeters (22-26 inches) ranged from 10.9 to 28.1 parts per million with an average of 18.8 parts per million. Dieldrin concentrations ranged from 0.14 to 0.45 parts per million with an average of 0.27 parts per million. Three smaller lake trout of 320, 366, and 483 millimeters contained 3.9, 6.2 and 11.1 parts per million of DDT and 0.18, 0.15, and 0.20 parts per million of dieldrin respectively. One large fish (736 millimeters) contained 22.7 parts per million DDT and 0.2 parts per million dieldrin.

Thirty chubs were collected on September 23 off Saugatuck, Michigan. Each was analyzed and had DDT concentrations between 4.7 to 19.7 parts per million with an average of 10.2 parts per million. Dieldrin concentrations ranged from 0.12 to 0.28 parts per million with an average of 0.19 parts per million.

Five coho salmon from the 1968 year class were collected off Waukegan, Illinois, in early May and measured 434 millimeters to 510 millimeters with an average of 477 millimeters total length. Weight ranged from 493 grams to 1,232 grams with an average of 967 grams. DDT concentrations were from 2.1 to 3.2 with an average of 2.8 parts per million. Dieldrin concentrations were from 0.05 to 0.09 parts per million and averaged 0.07 parts per million.

Twelve coho salmon collected off Ludington, Michigan, in late August were from 568 to 730 millimeters in length (average 658 millimeters) and weighed from 2,785 grams to 5,178 grams with an average of 3,663 grams. DDT concentrations in these fish ranged from 9.0 to 16.7 parts per million and averaged 14.1 parts per million. Dieldrin concentrations were from 0.05 parts per million to 0.18 parts per million with an average of 0.12 parts per million. A comparison of DDT and dieldrin concentrations between fish collected in 1970 and 1969 indicates there has been no detectable change in the concentrations of these insecticides (Appendix IV, Table 2).

The Bureau of Commercial Fisheries evaluated the analytical reliability of pesticide measurements in fish flesh. One hundred twenty analyses were made from a single collection of chubs (Coregonus hoyi). Total DDT ranged between 6.5 and 15.3 parts per million with a mean of 9.9 (Appendix IV, Table 3). The standard deviation was 1.84, indicating a coefficient of variation of 18 percent, entirely acceptable considering the analytical difficulties involved. This program substantiates the reliability of fish sampling at least as long as analyses are confined to one laboratory. The data may not be entirely accurate but precision is good and the data can be used to make location comparisons and establish residue trends in the fish.

Although too few fish analyses from the mid-1960's are available to predict long-term residue trends, the data from 1969 and 1970 are sufficient to be used for this purpose. The data suggest no significant difference between 1969 and 1970 between the southern and northern basin. It is obvious there are differences among species and larger fish tend to accumulate higher levels of DDT. Significantly, the larger fish with the high residue levels are those species of highest commercial value and these generally exceed the action level established by the Food and Drug Administration.

The State of Wisconsin Department of Natural Resources also analyzed fish samples from Lake Michigan for chlorinated hydrocarbons. The results of that survey are tabulated in Wisconsin Department of Natural Resources Management Report #34 and a summary of the data is tabulated in Appendix IV, Table 4 of this report. A total of 563 samples was analyzed for total DDT and dieldrin. These data also indicate that the larger trout and salmon generally exceeded the five parts per million action level established by the Food and Drug Administration but dieldrin levels did not exceed the 0.3 parts per million action level for that insecticide.

The Illinois Environmental Protection Agency processed 11 fish samples from Lake Michigan and found less DDT and dieldrin than Wisconsin and the Bureau of Commercial Fisheries (Appendix IV, Table 5). There is no obvious explanation for this difference.

The Bureau of Sport Fisheries and Wildlife, Fish-Pesticide Research Laboratory has long recognized the analytical complication of polychlorinated biphenyls in fish pesticide residue data. Fish samples from Lake Michigan were processed both with and without polychlorinated biphenyl separation. Those tabulations are recorded in Appendix IV, Table 6. The data show that some of what is recorded as total DDT is most likely part of the polychlorinated biphenyl complex, but the polychlorinated biphenyl complex is not additive with the DDT complex.

The polychlorinated biphenyl data of the Bureau of Sport Fisheries and Wildlife indicates that future analysis will require a separation of polychlorinated biphenyls from the chlorinated hydrocarbon insecticides. Most existing residue data in fish include the polychlorinated biphenyls with the insecticides. This analytical combination makes it conceivable that a future reduction in the insecticide residue level could go undetected if the polychlorinated biphenyl residues continued to increase.

Appendix IV, Table 7 is a summary of relative polychlorinated biphenyl pesticide residue levels in fish eggs and fry and Appendix IV, Table 8 is a summary of 79 analyses for total DDT-polychlorinated biphenyl levels.

SECTION IX

ADDITIONAL INVESTIGATION

The Michigan Water Resources Commission recognized the potential contamination of Lake Michigan from a dieldrin application intended for Japanese beetle control and in 1968 initiated an investigation to evaluate the impact of this specific application on the environment, including Lake Michigan. In the fall of 1968, the Michigan Department of Agriculture approved the application of dieldrin and chlordane on 4,225 acres of Chikaming Township, Berrien County. In October, the application was made using 6,227 pounds of dieldrin and 10 pounds of chlordane. Residue measurements of dieldrin and chlordane were made on water, sediments and tissues from caged mussels, both before and after treatment on four stream locations and two control streams (Fetterolf, 1971).

Prior to treatment, mean concentrations of chlordane were less than 0.2 parts per billion in water, less than 50 parts per billion in sediments and less than 34 parts per billion in mussel tissues. The mean dieldrin concentrations prior to treatment were less than 0.02 parts per billion in water, five parts per billion in sediments and 7.8 parts per billion in mussel tissues. Following treatment, the chlordane concentrations in water, sediments and mussels reached individual station highs of 3.4, 22,000 and 7,530 parts per billion, respectively; and the dieldrin concentrations reached 2, 2,000 and 1,137 parts per billion, respectively.

Movement of chlordane from treated land to stream waters occurred primarily in the first three months after application. Dieldrin concentrations in stream waters were lower initially but persisted throughout the 21 months of measurements.

Chlordane concentrations in stream sediments remained low but measureable up to one year after treatment. In October, 1969, subsequent applications of chlordane to portions of the previously treated watersheds reduced the value of continued monitoring. Dieldrin was still present in the sediments 21 months after application and at concentrations between 60 and 250 parts per billion.

Nine months after the insecticide applications, mussels at test stations contained chlordane concentrations as much as 33 times higher and dieldrin concentrations 112 times higher than at control stations. These levels dropped sharply by the end of the first year of sampling. An estimated 11.3 pounds of dieldrin were contributed to Lake Michigan in stream water in the 21 months following treatment representing 0.18 percent of the total 1968 applications.

Bedload, allochthonous and autochthonous organic materials appeared to play a significant but unmeasured role in the transport of insecticides in the streams. The biological significance of insecticides found in this manner in Lake Michigan are unknown. Resident fish populations were reduced in numbers and altered in species composition for as long as 12 months following the insecticide applications.

The Wisconsin Department of Natural Resources, in conjunction with the tributary stream monitoring program, included residue analysis of resident invertebrates. The data are included in the tabulation presented in Appendix III, Table 1 (Lueschow et al., 1970). Nearly 50 percent of all invertebrate sample analyses for chlorinated hydrocarbons fell below ten parts per billion DDT (ng/kg), a level which was considered to be background. As with mussel samples, those invertebrate samples where the concentration of DDT exceeded ten parts per billion were considered significantly contaminated and follow-up investigations at those sites have been initated to identify point sources.

Over 80 percent of all samples had dieldrin concentrations less than ten parts per billion. Many samples were less than two parts per billion. The sample distribution of highest chlorinated hydrocarbon residues was found to be remarkably consistent with the fish residue observations by Kleinert et al., 1968. Where point sources were identifiable, enforcement action is underway.

In 1969, the Wisconsin Department of Natural Resources promulgated relatively stringent restrictions on all chlorinated hydrocarbons which effectively prohibited their use for most routine purposes (NR 8 Administrative Code). Particularly DDT and dieldrin were restricted and essentially none was used in Wisconsin subsequent to the 1969 season. Selected follow-up biological investigations on the Wisconsin tributaries will be conducted in 1971 to evaluate the trend in the invertebrate population.

The Indiana Board of Health also analyzed resident invertebrates, in addition to the mussel samples (Appendix III, Table 3). The Indiana experience suggested that the resident invertebrates revealed significantly higher residue levels and were the organisms of choice to evaluate low pesticide loads in the tributary streams.

The Indiana Board of Health conducted a more extensive investigation on Trail Creek in an attempt to establish the important sources of DDT and dieldrin. Water samples from all stations were highest in August at a time when stream flows were lowest and runoff was least. Industrial sources such as dry cleaning establishments were viewed as unlikely contributors. This left groundwater as a potential source and analyses of artesian water correlated closely with Trail Creek waters.

The Wisconsin Department of Natural Resources also initiated monitoring program of municipal waste sources. Samples were both grab and 24-hour composites, collected and returned to the laboratory for extraction.

One hundred twenty-five samples were processed and are tabulated in Appendix V, Table 1. In general, the limit of detectability was ten parts per trillion. The most extensive monitoring was done at the Milwaukee Jones Island plant, Grafton, Racine and Oshkosh. Milwaukee and Oshkosh were considered typical communities with no known industrial wastes contributing chlorinated hydrocarbons. The weekly monitoring was initiated at the request of the enforcement personnel to cover the spring cleaning season when stores of recently restricted DDT would or might be discharged into a drain system. Racine, Grafton and Portage were selected for more extensive sampling because these communities had known sources of dieldrin. High pesticide levels recorded at Plymouth and Sheboygan are probably influenced by polychlorinated biphenyls.

The Wisconsin Department of Natural Resources in the stream monitoring program observed unusually high dieldrin levels below wool processing plants. A relatively comprehensive evaluation of this type of discharge was made at Grafton, Wisconsin, and reported in June, 1969 (Lueschow). This particular discharge was responsible for a dieldrin concentration in river water of 500 parts per trillion where background levels were less than 20 parts per trillion. The dieldrin concentration in invertebrates was approximately four parts per million and background was 0.015 parts per million. Enforcement action was completed before mussels were placed in this section of the stream. Information obtained in this investigation was the basis for enforcement action at other similar industrial sites located in the Lake Michigan Drainage Basin.

The Wisconsin Department of Natural Resources and Michigan Water Resources Commission noted in numerous situations the presence of peaks on the gas chromatograph that were typical of polychlorinated biphenyl contamination. A subcommittee of the Lake Michigan Enforcement Conference Pesticide Committee recommended a survey of industries suspected of discharging these products. A review of potential polychlorinated biphenyl users in the state suggested there were far more than could conveniently be investigated. Therefore, Michigan and Wisconsin elected to conduct a mail survey of those industries that had potential discharges of polychlorinated biphenyls. The questionnaire used by Wisconsin is represented in Appendix VI and a similar one was used in Michigan.

A total of 112 questionnaires was sent and 58 were returned (52%). Fifty-two industries reported they were not now using polychlorinated biphenyls and 47 suggested they never had been used. Three industries were currently using polychlorinated biphenyls and five industries reported using them within the last three years. The Michigan Water Resources Commission initiated 46 questionnaires and had 22 returned (48%).

It was concluded that the majority of industries that were using polychlorinated biphenyls, particularly as a component in a product, were not aware of them. In general, those sources that did not know of polychlorinated biphenyls in a raw material or product had relatively little potential loss or at least little loss would be on a sustained basis. Any losses would more likely be a result of accident, clean-up or some inadvertent loss of a raw material with polychlorinated biphenyls as a component.

Wisconsin has not initiated further industrial investigations nor taken enforcement action against polychlorinated biphenyl discharges at this time. WARF, Inc., in the July, 1969, survey provided sediment analyses on Lake Michigan tributary rivers. The analytical procedures are outlined in Appendix VII, Procedure 1. The data are tabulated in Appendix VII, Table 1. In general, the chlorinated hydrocarbons in stream sediments were consistent with stream water trends except the characteristic benzene hexachloride peak was not observed. It did appear that the southern portions of the lake (urbanized) had higher chlorinated hydrocarbons in the sediment than did the northern basin. The different sediment type between the two areas could be partly responsible.

The Illinois Environmental Protection Agency collected seven grab samples at sewage treatment plants tributary to Lake Michigan in Lake County, Illinois in 1970. Total DDT values ranged from 2.5 to 11.2 parts per trillion (Appendix V, Table 2). These values are low compared to results found by Wisconsin.

The Illinois Environmental Protection Agency also analyzed thirteen sediment samples for pesticides in 1970. Samples were collected at tributary streams, ravines, and offshore from sewage treatment plants tributary to Lake Michigan. Total DDT values were found in the part per million range and were comparable to values found by WARF in stream sediments (Appendix VII, Table 1).

SECTION X

IMPACT OF CHLORINATED HYDROCARBON CONTAMINATION ON THE LAKE MICHIGAN ECOSYSTEM AND ECONOMY

Hazards to Human Health

In November, 1968, when the enforcement conference report was published, the United States Food and Drug Administration had a "no tolerance" level of insecticides in fish used for human consumption. The Bureau of Commercial Fisheries had analyzed approximately 30 species of fish collected from Lake Michigan and had observed insecticides in all species (Carr, 1968). In general, the levels of insecticides in Lake Michigan fish were two to five times greater than levels observed in the same species of fish from other Great Lakes and substantially higher than fish collected from smaller Wisconsin lakes (Kleinert, et al., 1968). The committee formally requested an interpretation of this conflict from the Food and Drug Administration and was advised that the Food and Drug Administration had no petition for a tolerance in fish and no plans for establishing tolerances on the initiative of the Commissioner (Food and Drug Administration correspondence, June 4, 1968). The Food and Drug Administration correspondence further stated that they were in no position to comment on the effect of pesticide contaminants on human health. The Food and Drug Administration did say, however, that 0.3 parts per million of aldrin, dieldrin, endrin, heptachlor or heptachlor epoxide in the edible portions of the fish warranted legal action. In general, the Lake Michigan fish analyzed by the Bureau of Commercial Fisheries, Wisconsin Department of Natural Resources, and the Illinois Environmental Protection Agency do not exceed these concentrations.

In April, 1969 the Food and Drug Administration established a five parts per million interim guideline for DDT plus analogs in fish and began seizing interstate commercial shipments of Lake Michigan fish. The governors of five states bordering Lake Michigan and Lake Superior subsequently appointed an interdisciplinary committee to review the consequences of this action. In October, 1969, as a result of action by the Five States Interdisciplinary Committee on Pesticides, the Michigan Health Department transmitted a petition to the Food and Drug Administration requesting a residue tolerance for DDT and its analogs of 15 parts per million in the edible portion of other fish. The petition reviewed the toxicological support for the acceptability of these levels. In early 1970, the State of Michigan held public hearings to establish the requested levels of DDT plus analogs in fish shipped within the State of Michigan. The Food and Drug Administration in July, 1970, rejected the Michigan petition for the increased federal tolerance on DDT plus analogs because DDT is a potential carcinogen (Food and Drug Administration correspondence, July 16, 1970).

Impact of Insecticide Residues on Commercial Fishing

The Food and Drug Administration interim guideline of five parts per million DDT plus analogs on fish shipped in interstate commerce will have essentially no effect on the commercial fishing of Lake Erie or Lake Ontario where concentrations are generally less than five parts per million of DDT plus analogs. Lake Michigan fish, on the other hand, where the principal commercial species are coho, chubs and whitefish, have DDT concentrations which generally exceed the five parts per million interim guideline. The Bureau of Commercial Fisheries, 1966, catch value records indicate a commercial catch value on Lake Michigan of $2,816,000 (Reinert, 1970). By applying the five parts per million DDT interim guideline to this catch, approximately 80% of the Lake Michigan commercial catch is nonmarketable in interstate commerce. Approximately eight percent of the commercial catch from Lake Superior would exceed the five parts per million DDT maximum (lake trout) and be unacceptable for interstate commerce.

Lake Superior chubs, whitefish and lake herring would not be affected by the interim guideline since residue levels in these species are less than five parts per million. Based on the 1966 catch estimates for the entire Great Lakes, approximately 42 percent of the commercial catch would be unacceptable for interstate commerce.

The impact of pesticide residues on the commercial fishery is only one in a series of difficulties encountered by the commercial fishing industry on the Great Lakes. Commercial fishing for lake trout, chubs, herring and walleyes has been reduced in recent years due to sea lamprey predation, over-exploitation and alewife competition.

Impact of Insecticide Residues on Sport Fishing

The sport fishing for coho salmon and other anadromous fishes has been burgeoning in the last three to four years, despite the publicity of pesticide residues in these species. Since sport fishing has undergone such a dramatic increase, it is virtually impossible to establish the trend that might have been characteristic if the insecticide residues had not been involved.

It seems unlikely that pesticide residues will influence sport fishing when the objective is for sport or trophy only and fish are readily available. Sport fishing for food, however, could be influenced by the well-publicized seizures of "contaminated" fish. A Michigan survey of salmon fisherman expenses (1967) indicated a trip cost of $19.50 per angler day. In view of this relatively high cost of sport fishing, it seems more than likely that sport fishing is predicated on sport and trophy rather than food. Recent publicity regarding filleting and cooking techniques and the safety factor associated with the five parts per million residue level may also have contributed to a general disregard of the contaminants among sport fishermen.

Although the sport fishermen appear to be disregarding the implications of insecticide residues in Great Lakes fish, it remains to be seen if the general public, that acts through legislative processes to support the sport fishery, will also ignore the residue implications. The state legislatures and the Great Lakes Fishery Commission will be responding to the general public as well as to the sportsmen.

Hazards to Fish Production

The effects of organochlorine pesticides on fish production have been studied by numerous investigators, including Allison et al., 1964; Boyd, 1964; Burdick et al., 1964; Cuerrier et al., 1967; Johnson, 1967; Macek, 1968; and Johnson and Pecor, 1969. Allison (1964) found a high mortality of cutthroat trout sac fry whose parents had been exposed to 0.3 and 1.0 parts per million DDT in water for 30 minutes once each month for about 15 months or to one mg/kg in the food once each week for about 15 months. There was no mortality at lower concentrations.

Boyd (1964) observed abortion of young in mosquitofish (Gambusia affinis) which survived exposure to concentrations of organochlorine pesticides that killed other mosquitofish.

Several researchers have found that organochlorine pesticides accumulated in the eggs of "normal" adult fish may be toxic to the fry during the last stages of yolk absorption or when the fry begin to feed (Burdick, 1964; Cuerrier, 1967; Johnson, 1967; and Macek, 1968).

Johnson and Pecor (1969) reported an unusual sac fry mortality which occurred in Michigan trout hatcheries in 1967. The syndrome was particularly apparent on coho salmon fry that had progressed to the latter stages of yolk sac absorption. Eggs taken from Lake Michigan brood stock had a substantially greater sac fry mortality than eggs taken from Lake Superior or far west brood stock. The investigators noted that the concentration of DDT and analogs of Lake Michigan brood stock eggs were three to five times higher than Lake Superior brood stock eggs. They further suggested that higher concentrations of DDT were found in affected fry than in normal fry from the same parent. The concentration of DDT and analogs (wet weight) from Lake Michigan fish ranged between 1.09 and 2.76 parts per million, with the higher concentration associated with a higher mortality in the sac fry. Johnson and Pecor (1969) further postulated a mechanism that could account for the mortality. It was observed at the time of fry mortality that the last fraction of yolk present in the gut contained 6 to 12 times more DDT than the general body tissues and that absorption of this most concentrated fraction could have killed the fry. Johnson has continued to monitor the hatchery mortalities in 1968 and 1969. In September, 1970, Johnson suggested the results were inconsistent and he could not establish a distinct correlation between mortalities and DDT concentrations. He further observed that the question is academic since the hatcheries are able to rear adequate numbers of fry despite a loss during yolk sac absorption.

The recorded observations on lake trout and the observed effects on coho salmon still suggest a real threat to the Lake Michigan lake trout population. Even if the lamprey control programs are successful, there still appears to be a strong possibility that the lake trout population will be unable to recover due to fry mortality.

Hazards to Bird Reproduction

Hickey *et al.*, (1966) working in the Green Bay area concluded that there were DDT and analogs in all trophic levels of the Lake Michigan ecosystems, and further suggested concentration factors for several trophic stages. The most striking aspect of this work was not the concentration factor or the fact that the organochlorine pesticides were ubiquitous but was the quantity of organochlorine present in the various trophic levels of the Lake Michigan ecosystem. Keith (1966) suggested that DDT residues in Green Bay herring gulls were related to lower egg hatchability, but had little effect on chick survival. He concluded the data were not consistent with earlier works where DDT fed in diet of quail and pheasant affected chick survival and not hatchability. Hickey (1968) makes a strong case of the correlation between the introduction of DDT and the simultaneous demise of raptorial bird populations due to metabolic reproductive failure. Current research in Wisconsin by Hickey and others suggests that the nesting populations of the bald eagle in Lake Michigan and Lake Superior have been adversely affected by chemical pollutants.

Reproductive Failure in Mink

The Mink Ranchers Association representatives have suggested that mink that were fed Lake Michigan fish have failed to reproduce. The implications have been that Lake Michigan fish have higher pesticide levels and could be responsible for the reproductive failure.

Mr. H. F. Travis, United States Department of Agriculture, has recently attempted to correlate the reproductive failure in mink with insecticide levels and has suggested that reproductive failures can indeed be induced by feeding Lake Michigan coho salmon and by feeding other foods spiked with DDT plus analogs and dieldrin at a concentration comparable to the residue levels in Lake Michigan fish. This work is yet unpublished, along with other investigations currently under way to resolve this question.

SECTION XI

STATUS OF LEGISLATION AFFECTING PESTICIDE USAGE IN THE LAKE MICHIGAN BASIN

Recommendation Number 2 of the Lake Michigan Enforcement Conference Pesticide Report of November, 1968, called for appropriate legislation to regulate insecticide usage. Appendix VIII is a summary of the status of legislation germane to insecticide use control in the five states as compiled by the Governors' Five State Interdisciplinary Committee on Pesticides. The basic residue problem on Lake Michigan has been with chlorinated hydrocarbons and particularly DDT. Illinois, Michigan and Wisconsin all have restrictions on the use of DDT. Wisconsin further considers most of the chlorinated hydrocarbons as restricted materials typically requiring special permit for application. At this time, Michigan, Illinois, and Indiana have some legislation that regulates commercial applicators while Wisconsin has not yet enacted this type of legislation.

The State of Illinois has enacted rules jointly with the Department of Agriculture and the State Board of Health that prohibit the use of DDT except by permit and specifically prohibit the use of DDT for Dutch elm disease control effective January 1, 1970. This regulation should prevent DDT contamination of Lake Michigan since it restricts sale and urban use as well as agricultural use. Other chlorinated hydrocarbon insecticides are not regulated.

The State of Indiana regulates pesticides through the State chemist's office. Senate Enrolled Act Number 559, 1971, authorizes the Indiana State chemist to identify restricted pesticides and prepare rules and regulations concerning these pesticides. The identification of the restricted products and publication of rules have not yet been completed, but the legislative intent seems adequate to protect Lake Michigan from chlorinated hydrocarbon insecticides.

Michigan was the first Lake Michigan state to enact legislation restricting the sale of DDT. This legislation did not pertain to use or transport so recently the State Legislature has passed an amendment to its economic poison law (effective January 1, 1972) that provides for a list of restricted use pesticides as well as licensing of restricted use pesticide dealers. The State agencies are currently in the process of promulgating rules to implement the intent of this Legislature.

SECTION XII

ACKNOWLEDGEMENTS

This report to the Lake Michigan Enforcement Committee was prepared by the Pesticide Committee in response to Recommendation Number 15 of the conference held in January and March, 1968. The first report was submitted in November, 1968, by the following committee representatives.

Dr. Donald Mount, Federal Water Pollution Control Administration, Chairman

Mr. Benn J. Leland, Illinois Sanitary Water Board

Mr. Stephan Kin, Indiana Water and Waste Laboratory

Mr. John Favinger, Indiana Natural Resources Department

Mr. Carlos Fetterolf, Michigan Water Resources Commission

Mr. Lloyd A. Lueschow, Wisconsin Department of Natural Resources

Mr. John Carr, Bureau of Commercial Fisheries

Dr. Oliver Cope, Bureau of Sport Fisheries and Wildlife

In the three years of this study, the committee membership has reflected the personnel changes inherent in a long-term study. The present committee hereby presents to the Enforcment Conference the current report of the committee. The report has been prepared by Lloyd A. Lueschow of the Wisconsin Department of Natural Resources and reflects the input of all four state representatives, as well as the Federal agencies participating in the pesticide committee. The present committee members include:

Dr. Donald Mount, United States Environmental Protection Agency, Chairman

Mr. Lloyd A. Lueschow, Wisconsin Department of Natural Resources

Mr. Stephan Kin, Indiana Water and Waste Water Laboratory

Mr. John Favinger, Indiana Natural Resources Department

Dr. Jim Bedford, Michigan Water Resources Commission

Mr. John Carr, Bureau of Sport Fisheries and Wildlife

Dr. Dick Schoettger, Bureau of Sport Fisheries and Wildlife

Mr. Robert Schacht, Illinois Environmental Protection Agency

The committee received invaluable counsel and guidance from a substantial number of representatives of other private and public agencies. Particular mention should be made of the contribution provided by Dr. John Birdsall, Wisconsin Alumni Research Foundation; John Neal, Ontario Water Resources Commission and LeRoy Scarce, United States Environmental Protection Agency.

The rapid and extensive accumulation of data by the state agencies involved was made possible by the Environmental Protection Agency Research Grants EYV, EYS, EPU, ESP 16050 to each of the participating states. This report also serves as partial fulfillment of the grant obligation to the Environmental Protection Agency by Wisconsin, Indiana, and Michigan. Illinois has elected to provide a separate report at a later date.

SECTION XIII

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APPENDIX I

CHLORINATED HYDROCARBON INSECTICIDES IN LAKE MICHIGAN WATERS

APPENDIX I, PROCEDURE 1

ANALYTICAL TECHNIQUES USED IN LAKE WATER ANALYSES BY THE LAKE MICHIGAN BASIN OFFICE OF THE UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ANALYTICAL CONDITIONS

All samples were analyzed according to the "FWPCA Method for Chlorinated Hydrocarbon Pesticides in Water and Wastewater-1966" with Lake Michigan Basin Office modification (employing tall form 600 ml beakers for concentration of samples under a filtered air stream, instead of the Kuderna-Danish concentration system).

AQUEOUS SEPARATION PROCEDURE

The total volume of each sample (one gallon) was extracted twice with 240 ml of 15 percent ethyl ether in hexane. Then 140 ml of sodium sulphate-saturated water was added to each sample, then extracted with 240 ml of hexane. Extracts were then dried with anhydrous sodium sulphate (prerinsed with hexane), combined and evaporated to approximately 40 ml. Extracts were then placed on a florisil column.

The column was pre-eluted with 75 ml of hexane. The pre-eluted extract was discarded and just prior to exposure of the sodium sulphate layer to air, the 40 ml of extract was placed on the column and eluted with 200 ml of six percent ethyl ether in hexane and then with 200 ml of 15 percent ethyl ether in hexane. The eluates are collected in 600 ml tall form beakers and evaporated at room temperature under a stream of carbon filtered dried air to 10 ml or less. The concentrates were then quantitatively transferred to a graduated 10 ml centrifuge tube/ ground glass stopper. The eluate fraction was further concentrated to approximately 0.2 ml.

GAS LIQUID CHROMATOGRAPHY

Reasonably positive indentification of a pesticide residue was indicated by analyzing samples on two different gas chromatographic columns. To economize time of analyses, two gas chromatograph units were employed, set up as follows:

1. Tracor Instruments, Inc., Model MT-220 Instrument Conditions: Column: (Semi-Polar); Glass - 6 feet by $\frac{1}{4}$ inch outside diameter; Support-Chromosorb W (HP); 80/100 mesh; Liquid Phase - 5 percent QF-1, 3 percent DC-200 LMBO Nos. 7141 and 7678 (2/24/71). Carrier Gas: Nitrogen, prepurified, Matheson; 55 ml per minute. Temperatures: Injection - 250° C; Column Oven - 200° C; EC Detector (Ni^{63}) - 360° C.

2. MicroTek, Inc., Model GS-200R Instrument Conditions:
   Column: (Non-Polar); Aluminum - 6 feet by $\frac{1}{4}$ inch outside diameter; Support - Gas Chrom Q (60-80 mesh); Liquid Phase - OV-17; Carrier Gas: Nitrogen, prepurified, Matheson, 80 ml per minute. Temperatures: Injection - 250° C; Column Oven - 165° C; EC Detector (Ni^{63}) - 350° C.

Approximately 1 - 3 μl of sample was injected into the inlet block or column of the gas chromatograph unit for analysis. Quantitation was accomplished by employing peak-area with base line correction procedure calculation. Two water samples were spiked with known quantities of the various pesticides and for DDT and analogs and dieldrin. The recovery efficiencies are tabulated.

Lake Michigan Water			12/14/70	(ng/l)				
	Analysis		Amount	Est	Analysis			%
Parameter	1	2	Added	Total	1	2	Av	Recovery
p, p'-DDE	3.7	--	5.4	9.1	7.3	7.1	7.2	79
o, p'-DDE	6.4	--	5.4	11.8	15.0	17.4	16.2	137
o, p'-DDD	2.8	--	5.4	8.2	5.2	5.8	5.5	67
p, p'-DDT	6.5	--	8.1	14.6	15.0	12.7	13.9	95
o, p'-DDT	3.0	--	8.1	11.1	8.5	5.9	7.2	65
total DDT	22.4	--	32.4	54.8	41.0	48.7	43.8	90
Dieldrin	5.6	--	5.4	11.0	10.3	5.8		74

APPENDIX I, TABLE 1

CHLORINATED PESTICIDE ANALYTICAL DATA FOR LAKE MICHIGAN

(results expressed in ng /l)

Sample Location: Chicago Central Filtration Plant Raw Water Intake

Analysis reported by Lake Michigan Basin Office USEPA

Parameter	4/1/69	4/29/70	5/4/70	5/12/70	5/18/70	5/26/70	6/1/70	6/8/70	6/15/70	6/25/70	6/29/70	7/6/70	7/13/70	7/21/70	7/22/70	8/3/70	8/10/70	8/17/70	11/3/70	12/14/70	1/11/71
Lindane	3	NF*	NF	1	5	3	3	4	NF	7	8	3	4	1	4	4	2	4	4	4	2
Heptachlor	NF	1	2	5	NF	NF	4	NF	4	4	4	5	4	2	4	3	2	2	NF	2	3
Aldrin	5	1	2	NF	NF	1	5	NF	8	NF	4	2	5	3	9	4	3	5	2	2	3
Heptachlor Epoxide	6	1	2	3	3	2	2	5	NF	NF	8	7	4	6	NF	6	5	6	7	7	7
Endrin	NF	4	5	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	1
Dieldrin	NF	3	NF	6	NF	4	NF	NF	3	NF	NF	35	43	20	4	17	17	18	3	6	4
Methoxychlor	NF	NF	17	14	14	16	NF	5	5	NF	NF	NF	8	6	NF	NF	6	NF	3	13	NF
DDE	NF	NF	3	NF	NF	NF	NF	NF	2	12	21	14	18	16	3	11	4	14	NF	10	10
DDD	NF	NF	3	4	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	12	NF	NF	NF	2	3	2
DDT	21	25	20	NF	NF	NF	NF	5	3	40	17	41	48	29	19	36	21	51	10	10	10
Total DDT	21	25	26	4	NF	NF	NF	5	5	52	38	55	66	45	34	47	25	65	12	23	22

*None Found

APPENDIX I, TABLE 2

DATA COMPARISON

LAKE MICHIGAN INTERSTATE PESTICIDE COMMITTEE ANALYTICAL QUALITY CONTROL INVESTIGATIONS

(results expressed in ng/l, ppt)

Date	7/22/70							11/3/70							
Laboratory	LMBO	WDNR	ISBH	BSFW[1]	BCF	WARF	MBWM	LMBO	WDNR	ISBH[2]	BSFW[3]	WARF	MBWM	OWRC	AQCL
Pesticide															
Lindane	4	< 1	< 1		< 1	NT	NT	4	< 1	< 1	< .5	NT	< 1	< 1	< 1
Heptachlor	4	< 1	< 1		< 1	NT	NT	< 1	< 1	< 1	NT	NT	< 1	< 1	< 1
Aldrin	9	< 1	< 1		< 1	NT	NT	2	< 1	< 1	NT	NT	< 1	< 1	< 1
Heptachlor Epoxide	< 1	< 1	NT		< 1	NT	NT	7	< 1	NT	NT	NT	NT	< 1	< 2
Methoxychlor	< 1	< 1	NT		NT	NT	NT	3	< 1	NT	< .5	NT	< 1	NT	< 10
Dieldrin	4	< 1	1		1	NT	2	3	< 1	< 1	1	NT	2	2	2
Endrin	< 1	< 1	< 1		< 1	NT	NT	< 1	< 1	< 1	NT	NT	< 1	< 1	< 5
DDE	4	3	< 1		< 1	4	3	NT	< 1	< 1		2		4	< 2
o,p-DDE								< 1			5				
p,p-DDE								< 1			2		4		
p,p'-DDD	8	< 1	< 1		< 1	3	NT	NT	< 1	< 1	1	2	NT	6	< 5
o,p-DDD	4	< 1	< 1		< 1	NT	NT	2	< 1	NT	NT	NT	NT	NT	
p,p'-DDT	13	6	6		3	6	10	7	< 1	14	1	2	13	8	< 5
o,p-DDT	6	< 1	< 1		< 1	NT	3	3	< 1	< 1	NT	NT	7	NT	

Date	12/14/70																		
Laboratory	LMBO	WDNR[4]	ISBH	BSFW[6]	WARF	MBWM	AQCL	OWRC	LMBO	WDNR	ISBH	BSFW[6]	WARF	MBWM	AQCL	OWRC	IEPA	No. results	Range
Pesticide																			
Lindane	4		< 1	20	NT	< 1	< 1	< 1	2	< 1	< 1	< .5		< 1	< 1	< 1	NT	24	< .5-20
Heptachlor	2		< 1	NT	NT	< 1	< 1	< 1	3	< 1	< 1	NT		< 1	< 1	< 1	NT	21	< 1.0-4
Aldrin	2		< 1	NT	NT	< 1	< 1	< 1	3	< 1	< 1	NT		< 1	< 1	< 1	NT	21	< 1.0-9
Heptachlor Epoxide	7		NT	NT	NT	NT	< 2	< 1	7	< 1	NT	NT		< 1	25	< 1	< 1	16	< 1.0-25
Methoxychlor	13		NT	10	NT	< 1	< 10	NT	< 1	< 1	NT	< .5		< 1	< 10	NT	NT	16	< .5-13
Dieldrin	6		< 1	2	NT	1	< 2	2	4	< 1	< 1	< .5		1	< 2	3	1	26	< .5-6
Endrin	< 1		< 1	NT	NT	< 1	< 5	< 1	1	NT	< 1	NT		< 1	< 5	< 1	NT	20	< 1.0 -< 5.0
DDE			< 1	< .5	2	6	< 2			3	< 1			14	40			20	< .5-40
o,p-DDE	6							NT	6			8				NT	NT	5	< 1.0-8
p,p-DDE	4							4	4				4			17	1	9	< 1.0-17
p,p'-DDD	NT		< 5	1	2	NT	< 5	7	< 1	< 1	< 1	5[7]	4	6	< 5	6	2	21	< 1.0-8
DDD																		4	< 5.0-< 5.0
o,p-DDD	3			NT	NT	NT		NT	2	NT	< 1	NT		< 1		NT	NT	10	< 1.0-4
p,p'-DDT	7		20[5]	2	11	13	< 5	8	9	2	16	< .5	7	34	< 20	10	9	27	< .5-34
DDT																		3	< 5 -20
o,p-DDT	3		< 1	NT	NT	7		NT	1	NT	< 1	NT		21		3	2	17	< 1.0-21

1/ No results - sample broken in transit. 2/ Used only one liter for analysis. 3/ Analyzed for PCB, di-2-ethyl hexyl phthalate and di-n-butyl phthalate only but no laboratory blank available; laboratory contamination with PCB's and phthalate esters indicated. 4/ No results per instrumental difficulties. 5/ Considerable interference observed. 6/ All samples corrected for laboratory blank for PCB's and phthalates. 7/ Identity of peak questionable.

LMBO=Lake Michigan Basin Office
WDNR=Wisconsin Dept. of Natural Resources
ISBH=Indiana State Board of Health
BSFW=Bur. of Sport Fisheries & Wildlife
WARF=Wisconsin Alumni Research Foundation
MBWM-Michigan Bureau of Water Management
AQCL=Analytical Quality Control Lab - EPA
OWRC=Ontario Water Resources Commission
IEPA=Illinois Environmental Protection Agency

APPENDIX I, TABLE 3

CHLORINATED PESTICIDE ANALYTICAL DATA FOR LAKE MICHIGAN

(results expressed in ng/l)

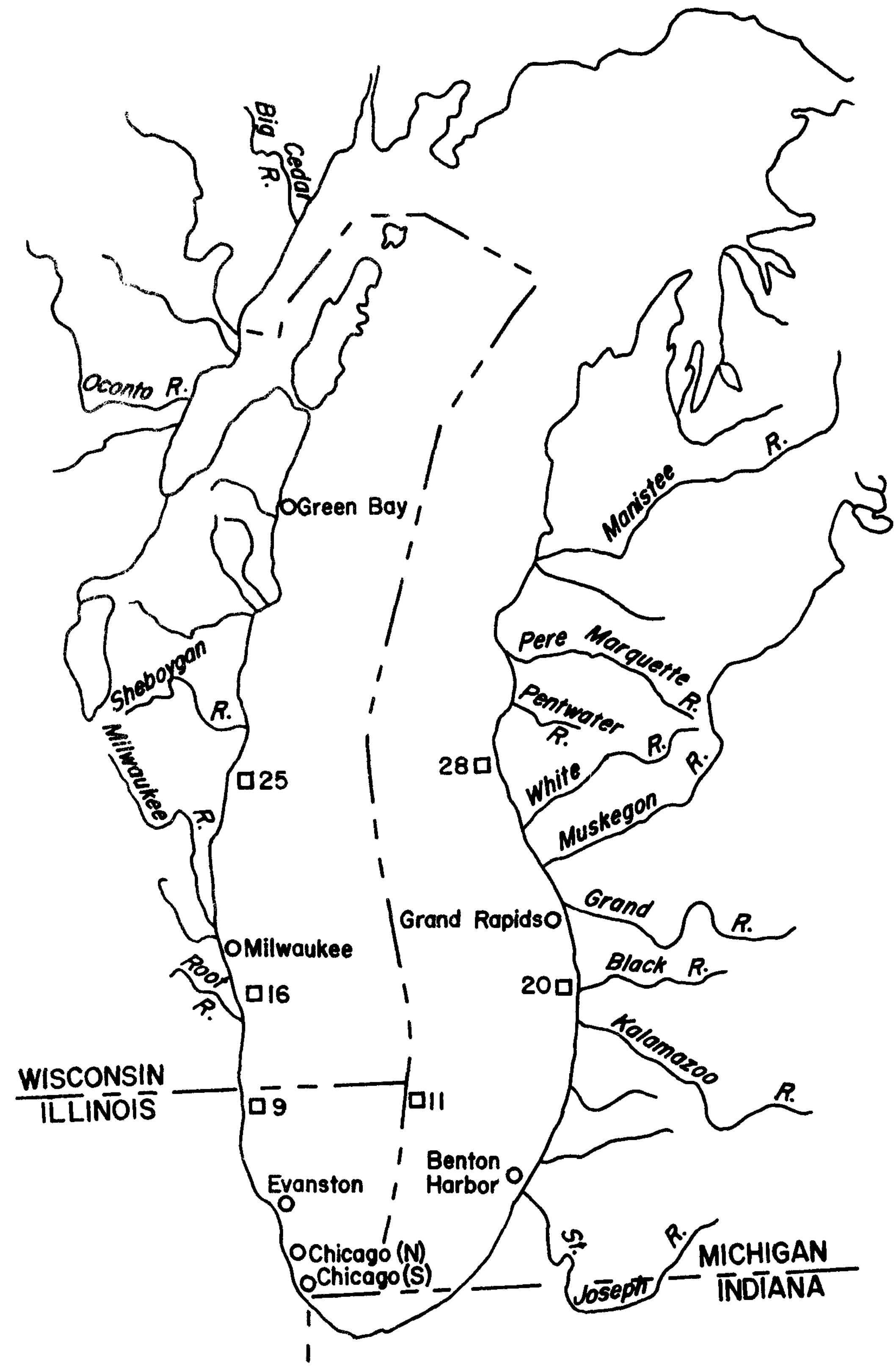
Analyses Reported by Lake Michigan Basin Office - US EPA

Station*	9				11		16				20				25				28			
	Surface 11/6/69	Bottom 11/6/69	Surface 11/6/70	Bottom 11/6/70	Surface 10/30/69	Surface 10/30/70	Surface 11/6/69	Bottom 11/6/69	Surface 11/6/70	Bottom 11/6/70	Surface 10/30/69	18 meter 10/30/69	Surface 10/30/70	18 meter 10/30/70	Surface 11/6/69	Bottom 11/6/69	Surface 11/6/70	Bottom 11/6/70	Surface 10/28/69	12 meter 10/28/69	Surface 10/30/70	Bottom 10/30/70
<u>Parameter</u>																						
Lindane	1.2	NF	NF	NF	1.5	1	.6	NF	NF	NF	NF	NF	NF	NF	NF	1.8	NF	2	1.5	1.9	NF	1
Heptachlor	2.2	.9	1	1	2.9	2	1.2	1.7	NF	1	.7	1.5	1	1	1	3.1	1	2	1	2.2	1	2
Aldrin	1.8	.5	3	1	1.1	1	.6	1.1	4	NF	1.9	.8	3	2	1.5	1	2	5	1	.9	4	NF
Heptachlor Epoxide	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Endrin	3.5	4.8	NF	NF	2.1	NF	1.7	3.6	NF	NF	5.3	4.5	NF	NF	3	4.2	NF	NF	2.6	3.1	NF	NF
Dieldrin	3.7	NF	NF	NF	3.1	NF	2.1	2.6	1	3	NF	NF	NF	NF	3	4.2	NF	5	3	3.6	NF	NF
Methoxychlor	NA	NA	NF	NF	NA	NF	NA	NA	NF	NF	NA	NA	NF	NF	NA	NA	NF	NF	NA	NA	NF	NF
DDE	5.1	2.9	3	2	5.4	2	3.6	6.5	NF	NF	4	5.4	3	3	5	1.9	NF	NF	5.6	7.6	NF	NF
DDT	9.7	11	6	7	14.1	7	10.6	18.5	5	4	8.1	11.6	8	7	14.2	7.5	4	4	14.8	16.0	3	7
DDD	4	2.7	NF	NF	3	NF	5.4	9.8	NF	NF	2	3.7	NF	NF	NF	1.4	NF	NF	NF	4.6	NF	NF
Total DDT	18.8	16.6	9	9	22.5	9	19.6	34.8	5	4	14.1	20.7	11	10	19.2	10.8	4	4	20.4	28.2	3	7

* refer to map, Appendix I, Figure 1

NF = none found

NA = not analyzed



APPENDIX I, FIGURE 1

LAKE MICHIGAN BASIN OFFICE OPEN LAKE SAMPLE STATIONS

APPENDIX I, TABLE 4

PESTICIDES IN LAKE WATERS (ppt)
DATA FROM THE WISCONSIN DEPARTMENT OF NATURAL RESOURCES

Location	Lab No.	Date	Limit of Detectability	DDT Complex	Dieldrin	Remarks
LAKE MICHIGAN - GREEN BAY						
Entrance Light	362	6/04/69	5	none	none	Ragged base line
	480	7/21/69	2	4.8		
	481	7/21/69	2	17.5	2.5	
	657	8/19/69	2	none	none	
	664	9/23/69	2	none	none	
Sturgeon Bay Area	363	6/05/69	2	none	none	GC peak where Aldrin would be identified
	484	7/22/69	2	none	none	GC peak where Hept. Epoxide would be identified
	658	8/19/69	70			Insufficient instrument injection
	665	9/23/69				GC peak where Lindane would be identified (See 663 for curve comments)
In Sturgeon Bay	659	8/19/69	10	none	none	Interference
Washington Island Area	364	6/05/69	2	none	none	GC peak where Aldrin would be identified No Strip Chart.
Washington Island Area	479	7/22/69				Interference
Ellison Bay Area	660	8/21/69				Interference
LAKE MICHIGAN						
0.5 mi. off Sturgeon Bay	360	6/05/69	2	22		Base line interference
0.5 mi. off Sturgeon Bay	485	7/22/69	2	5.5		
0.5 mi. off Sturgeon Bay	656	8/19/69	10	none	none	Interference
0.5 mi. off Sturgeon Bay	663	9/23/69	2	none	none	Drifting base line. Peak of Heptachlor
*5.0 mi. off Sturgeon Bay	359	6/05/69		1,510	none	
5.0 mi. off Sturgeon Bay	486	7/22/69	2	21.1	none	13.6 ppt DDT & 75 ppt DDE
5.0 mi. off Sturgeon Bay	655	8/19/69	2	none	none	
5 mi. SE Kewaunee	776	6/11/70	2	11	none	Profile
5 mi. SE Kewaunee	780	6/11/70	2	none	none	Peak where Aldrin would be identified
*2 mi. off Two Creeks	162	11/12/68	2	20.5	3	
7 mi. off Two Rivers	782	6/11/70	2	none	none	
10 mi. off Two Rivers	896	8/05/70	2	2	none	325 feet deep
0.5 mi. off Manitowoc	361	6/06/69	5	none	none	
0.5 mi. off Manitowoc	483	7/23/69	2	none	none	Peak where Heptachlor Epoxide would be identified
0.6 mi. off Manitowoc	661	8/22/69	2	none	none	
NE Sheboygan	781	6/11/70	2	6	none	6 ppt as DDE:trace DDT (pp)
0.5 mi. off Milwaukee	330	6/18/69	2	none	none	Peaks at Lindane & Heptachlor Epoxide
0.5 mi. off Milwaukee	478	7/25/69				Interference
25 mi. off Milwaukee	779	6/11/70	1	3	none	Profile sample:3 ppt as DDE
25 mi. off Milwaukee	777	6/11/70	1	3	none	Profile sample:3 ppt as DDE
0.5 mi. off Kenosha	371	6/18/69	2	none	none	Peaks at Lindane & Heptachlor Epoxide
0.5 mi. off Kenosha	477	7/25/69	2	5.2	none	
0.5 mi. off Kenosha	662	9/22/69	2	none	none	
5.0 mi. off Kenosha	372	6/18/69	1	none	none	Peak at Heptachlor Epoxide
5.0 mi. off Kenosha	472	7/25/69	1	3	none	

APPENDIX I, PROCEDURE 2

ANALYTICAL TECHNIQUES USED IN LAKE AND RIVER WATER ANALYSIS BY THE WISCONSIN DEPARTMENT OF RESOURCES - LABORATORY OF HYGIENE

Water samples were collected in hexane mixed glass bottles with caps protected by aluminum foil. They were transported to the Madison laboratory where extraction and analyses were conducted. The time between collection and analysis varied between one day and two weeks. The general procedures included hexane extraction, florisil column clean up and gas chromatographic identification and quantitation. Some samples were confirmed with thin layer chromatography and some were confirmed by mass spectrophotometer analysis at the Athens laboratory of the United States Environmental Protection Agency.

Water samples of 2,000 ml were extracted three times in teflon stopcock separatory funnels, first with 100 ml of hexane twice with 50 ml hexane. If an emulsion appeared it was broken by hot and cold water treatment, the addition of propanol or addition of sodium chloride. The three hexane extracts were combined and dried with sodium sulphate, then concentrated to 10 ml with a dry air stream on a 38° C water bath. The 10 ml hexane extract with pesticide residue was florisiled at this point to separate fats, pigments and other contaminants.

The extraction procedure efficiently partitions fats and oils from the sample into the hexane carrier solvent. The fats and oils contain most of the insecticides present in the organisms due to their solubility in the fats and oils and their insolubility in water. Along with the lipid soluble pesticides, the extraction process also extracts other organic compounds that could have a high electron affinity and thus cause erroneous electron capture detector responses. To remove the interfering substances from the hexane extract, absorption chromatography is used. The absorption material is a commercial diatomaceous earth purchased as florisil. The florisil is activated by heating to 100° C for 24 hours, followed by deactivation to a specific level by adding one to three percent water. This enables efficient separation of the insecticides on the florisil column. The column holder is a pyrex glass tube with a 22 mm inside diameter and of adequate length to contain 300 ml of hexane solvent. It has fritted glass and teflon stopcock at the bottom to permit a regulated flow through the system. One-half inch of sodium sulphate is added to the column and 40 grams of deactivated florisil which is covered with another one-half inch of sodium sulphate.

The florisil column is prewashed with 50 ml of hexane. The concentrated hexane extract of the sample is then added to the column. The sample container is washed with 200 ml of six percent ethyl ether and 94 percent hexane solvent mixture. This mixture is added to the florisil column and eluted through the column at a rate not to exceed five ml per minute. When the column is almost empty, 200 ml or 20 percent ethyl ether and 80 percent hexane is added to the florisil column. Each one of the elutions (94/6, 80/20) is collected and analyzed separately.

The two elutions and properly deactivated florisil will remove most interferences and separate some of the insecticides. The first elution (six percent ethyl ether) will contain:

Lindane	DDT
BHC	Perthane
Kelthane	Methoxychlor
Aldrin	Toxaphene
Heptachlor	Strobane
Heptachlor Epoxide	Chlordane
DDE	DDD (TDE)

The second elution (20 percent ethyl ether) will contain:

Dieldrin	Endrin
Lindane (Trace)	Kelthane (Trace)

The two elutions are concentrated with a dry air stream to 10 ml or less, depending on the suspected insecticide concentration in the sample. These concentrated samples are at this time ready for injection into the gas chromatograph.

The gas chromatograph used for the analyses was a Hewlett Packard, dual channel (Model 402). Both channels were equipped with Ni_{63} electron capture detectors. The instrument columns were two to six feet V-tubes of pyrex glass. These columns were packed with three percent OV-17 (Phenyl methylsilicone, 50 percent phenyl), ten percent silicone DC-200 (12,500 cstk), and ten percent silicone DC QF-1 on a solid support of gas chrom Q (60-80 mesh) either singly or in varying concentrations of each.

The analysis of environmental samples is a problem because the extraction process removes substances from the sample which the florisil cleanup misses and these substances are detected by electron capture systems and cause interferences.

One of the most common interferences with the analysis of the DDT complex is the polychlorinated biphenyl (PCB). Because of the structural similarity between PCB's and some pesticides, the electron capture detector will give the same response for both. The PCB's have 210 isomeric formations that are detectable and the DDT complex has only six formations that could be detected with electron capture detector.

APPENDIX I, TABLE 5

WATER TREATMENT PLANTS[1] (ppt)

Municipality	Lab No.	Date Collected	Limit of Detect.	DDT Complex	Dieldrin	Remarks
BROWN COUNTY						
Green Bay	785	6/11/70	10	110	none	Raw
Green Bay	786	6/11/70	2	15	none	Settled
Green Bay	877	7/22/70	2	30	none[2]	Final
Green Bay	887	8/14/70	1	none	none	Settled
Green Bay	888	8/14/70	1	none	none	Final
KENOSHA COUNTY						
Kenosha	806	6/23/70	1	none	none	Raw
Kenosha	807	6/23/70	1	25	none	Settled
Kenosha	808	6/23/70	1	3	none	In plant
MILWAUKEE COUNTY						
Milwaukee[3]	759	6/05/70	2	20	none	Raw
Milwaukee	760	6/05/70	2	20	PCB's none	In plant, PCB's
Milwaukee	761	6/05/70	1	none	PCB's none[4]	Final
Milwaukee	762	6/05/70	1	221	none	Floc
Milwaukee	849	7/10/70	1	none	PCB's none	Final
Milwaukee	850	7/10/70	1	none	none	Final
Milwaukee[5]	765	6/05/70	1	none	none	Final
Milwaukee	763	6/05/70	2	28	none	Raw
Milwaukee	853	7/10/70	1	none	none	Filtered
Milwaukee	854	7/10/70	1	none	none	Final
RACINE COUNTY						
Racine	802	6/23/70		9	none	In plant
Racine	803	6/23/70		8	none	Finished
Racine	804	6/23/70		11		Raw
SHEBOYGAN COUNTY						
Sheboygan	846	7/10/70	1	none	none	Final

[1]Data from the Wisconsin Department of Natural Resources
[2]Peak at Heptachlor Epoxide
[3]Howard Street
[4]Fading base line with numerous peaks
[5]Linnwood Water Treatment Plant

APPENDIX I, TABLE 6

PESTICIDES IN LAKE MICHIGAN MUNICIPAL WATER INTAKES*, 1970
(Concentrations in ppt)

Location	Date Sampled	DDE	TDE	o,p-DDT	p,p'DDT	Total DDT	Dieldrin
Bridgeman	11/24/70	<1	<1	<1	<1	<1	ND**
Benton Harbor	12/10/70	<1	2	<1	3	<5	1
St. Joseph	12/10/70	4	26	14	24	67	<1
South Haven	12/10/70	<1	<1	6	20	26	1
Holland	12/10/70	<1	<1	<1	<1	<1	ND
Wyoming	12/10/70	<1	<1	<1	<1	<1	ND
Grand Rapids	12/10/70	<1	<1	<1	<1	<1	ND
Grand Haven	12/10/70	<1	<1	<1	3	3	ND
St. Joseph	2/16/71	<1	ND	<1	5	5	1
Benton Harbor	2/16/71	<1	<1	<1	<1	<1	1
South Haven	3/09/71	2	3	6	21	32	1
Holland	4/14/71	<1	2	<1	1	3	1
Grand Rapids	4/14/71	<1	<1	<1	<1	<1	<1
Muskegon	3/09/71	<1	<1	4	8	13	1
Ludington	3/09/71	2	5	19	68	93	5
Traverse City	3/02/71	4	5	21	19	49	ND
Escanaba	2/25/71	10	13	33	52	119	2
Gladstone	2/25/71	<1	<1	10	12	23	2
Menominee	3/23/71	<1	<1	4	16	21	<1
Bridgeman	4/14/71	<1	<1	<1	<1	<1	ND

* Data from the Michigan Water Resources Commission
**None detected

APPENDIX I, TABLE 7

PESTICIDES IN LAKE MICHIGAN WATER INTAKES*
(Concentrations in ppt)

Sample Site**	pp'DDT	pp'TDE	opDDT	pp'DDE	Total DDT	Dieldrin
Waukegan	0.47	0.06	0.32	0.07	0.92	0.13
North Chicago	0.26	0.12	0.10	0.03	0.51	0.07
Highland Park	0.18	0.08	0.13	0.04	0.43	0.09
Evanston	0.32	0.03	0.17	0.04	0.56	0.10
Chicago Central	0.15	0.03	0.02	0.09	0.29	0.09
Chicago South	0.16	0.04	0.07	0.01	0.28	0.10

* Data provided by the Illinois Environmental Protection Agency
** Date of collection not recorded

APPENDIX I, PROCEDURE 3

WATER ANALYSIS PROCEDURE
WISCONSIN ALUMNI RESEARCH FOUNDATION

OFFSHORE WATER SAMPLES

The sample was mixed well before sub-sampling. Four 2,000 ml portions were measured and placed in four clean nanograde solvent bottles. Two hundred milliliters of hexane were added to each bottle. The bottles were placed in a case and put on a shaker for five minutes. The bottles were removed from the case and shaken by hand for three minutes. The bottles were allowed to stand for four hours and the above method of shaking was repeated. The samples were then transferred to 2,000 ml separatory funnels and the layers allowed to separate. After separation, the lower layer was drained back into the extractor bottles. The hexane layers were combined and dried with sodium sulphate. The hexane was transferred to a two liter flask. The hexane was concentrated to two to three ml on a steam bath and then transferred to a florisil column and eluted the same as the inshore water samples. The elutions were evaporated and made to two ml and injected into a gas chromatograph.

APPENDIX I, TABLE 8

LAKE MICHIGAN OPEN WATER PESTICIDES*
July 1969
(Results expressed in ng/l)

Sample No.	Location (½ mile off shore)	Total DDT	Dieldrin	BHC	Estimated PCb
3	Little Suamico River	<1	1.1	111	2.5
4	Pensaukee River	2.6	2.6	140	6.5
5	Oconto River	12.7	1.3	50.3	
6	Peshtigo River	<1	<1	33.0	2.8
7	Menominee River	1.1	1.5	16.5	2.5
9	Clark Lake Creek	3.5	1.5	13.7	9.0
11	Kangaroo Lake Creek	<1	1.7	8.0	Off Scale
14	Ahnapee River	15.3	1.0	23.3	50.8
15	Kewaunee River	<1	1.1	8.5	
16	East Twin River	8.8	2.2	20.0	19.5
21	Pine Creek	31.2	2.6	7.5	Off Scale
26	Pigeon River	<1	<1	11.2	2.5
30	Kinnickinnic River	5.5	2.2	8.0	9.5
31	Menominee River	12.0	1.1	20.2	15.0
32	Oak Creek	10.8	3.3	22.8	27.2
33	Root Creek	5.9	4.5	110.0	5.5
34	Pike River	2.1	3.1	27.8	
35	Barnes Creek	5.0	1.9	9.0	
36	Calumet River at Calumet City	4.1	2.1	7.8	55.9
37	Burns Ditch	4.7	2.3	8.3	9.3
38	Trail Creek	3.5	2.1	1.5	6.5
39	Galien River	10.1	3.4	4.5	15.0
40	Drain at Sawyer	1.5	1.9	7.4	
42	PawPaw River	11.1	3.0	34.3	28.3
43	Black River	1.2	1.8	1.8	2.5
48	Muskegon River at mouth into Muskegon Lake	1.4	1.6	12.3	2.5
49	White River	1.4	1.5	18.1	2.0
50	Pentwater River	5.0	2.7	5.8	12.5
52	Manistee River	<1	<1	5.9	2.5
53	Betsie River	1.3	1.2	6.2	
54	Platte River	2.5	1.4	9.9	5.0
60	Bear River, Petoskey	1.5	1.3	2.1	
62	Manistique River	11.1	1.6	6.5	
65	Escanaba River	<1	<1	16.1	2.0

* Data from the Wisconsin Alumni Research Foundation

APPENDIX II

CHLORINATED HYDROCARBON INSECTICIDES IN LAKE MICHIGAN TRIBUTARY WATERS

APPENDIX II, TABLE 1

TRIBUTARY MONITORING STATION FOR INSECTICIDES
LAKE MICHIGAN DRAINAGE BASIN

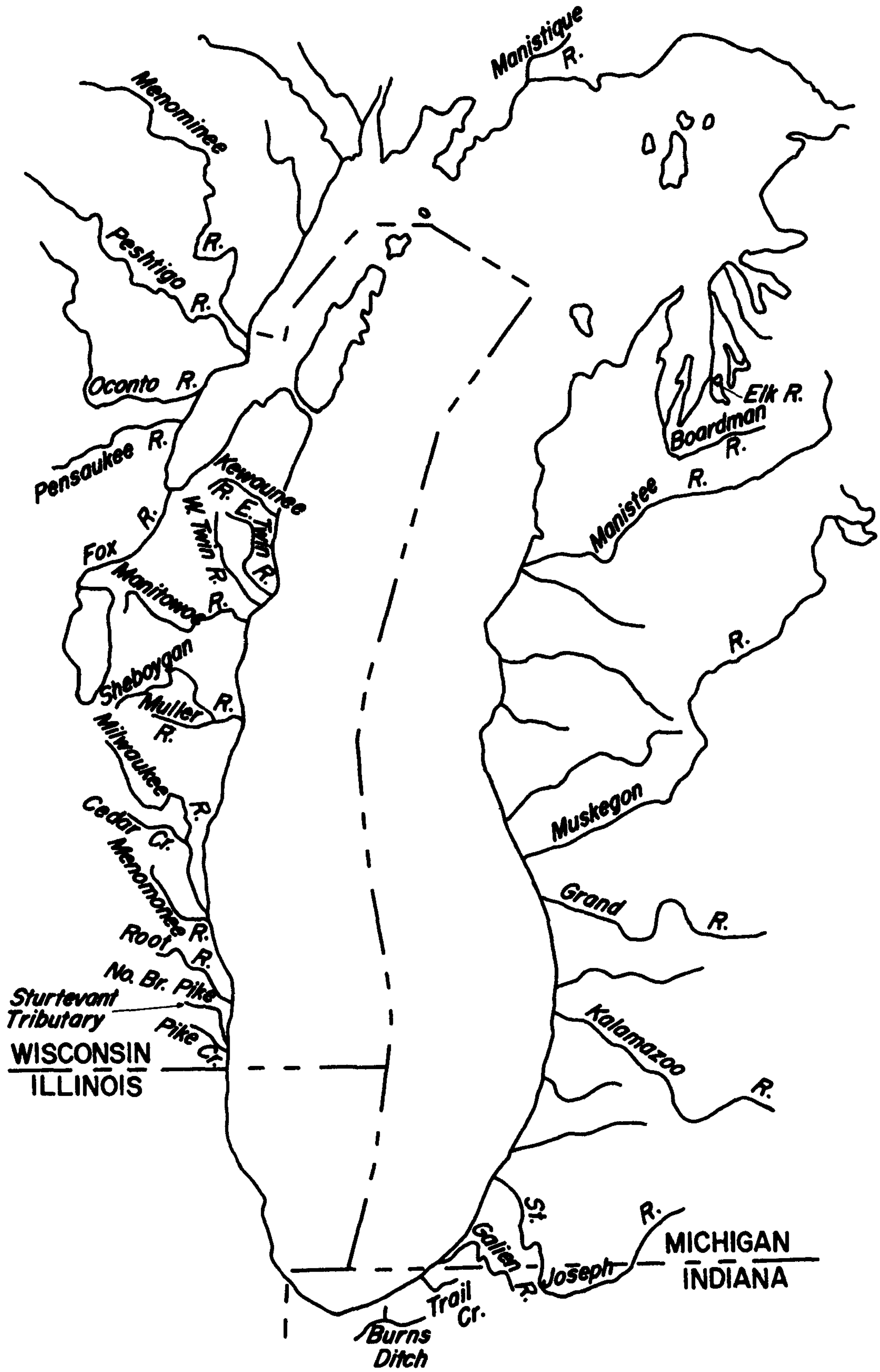
River	Sample Site	Annual Flow[a] CFS	High Flow[a] CFS	Low Flow[a] CFS	Watershed (sq mi)	Percent of Basin (gauged)
Fox*	Green Bay, WI	4154	12,893	1207	6150	
Grand-Calumet**	East Chicago, IN	864			37	
Grand	Grand Haven, MI	4000	23,820	924	5570	88
Kalamazoo	Saugatuck, MI	1722	5,812	512	2060	78
Manistee	Manistee, MI	2312	5.937	1322	2130	93
Menominee	Marinette, WI	3382	15,150	994	4070	93
Milwaukee***	Milwaukee, WI	385	4,640	28	686	
Milwaukee	Above urban area		Not available			
Muskegon	Muskegon, MI	2176	7,750	698	2660	88
St. Joseph	St. Joseph, MI	2312	5.937	1322	2130	93

* Data from Wrightstown, Wisconsin

** Data from Gary, Indiana. Stage-flow relationship plus industrial and municipal discharges.

*** Data from six miles above mouth.

a Established mean flows



APPENDIX II, FIGURE 1

LAKE MICHIGAN BASIN MAJOR RIVER PESTICIDE SAMPLING STATIONS

APPENDIX II, TABLE 2

PESTICIDE CONCENTRATIONS IN WISCONSIN RIVER WATERS
DATA FROM THE WISCONSIN DEPARTMENT OF NATURAL RESOURCES

River Waters (ng/l)

County and Source	Lab No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Remarks
BROWN COUNTY						
Fox River 314 RM*	666	8/27/69	10	38	20	Grab
Fox River 314 RM	667	8/28/69	10	183	none	Grab
Fox River 314 RM	668	8/29/69	10	none	none	Grab
Fox River 314 RM	669	8/29/69	10	10	none	Grab
Fox River 0.1 RM	670	8/27/69	5	16	none	55 hr composite
Fox River 0.1 RM	735	5/07/70	50	none	none	Interference - possible PCBs
Fox River 0.1 RM	839	6/13/70	10	none	none	Interference - composite
Fox River 0.1 RM	912	9/01/70	10	none	none	Composite
Fox River 0.1 RM	883	8/21/70				No analysis
Fox River 0.1 RM	891	8/28/70	2	none	none	Grab
Fox River 0.1 RM	864	7/14/70	2	none	none	Composite
KENOSHA COUNTY						
Pike River County Highway A	253W	4/11/69	2	none	23	Grab
KEWAUNEE COUNTY						
Kewaunee River DodgeSt.	889	8/18/70	1	none	none	Composite
MANITOWOC COUNTY						
East Twin River 22nd St.	884	8/10/70	1	none	none	Composite
Manitowoc River 8th St.	160	11/12/68	10	none	none	
Manitowoc River 8th St.	841	7/02/70	10	none	none	Fading base line
West Twin River	885		1	none	none	Composite

* River miles above mouth

APPENDIX II, TABLE 2
continued

River Waters (ng/l)

County and Source	Lab No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Remarks
MARINETTE COUNTY						
Menominee 0.2 RM*	754	5/13/70	2	none	none	Composite
Menominee 0.2 RM	861	6/26/70	10	none	none	Composite - fading base line
Menominee 0.2 RM	913	9/10/70	2	none	none	Composite
Menominee 0.2 RM	890	8/28/70	2	none	none	Composite
Peshtigo River - in Peshtigo	869	7/24/70	2	none	none	Composite
MILWAUKEE COUNTY						
Milwaukee River**	732	4/23/70		460	650	Composite
Milwaukee River**	755	5/20/70	5	65	none	Composite
Milwaukee River**	787	6/17/70	10	85	none	Composite
Milwaukee River**	842	7/09/70	5	none	35	Composite
Milwaukee River**	915	9/04/70	15	none	none	Composite interference
OCONTO COUNTY						
Oconto River - Oconto	865	7/17/70	2	none		Composite
Pensaukee River - Pensaukee	892	8/24/70	2	none		Composite
OZAUKEE COUNTY						
Milwaukee River***	758	6/05/70	2	16	none	Composite (as DDE)
Milwaukee River***	843	7/10/70	5	none	7	Composite - interference late on the base line
Milwaukee River***	914	9/04/70	2	none	none	Composite
Milwaukee River***	753	5/20/70	2	none	none	Composite
Milwaukee River***	933	9/29/70	2	none	none	Composite

* River miles above mouth
** Wells Street
*** Above Grafton

APPENDIX II, TABLE 2
continued

River Waters (ng/l)

County and Source	Lab No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Remarks
RACINE COUNTY						
No. Br Pike River - Highway 20	254W	4/11/69	5	29	54	Grab
No. Br Pike River - Highway 20	252W	4/11/69	15	60	none	Grab
No. Br Pike River - Highway 11	792	6/23/70	10	none	68	Grab
No. Br Pike River - Highway 11	793	6/23/70	10	30	31	Grab
No. Br Pike River - Co. Highway R	798	6/23/70				Grab
Sturtevant Tributary	257	4/11/69	10	none	93	Grab - Aldrin peak?
Sturtevant Tributary	258	4/11/69	10		83	Grab - Heptachlor epoxide peak?
SHEBOYGAN COUNTY						
Mullet River Co. AC	244W	4/10/69	2	none	none	Grab
Mullet River Co. PP	245W	4/10/69	20	none	none	Interference
Sheboygan River - Sheboygan	246W	4/10/69	5	none	none	
Sheboygan River - STH 28	247	4/10/69	5	none	none	
Sheboygan River - STH 28	249	4/10/69	5	none	none	
Sheboygan River - 1 mi below Sheboygan Falls	250	4/10/69	5	none	none	
Sheboygan River - below Sheboygan Point	789	6/22/70	5	40	150	PCBs
Sheboygan River - Meadowlake Road	788	6/22/70	1	none	none	
Sheboygan River - Kiel	790	6/22/70	2	3	none	
Sheboygan River - Sheboygan	840	6/22/70	2	none	none	Composite

APPENDIX II, TABLE 2
continued

River Waters (ng/1)

County and Source	Lab No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Remarks
WASHINGTON COUNTY						
Milwaukee River - Hwy 33 West Bend	795	6/24/70	1	none	none	
Milwaukee River - West Bend	801	6/24/70	2	6	none	
Cedar Creek - Cedarburg	796	6/24/70	5	52	none	

APPENDIX II, TABLE 3

PESTICIDES IN RIVER WATER SAMPLES***
Michigan Drainage, 1970
(Concentrations in ppt)

River and Location**	Date	p,p-DDE	p,p-DDD	o,p-DDT	p,p-DDT	Total DDT	Dieldrin	Est PCB
Galien	10/23/70*	12	5	35	44	96	< 1	
New Buffalo	6/24/71*	2	< 1	4	10	17	< 1	< 10
St. Joseph	10/23/70	14	7	34	58	113	2	
U. S. 31 Bridge	3/25/71	< 1	2	< 1	9	11	< 1	< 10
St. Joseph	6/24/71	< 1	2	< 1	3	5	3	< 10
Kalamazoo	10/23/70	10	6	28	40	84	1	
Bureau of Sport Fisheries Dock	3/25/71	< 1	2	< 1	9	11	ND	11
Saugatuck	6/24/71	< 1	2	< 1	< 1	2	< 1	28
Grand	10/23/70	12	7	35	65	119	< 1	
Coast Guard Station	3/25/71	< 1	6	< 1	16	22	< 1	47
Grand Haven	6/24/71	< 1	< 1	< 1	10	12	1	< 10
Muskegon	10/23/70	18	7	55	72	152	< 1	172
Coast Guard Station	3/25/71	< 1	2	< 1	10	12	< 1	10
Muskegon	6/24/71	< 1	< 1	< 1	< 1	< 1	< 1	< 10
Manistee	10/23/70	21	9	72	83	184	ND	210
Maple Street	3/25/71	< 1	< 1	< 1	6	7	ND	< 10
Manistee	6/24/71	< 1	< 1	< 1	10	11	< 1	< 10
Boardman	11/05/70	6	16	25	112	159	2	
U. S. 31	4/09/71	< 1	< 1	< 1	< 1	< 1	ND	< 10
Traverse City	7/08/71	5	3	24	34	65	2	26
Elk	11/05/70	10	6	29	47	92	2	
Dam	4/09/71	< 1	2	< 1	3	5	ND	< 10
Elk Rapids	7/08/71	< 1	2	2	11	14	1	< 10

* Grab Sample
** Refer to Appendix II, Figure 1
*** Data from Michigan Water Resources Commission

APPENDIX II, TABLE 3
continued
(Concentrations in ppt)

River and Location**	Date	p,p-DDE	p,p-DDD	o,p-DDT	p,p-DDT	Total DDT	Dieldrin	Est. PCB
Manistique								
U. S. 2	11/11/70	< 1	< 1	< 1	11	11	ND	
Manistique	5/05/71	< 1	3	< 1	5	8	ND	< 10
	7/13/71*	< 1	< 1	< 1	2	2	< 1	< 10
Menominee	11/11/70	< 1	< 1	< 1	4	4	< 1	
North Channel Wall	5/05/71	< 1	1	2	16	19	ND	< 10
Menominee	7/13/71*	< 1	1	< 1	2	4	< 1	< 10

* Grab sample

APPENDIX II, PROCEDURE 1

MICHIGAN WATER RESOURCES COMMISSION
FIELD AND ANALYTICAL PROCEDURES

To obtain representative water samples from the major tributaries, the Pesticides Committee of the Lake Michigan Conference recommended that a continuous flow apparatus be used over a three day period. This technique should moderate possible fluctuations in pesticide concentrations over time. Michigan designed a completely submersible sampler consisting of a five gallon carboy, two pieces of heavy-walled glass tubing fitted through a rubber stopper, a 30-gauge hypodermic needle and a perforated metal case (see attached diagram).

When the sampler is submerged to operating depth (18 inches below the surface), a small amount of water enters the bottle through the water-intake tube until water pressure outside the bottle equals air pressure within the bottle. Air then gradually escapes through the air-outlet needle at a rate fixed by the size of the needle opening. As air escapes, water slowly fills the carboy at a proportional rate over the sampling period until the water level reaches the bottom of the air-outlet tube. Sampling is then complete. Time required to fill a five gallon carboy when a 30-gauge needle is used is approximately 30 hours. This time period could be extended by using a smaller diameter needle or orifice.

Some of the advantages of this sampler are: 1. It is entirely submersible, thus reducing chances of vandalism; 2. It is entirely independent of a power source, thus allowing increased versatility and reduced chances of failure; 3. It fills at a uniform rate throughout the sampling period; and 4. It is simple in construction and quite inexpensive.

Immediately after removal from the stream, the composite sample is mixed well and a one gallon aliquot for insecticide analysis poured into a clean glass bottle containing 100 milliliters of hexane. All gallon bottles had either teflon or aluminum-lined caps to avoid contamination. A 250 milliliter aliquot is removed for turbidity and suspended solids determination. The remainder of the sample is discarded.

In streams where time did not permit a composite sample to be taken or where it was impossible to use the continuous sampler, grab samples were obtained by submerging a one gallon glass bottle to a depth approximately 18 inches below the surface and allowing it to fill. Prior to sampling 100 milliliters of n-hexane was added to the bottle. Extreme care was taken to avoid any loss of the hexane during sampling.

Samples of raw water at municipal water intakes were obtained by filling a clean one gallon glass bottle (containing 100 milliliters of n-hexane) from the raw water tap within the treatment facilities.

Mussels used as biological monitors of pesticides were held captive in tributaries in chrome-plated barbecue baskets. The mussels were placed in the streams at least one month prior to the anticipated sampling date to allow ample time for them to reach equilibrium with pesticide concentrations in the water. Studies have demonstrated that at normal temperatures, equilibrium occurs within one to three weeks. A sample consisted of three mussels which were placed in Whirlpak bags for transportation to the laboratory. The source of mussels for this study was the shallow sandy shoal areas of Gun Lake, Barry County, Michigan.

LABORATORY PREPARATION AND ANALYSIS

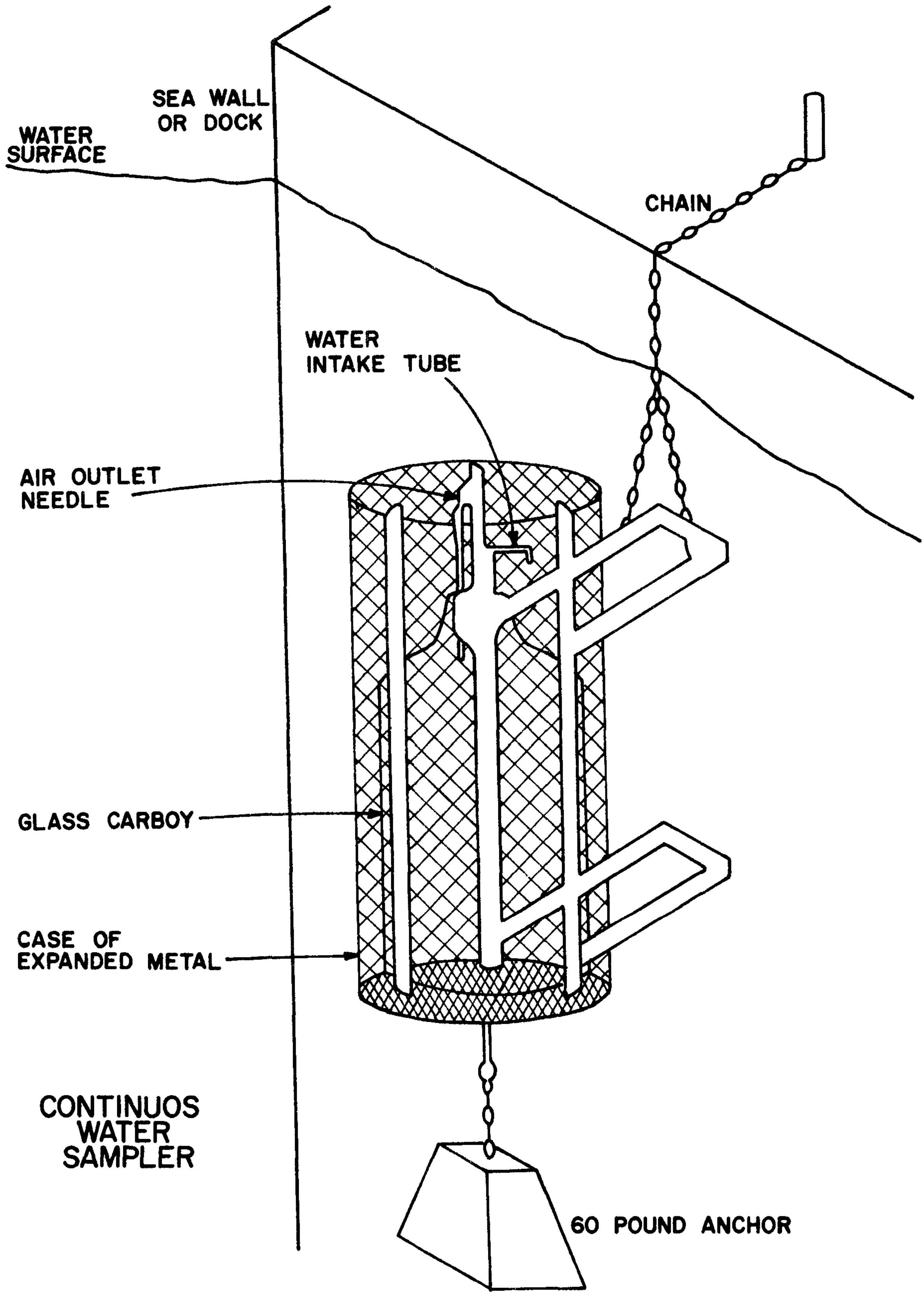
The water samples were extracted according to the FWQA method (U. S. D. I., 1969). The extracts were concentrated over stream to approximately five milliliters and further concentrated to one milliliter in a tube heater (Kontes Model #K-72000).

Pyrex columns, 1.1 by 29 cm, fitted with a fritted glass disk, were packed with one gram of florisil: Celite (5:1) with a layer of anhydrous sodium sulphate above and below the packing. The florisil was used as received from Floridin, Inc., and was calibrated before use to ensure conformation to the elution procedure used. A 0.5 ml portion of the extract was first eluted with 30 ml of n-hexane and the eluate collected and reconstituted to 0.5 ml. The sample was then eluted with 20 ml of 15 percent ethyl ether in hexane and this eluate also reconstituted to 0.5 ml. The first eluate (n-hexane) would contain lindane, aldrin, heptachlor, heptachlor epoxide, DDE, DDD, DDT and chlordane; if present, while the second (15 percent ethyl ether) would contain dieldrin, endrin and methoxychlor.

An Aerograph 1740 gas chromatograph, equipped with two tritium foil detectors, was used for the analyses. It was fritted with a five foot by 1/8 inch aluminum column packed with S. E. 30 on Varaport 30 (100/120 mesh) and a five foot by 1/8 inch Pyrex column with four percent S. E. 30 and six percent QF-1 on Chrom. W A/W DMCS (80/100 mesh). The chromatograph was operated at a column temperature of 200° C and a 20 ml per minute nitrogen flow. The injection temperature was 275° C and the detector temperature 220° C. Standards were injected at the beginning of each run, after every five samples, and at the end of the run. Quantitations were based on peak heights.

Two mussels from each sample of three were individually prepared for analysis. Each mussel was removed from its shell, drained and weighed to the nearest mg and then blended with 50 ml of hexane-acetone (2:1) in a Sorvall Omni-Mixer for three minutes at 10,000 rpm. The solvent mixture was decanted and the sample blended twice more with 50 ml aliquots of additional solvent. The extract was dried over anhydrous sodium sulphate and a 10 ml aliquot removed for determination of percent fat by evaporation of the solvent in a vacuum at 60° C or over. The remaining extract was concentrated to 5 ml over a steam bath. The extracts were cleaned up in a manner similar to the water samples. In this case, 2 grams of florisil: Celite (5:1) were used as column packing and a two ml aliquot of the extract placed on the column. The samples were eluted with n-hexane (40 ml) and 15 percent ethyl ether in n-hexane (20 ml) and the eluates concentrated to 0.5 ml for gas chromatographic analysis.

The identities of the pesticides were confirmed on two different gas chromatographic columns, but further confirmation (e.g. thin-layer chromatography) has not been completed.



APPENDIX II, FIGURE 2

APPENDIX II, TABLE 4

PESTICIDES IN RIVER WATER SAMPLES**
Indiana Drainage, 1970
(Concentrations in ppt)

River	Location	Date	DDE	Dieldrin	DDD	DDT
Burns Ditch	Portage	6/11/70	*	*	*	*
Burns Ditch	Portage	7/03/70	*	*	*	*
Burns Ditch	Portage	8/04/70	*	*	*	47
Burns Ditch	Portage	9/01/70	*	*	*	*
Burns Ditch	Portage	10/06/70	*	*	*	*
Burns Ditch	Portage	11/03/70	*	*	*	13
Trail Creek	Michigan City	6/11/70	*	*	*	*
Trail Creek	Michigan City	7/03/70	*	*	*	*
Trail Creek	Michigan City	8/04/70	*	*	*	21
Trail Creek	Michigan City	9/01/70	*	*	*	*
Trail Creek	Michigan City	10/06/70	*	*	*	*
Trail Creek	Michigan City	11/03/70	*	*	*	15
St. Joseph	South Bend	6/10/70	*	*	*	15
St. Joseph	South Bend	7/02/70	*	*	*	*
St. Joseph	South Bend	8/05/70	*	*	*	28
St. Joseph	South Bend	9/02/70	*	*	*	*
St. Joseph	South Bend	10/07/70	*	*	*	*
St. Joseph	South Bend	11/04/70	*	*	*	*
St. Joseph	Bristol	6/09/70	*	*	*	22
St. Joseph	Bristol	7/02/70	*	*	*	*
St. Joseph	Bristol	8/05/70	*	*	*	16
St. Joseph	Bristol	9/02/70	*	*	*	*
St. Joseph	Bristol	10/08/70	*	*	*	*
St. Joseph	Bristol	11/04/70	*	*	*	11
Indiana Harbor		6/30/70	*	*	*	*
Indiana Harbor		8/11/70	*	*	*	23

* < 10.0 ppt
** Data from Indiana State Board of Health

NOTE: Lindane, heptachlor, aldrin and endrin were not detected in any sample.

APPENDIX II, TABLE 5

PESTICIDES IN RIVER WATER SAMPLES**
Illinois Drainage, 1970
(Concentrations in ppt)

River*	Location	Date	pp'-DDT	pp'-TDE	op'-DDT	op'-DDE	Total DDT	Heptachlor Epoxide	Dieldrin
Waukegan	Waukegan	11/02/70	2.76	1.84	.06	1.59	6.25	.96	1.40
Pettibone Creek	North Chicago	11/02/70	6.24	7.20	.90	.61	14.95	.07	.93

* 50 yards upstream from Lake Michigan

** Data from Illinois Environmental Protection Agency

APPENDIX II, TABLE 6

LAKE MICHIGAN RIVER WATER PESTICIDES**
July 1969
(Results expressed in ng/l)

Sample No.	Location	Total DDT	Dieldrin	BHC	Est. PCB
2	Big Suamico River	< 10	< 10	NC**	NC
3	Little Suamico River	< 10		NC	NC
4	Pensaukee River	< 10	< 10	NC	NC
5	Oconto River	< 10	< 10	NC	NC
6	Peshtigo River	< 10	< 10	73.5	NC
7	Menominee River	< 10	< 10	128.0	NC
8	Mud Lake Creek	< 10		16.0	NC
9	Clark Lake Creek	600*	10	17.8	NC
10	N Jacksonport Creek	< 10		43.3	NC
11	Kangaroo Lake Creek	14.4*	< 10	52.2	NC
12	Moonlight Bay	< 10	< 10	27.2	NC
13	Stony Creek	< 10	< 10	35.3	NC
14	Ahnapee River	360*	< 10	72.2	NC
15	Kewaunee River	< 10	< 10	13.3	NC
16	East Twin River	< 10	< 10	50.0	NC
17	West Twin River	27.6	< 10	14.4	
18	Manitowoc River	< 10	< 10	66.7	NC
19	Silver Creek	10.8	< 10	34.4	NC
20	Calvin Creek	< 10	< 10	< 10	NC
21	Pine Creek	574*	< 10	< 10	NC
22	Point Creek	< 10	< 10	< 10	NC
23	Fisher Creek	< 10	< 10	< 10	NC
24	Centerville Creek	< 10	< 10	174.0	NC
25	Seven Mile Creek	542*	< 10	20.8	NC
26	Pigeon River	< 10	< 10	< 10	NC
27	Sheboygan River	260*	< 10	5.2	Very possible
28	Black River	97.4*	< 10	18.4	V. pos. present
29	Sauk Creek	29.8*	< 10	19.5	Possible
30	Milwaukee	42.8*	28.8	44	Possible
31	Menominee River	53.8*	14	84	Possible
33	Root Creek	10.0	< 10	64	Possible
34	Pike River	49.1*	< 10	10.4	Possible
35	Barnes Creek	75.5*	< 10	< 10	Possible
36	Calumet River at Calumet City	50*	< 10	40.4	
37	Burns Ditch	< 10	< 10	17.9	NC
38	Trail Creek	93.6*	< 10	47	Possible
39	Galien River	56.9*	< 10	14	Possible

* Retention time not exact.
** Not calculated
***Data from the Wisconsin Alumni Research Foundation

APPENDIX II, TABLE 6
continued

(Results expressed in ng/l)

Sample No.	Location	Total DDT	Dieldrin	BHC	Est. PCB
40	Drain at Sawyer	16.0	<10	40	
41	St. Joseph River	<10	<10	23.0	30.0
42	Paw Paw River	36.0*	45.2	7.2	
43	Black River	82.2*	<10	<10	NC**
44	Kalamazoo River	<10	<10	33.0	NC
45	Black River	<10	<10	<10	<10
46	Pigeon River	<10	<10	10.0	NC
47	Grand River	11.4*	<10	<10	Possible
48	Muskegon River at mouth into Muskegon L.	<10	<10	<10	NC
49	White River	<10	<10	<10	NC
50	Pentwater River	<10	<10	<10	<10
51	Pere Marquette River	<10	<10	20	NC
52	Manistee River	24.4*	<10	<10	Possible
53	Betsie River	<10	<10	<10	NC
54	Platte River	<10	<10	<10	NC
56	Leelanan Lake	<10	<10	<10	NC
57	Boardman River	<10	<10	Inter	NC
59	Lake Charlevois Outlet	600*	<10	<10	NC
60	Bear River, Petoskey	<10	<10	NC	NC
61	Millecoquins Creek	<10	<10	NC	NC
62	Manistique River	<10	<10	<10	NC
63	Sturgeon River	<10	<10	<10	NC
64	Whitefish River	975*	<10	NC	NC
65	Escanaba River	<10	<10	<10	NC
66	Ford River	<10	<10	<10	NC

* Retention time not exact
** Not calculated

APPENDIX III

CHLORINATED HYDROCARBON INSECTICIDES IN BIOLOGICAL MONITORS

APPENDIX III, PROCEDURE 1

FIELD METHODS FOR BIOLOGICAL SAMPLING
WISCONSIN DEPARTMENT OF NATURAL RESOURCES

Both random sample sites and selected sample sites were established for the invertebrates organism analyses. Random sites were designed to establish regional background levels in the organisms and specific sites were established to evaluate specific waste sources. Aquatic invertebrate samples were collected by hand picking or with dip nets and minnow seines. At least ten grams wet weight were desirable but that quantity was often impossible to obtain. The samples were normally mixed species of immature insects, fresh water shrimp, crayfish, leeches and others. Fish samples were taken at some sites. In addition to the resident invertebrate organisms, clams (*Lampsilis sp.* and *Fusconia sp.*) were tethered at selected sites near the mouth of the rivers tributary to both Lake Michigan and Lake Superior. The objective of utilizing clams was to provide a biological filter that offered a consistent pesticide accumulation mechanism. Clams were collected from Oxbow Creek in Douglas County, the Eau Claire River in Douglas County and Namakegon River in Washburn County.

Background residue data on control clams were generally less than two parts per billion for DDT plus analogs at the time of collection. However, some of the controls ranged as high as 20 parts per billion DDT plus analogs at the time of collection. The background levels of DDT and its analogs must, therefore, be considered variable. Most usually the background residue levels were not considered important unless they were unusually high since it was anticipated that the organisms would reach a new residue level equilibrium in the new environment.

The clams were tethered in the stream by means of a nylon cord tied to a drill hole at the edge of one mantle. Recovery from the stream sites was generally good, as long as the tether lines were totally hidden and casual observers had no opportunity to interfere. The clams normally assumed the same attitude in the stream when tethered as they had assumed when they were originally collected, suggesting that tethering did not interfere with their normal habits.

Both invertebrate organism and clam collections were preserved in the field in glass containers with formalin and returned to the laboratory for subsequent analysis.

APPENDIX III, PROCEDURE 2

ANALYTICAL METHODS FOR BIOLOGICAL SAMPLES
WISCONSIN DEPARTMENT OF NATURAL RESOURCES

Water, clams, invertebrates and algae were processed in this study by hexane extraction, acetonitrile partitioning, florisil column cleanup, gas chromatrographic identification, and quantitation. Thin layer chromatography was used for identification and confirmation on some samples.

Water samples of 2,000 ml were extracted three times in teflon stop-cock separatory funnels, first with 100 ml of hexane, twice with 50 ml hexane. If an emulsion appeared, it was broken by hot and cold water treatment, the addition of propanol or addition of sodium chloride. The three hexane extracts were combined and dried with sodium sulphate, then concentrated to 10 ml with a dry air stream on a 38° C water bath. The 10 ml hexane extract with pesticide residue was florisiled at this point to separate fats, pigments and other contaminants.

Two or three clams from a site were removed from their shells and partially dried on filter paper to remove excess water. They were ground with a hand grinder and mixed to give a representative sample. Fifty grams of this sample were mixed with enough sodium sulphate to dry the sample. The 100 ml hexane extracts were combined and dried with sodium sulphate and concentrated with the dry air stream on a water bath to 10 ml. This final clam extract was then cleaned by a florisil column to remove traces of fats, pigments and other contaminants.

Invertebrates, other than clams, were drained on filter paper to remove excess water. Using 50 grams (if available) or less, the sample was ground with sodium sulphate in a mortar and pestle. After pulverization the sample was transferred to 250 ml centrifuge bottles. These bottles were then stoppered with either glass stoppers or aluminum foil-covered rubber stoppers and hexane was added. One hundred milliliters of hexane were first added to each bottle and the mixture was shaken for three minutes, followed by centrifuging at 1,500 rpms for 10 minutes. The supernatant was then decanted and the sample was again extracted with 50 ml of hexane and centrifuged for 10 minutes. The supernatants from both spinnings were combined and concentrated to 10 ml by a dry air stream and were then ready for florisil cleanup.

Algae samples were collected and as much algae as was available was used for extraction. The samples were filtered through tared, hexane-rinsed fiber glass filter pads with a buchner funnel. The samples were then dried in a dessicator for 15 minutes. The algae as well as filter paper were mascerated by mortar and pestle with enough sodium sulphate to dry the sample. The sample was then placed in a 250 ml centrifuge bottle with 100 ml of hexane and shaken for three minutes. The sample was then centrifuged for ten minutes at 1,500 rpms. The hexane was decanted and the sample re-extracted twice with 50 ml of hexane. The hexane supernatants were combined and concentrated to 10 ml by a dry air stream and were then ready for florisil cleanup.

The extraction procedure efficiently partitions fats and oils from the sample into the hexane carrier solvent. The fats and oils contain most of the insecticides present in the organisms due to their solubility in the fats and oils and their insolubility in water. Along with the lipid soluble pesticides, the extraction process also extracts other organic compounds that could have a high electron affinity and thus cause erroneous electron capture detector responses. To remove the interfering substances from the hexane extract, absorption chromatography is used. The absorption material is a commercial diatomaceous earth purchased as florisil. The florisil is activated by heating to 100° C for 24 hours followed by deactivation to a specific level by adding one to three percent water. This enables efficient separation of the insecticides on the florisil column. The column holder is a pyrex glass tube with a 22 ml inside diameter and of adequate length to contain 300 ml of hexane solvent. It has fritted glass and teflon stopcock at the bottom to permit a regulated flow through the system. One-half inch of sodium sulphate is added to the column and 40 grams of deactivated florisil which is covered with another one-half inch of sodium sulphate.

The florisil column is prewashed with 50 ml of hexane. The concentrated hexane extract of the sample is then added to the column. The sample container is washed with 200 ml of six percent ethyl ether and 94 percent hexane solvent mixture. This mixture is added to the florisil column and eluted through the column at a rate not to exceed five ml per minute. When the column is almost empty, 200 ml of 20 percent ethyl ether and 80 percent hexane are added to the florisil column. Each one of the elutions (94/6, 80/20) is collected and analyzed separately.

The two elutions and properly deactived florisil will remove most interferences and separate some of the insecticides. The first elution (six percent ethyl ether) will contain:

Lindane	DDT
BHC	Perthane
Kelthane	Methoxychlor
Aldrin	Toxaphene
Heptachlor	Strobane
Heptachlor Epoxide	Chlordane
DDE	DDD (TDE)

The second elution (20 percent ethyl ether) will contain:

Dieldrin	Endrin
Lindane (Trace)	Kelthane (Trace)

The two elutions are concentrated with a dry air stream to 10 ml or less, depending on the suspected insecticide concentration in the sample. These concentrated samples are at this time ready for injection into the gas chromatograph.

The gas chromatograph used for the analyses was a Hewlett Packard, dual channel (Model 402). Both channels were equipped with Ni_{63} electron capture detectors. The instrument columns were two to six feet V-tubes of pyrex glass. These columns were packed with three percent OV-17 (Phenyl methylsilicone, 50 percent phenyl), ten percent silicone DC-200 (12,500 cstk), and ten percent silicone DC QF-1 on a solid support of Gas Chrom Q (60-80 mesh) either singly or in varying concentrations of each.

The analysis of environmental samples is a problem because the extraction process removes substances from the sample which the florisil cleanup misses and these substances are detected by electron capture systems and cause interferences.

One of the most common interferences with the analysis of the DDT complex is the polychlorinated biphenyl compounds (PCB's), because of the structural similarity between PCB's and some pesticides, the electron capture detector will give the same response for both types of compounds. The PCB's have 210 isomeric formations that are detectable and the DDT complex has only six formations that could be detected with an electron capture detector.

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES*
Wisconsin Drainage, 1968-69
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
BROWN COUNTY				
Clams				
East River	322	5/04/69		
East River	493	7/16/69		
East River	548	8/19/69		
Fox River	13099	7/31/68	2	
Fox River	13100	7/31/68	2	
Suamico River	323	5/07/69		
Suamico River	494	7/15/69		
Suamico River	549			
Invertebrates				
Duck Creek	126A1	11/14/68	13.0	
Trout Creek	127A1	11/14/68	13.0	
Unnamed Creek	147	4/25/68	54.0	
CALUMET COUNTY				
Invertebrates				
Killsnake Creek	228A	4/07/69	Trace	Trace
Manitowoc River	149	5/14/68	Trace	
Manitowoc River	152	5/14/68	2900.0	
Manitowoc River	150	5/19/68	2000.0	
Pine Creek	151	5/14/68	28.0	8.0
Story Brook	148	5/14/68	84.0	16.0
DOOR COUNTY				
Clams				
Clarke Lake Outlet	330	5/06/69	27.4	
Clarke Lake Outlet	500	7/15/69	26.0	
Heine Creek	332	5/06/69		
Heine Creek	501	7/15/69	65.3	
Heine Creek	554	9/18/69	10.0	
Lily Bay Creek	329	5/06/69	23.9	
Lily Bay Creek	499	7/15/69	26.0	
Lily Bay Creek	553	9/18/69	10.0	

* Data from the Wisconsin Department of Natural Resources

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES
continued
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
DOOR COUNTY CONTINUED				
Clams continued				
Riebolts Creek	333	5/06/69		
Riebolts Creek	502	7/15/69	4.5	
Riebolts Creek	555	9/18/69	10.0	
Stoney Brook	334	5/07/69	6.9	
Stoney Brook	556	9/19/69		
Unnamed Creek	328	5/06/69		
Unnamed Creek	498	7/15/69		
Unnamed Creek	552	8/19/69	50.0	
Invertebrates				
Clark Creek	157	5/16/68		
Heine Creek	154	5/16/68	190.0	
Hubbards Creek	158	5/16/68	25.0	6.0
Lily Bay Creek	240A	4/09/69	2350.0	
Little Sturgeon Creek	241A	4/09/69		
Little Sturgeon Creek	243A	4/09/69		
Mink River	153	5/16/68	309.0	
North Bay River	159	5/16/68	34.0	
Shivering Sand Creek	238A	4/09/69		6.0
Shivering Sand Creek (Some fish also)	239A	4/09/69	89.0	33.0
Sugar Creek	242A	4/09/69		
Unnamed Creek	156	5/16/68	708.0	
FLORENCE COUNTY				
Invertebrates				
Lamon-Tangue Creek	304	4/10/69	63.0	
Popple River	303	4/10/69		
Popple River Trib	305	4/10/69	1.45	0.68
Popple River So Br	306	4/11/69		0.9
Riley Creek	301	4/10/69	3.2	1.8
Wakefield Creek (Some fish also)	300	4/10/69	3.2	
Woods Creek	302	4/10/69	1.16	0.58

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES
continued
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
FOREST COUNTY				
Invertebrates				
Pine River	648	7/07/69	49.0	
Wolf River	654	7/07/69	100.0	
GREEN LAKE COUNTY				
Invertebrates				
Sucker Creek	523	6/25/69		330.0
Sucker Creek	524	6/25/69	10.0	
KENOSHA COUNTY				
Clams				
Barnes Creek	307	5/26/69	12.2	
Pike River	516	7/16/69	4290.0	1350.0
Invertebrates				
Barnes Creek	14567	5/03/68	143.0	25.0
Pike River	253A1	4/11/69	2557.0	322.0
Pike River	14568	5/03/68	1210.0	589.0
Pike River	14569	5/03/68	150.0	30.0
Pike River So Br	69A	7/11/68	100.0	10.0
KEWAUNEE COUNTY				
Clams				
Ahnapee River	335	5/07/69	3.9	
Ahnapee River	503	7/15/69	10.6	
Kewaunee River	337	5/07/69	14.8	0.54
Kewaunee River	558	9/20/69	15.0	
Unnamed Creek	336	5/07/69	9.7	
Unnamed Creek	504	7/15/69	< 1.0	
Unnamed Creek	557	8/19/69		
Invertebrates				
Buck Creek	233A	4/08/69	16.0	
Casco River	236A1	4/08/69		
East Twin River	234A	4/08/69	12.0	
East Twin River (Some fish also)	235A	4/08/69	11.0	
Kewaunee River	237A	4/08/69		

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES
continued
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
LANGLADE COUNTY				
Invertebrates				
Hunting River	626	7/07/69	0.05	
Hunting River	644	7/11/69	<1.0	
Nine Mile Creek	636	7/10/69	53.0	
Pickerel Creek	628	7/09/69	< 1.0	
Swamp Creek	629	7/09/69	33.0	
Wolf River	633	7/10/69	< 0.1	
Wolf River	642	7/10/69	45.0	
MANITOWOC COUNTY				
Clams				
Calvin Creek	316	5/27/69	19.0	
Calvin Creek	507	7/16/69	5.0	
Calvin Creek	562	9/20/69	32.0	
Centerville Creek	320	5/27/69	< 1.0	
Centerville Creek	565	9/20/69	39.0	
East Twin River	314	5/27/69	8.8	
East Twin River	559	9/20/69		
Fisher Creek	319	5/27/69	35.0	
Fisher Creek	508	7/16/69	5.0	
Fisher Creek	564	9/20/69	< 1.0	
Manitowoc River	506	7/16/69	28.0	
Manitowoc River	13101	8/01/69	< 2.0	
Manitowoc River	13102	8/01/68	< 2.0	
Pine Creek	317	5/27/69	5.8	
Pine Creek	563	9/20/69	<1.0	
Point Creek	318	5/27/69	19.5	
Silver Creek	315	5/27/69	10.0	
Silver Creek	561	9/20/69	38.0	
West Twin River	505	7/16/69	<1.0	
West Twin River	560	9/20/69	21.0	
Invertebrates				
Branch River	230A	4/07/69	Trace	
Branch River Trib	231A	4/07/69		
East Twin River	119A1	11/12/68	13.0	
Francis Creek	121A1	11/12/68	13.0	

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES
continued
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
MANITOWOC COUNTY CONTINUED				
Invertebrates continued				
Molash Creek	232A	4/08/69		
Mud Creek	229A	4/07/69		
West Twin River	120A1	11/12/68	13.0	
MARINETTE COUNTY				
Clams				
Peshtigo River	327	5/07/69	2.5	
Invertebrates				
Beaver Creek	84	9/05/68		10.0
Harvey Creek	287	4/09/69	3.0	
Holme Creek	285	4/09/69	141.0	
Little Peshtigo River	282	4/08/69	62.0	20.5
Menominee River	283	4/09/69	Insufficient Sample	
Pike River Branch	288	4/09/69		
MARQUETTE COUNTY				
Invertebrates				
Chapman Creek	85A	11/05/68		<10.0
Fox River	92A	11/05/68	84.0	29.0
Klawitter Creek (Some fish also)	86A	11/05/68		<10.0
Lunch Creek	89A	11/05/68		< 2.0
Mecan River	88A	11/05/68		4.0
Mecan River (Some fish also)	91A	11/05/68	23.0	
Westfield Creek (Some fish also)	87A	11/05/68	23.0	6.0
White River (Some fish also)	90A	11/05/68	5.0	14.0
MENOMINEE COUNTY				
Invertebrates				
Pecore Creek	529A1	7/08/69	<10.0	
Wolf River W Br	527	7/08/69	<10.0	
Wolf River	528A1	7/08/69	<10.0	

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES
continued
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
MILWAUKEE COUNTY				
Clams				
Kinnickinnic River	514	7/15/69	10.0	
Menominee River	309	5/26/69	196.5	11.2
Menominee River	513	7/15/69	76.0	
Oak Creek	310	5/26/69		
Oak Creek	515	7/16/69	69.0	
Invertebrates				
Kinnickinnic River	14571	6/03/68	172.0	
Kinnickinnic River	14572	7/02/68	780.0	280.0
Lincoln Creek	47	10/22/68	234.0	40.0
Lincoln Creek	48	10/22/68	403.0	29.0
Lincoln Creek	46	10/24/68	740.0	
Little Menominee River	14574	5/29/68	365.0	26.0
Menominee River	14573	7/03/68	2226.0	163.0
Menominee River	80	6/05/68	430.0	104.0
Menominee River	81A	6/05/68	170.0	
Milwaukee River	14565	4/29/68	595.0	1596.0
Milwaukee River	82A	6/07/68	4100.0	
Milwaukee River	79A	6/11/68	287.0	19.0
Oak Creek	76A	5/28/68	13.0	4.0
Oak Creek	14570	6/03/68		
Root River	77A	5/28/68	451.0	27.0
Root River	78A	5/28/68	379.0	19.0
OCONTO COUNTY				
Clams				
Little Suamico River	324	5/07/69	16.0	
Little Suamico River	495	7/15/69		
Little Suamico River	550	9/18/69	$<$20.0	
Oconto River	326	5/07/69	16.0	
Oconto River	497	7/15/69	$<$1.0	
Pensaukee River	325	5/07/69	12.6	
Pensaukee River	496	7/15/69	23.0	
Pensaukee River	551	9/18/69	$<$10.0	

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES
continued
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
OCONTO COUNTY				
Invertebrates				
Daly Creek	299	4/11/69	2.5	
Kelly Brook	297	4/11/69	3.6	
Little River	295	4/11/69		
Little Suamico River	525A1	7/08/69	< 1.0	
McCaslin Brook	290	4/07/69		23.1
Oconto R, 1st S Br	292	4/07/69	433.0	
Oconto R, N Br	294	4/07/69		
Pensaukee River, N Br	526A1	7/08/69	<50.0	
Peshtigo River	293	4/07/69		
OUTAGAMIE COUNTY				
Invertebrates				
Bear Creek	123A	11/14/68	10.0	
Duck Creek	124A1	11/14/68	759.0	
OZAUKEE COUNTY				
Clams				
Milwaukee River	13661	6/27/68	36	51
Milwaukee River	50	8/30/68	65	60
Milwaukee River	51	8/30/68	68	
Milwaukee River	275	4/23/69	15	
Milwaukee River	276	4/23/69	16.5	3.5
Milwaukee River	277	4/23/69	10.3	4.6
Milwaukee River	278	4/23/69	20.7	9.4
Invertebrates				
Cedar Creek	14565	4/29/68	6060.0	1150.0
Cedar Creek	62A	5/24/68	78.0	18.0
Cedar Creek	14562	5/24/68	104.0	
Little Menominee River	64A	5/29/68	20.0	10.0
Milwaukee River	14564	4/29/68	5360.0	2430.0
Milwaukee River	61A	5/24/68	145.0	40.0
Milwaukee River	63A	5/27/68	124.0	37.0
Milwaukee River	14563	5/29/68	152.0	794.0

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES
continued
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
OZAUKEE COUNTY CONTINUED				
Invertebrates continued				
Milwaukee River	71A	6/11/68	60.0	29.0
Milwaukee River	72A	6/11/68	1986.0	2500.0
Milwaukee River	73A	6/07/68	90.0	394.0
Milwaukee River	74A	6/11/68	105.0	427.0
Milwaukee River	75A	6/07/68	1096.0	605.0
Sauk Creek	14561	5/13/68	19400.0	
Sauk Creek	59A	5/24/68	47.0	16.0
Sauk Creek	60A	5/27/68	18.0	27.0
Sucker Creek	58A	5/24/68	102.0	26.0
Sucker Creek	57A	5/27/68	42.0	15.0
RACINE COUNTY				
Clams				
Pike R, No. Br	49	8/29/69	40.0	1660.0
Root River	308	5/26/69	25.3	1.7
Root River	53	8/29/68	33.0	28.0
Invertebrates				
Pike River, No. Br	14575	5/06/68		262.0
Pike River, No. Br	14578	5/06/68	289.0	
Pike River, No. Br	252A	4/11/69	6.0	
Root River, E Br	14576	5/06/68	943.0	15.0
Root River, W Br	14577	5/06/68	144.0	46.0
Root River	14579	5/10/68	99.0	37.0
Root River	14580	5/10/68	71.0	21.0
Root River	14581	5/10/68	211.0	33.0
SHAWANO COUNTY				
Invertebrates				
Comet Creek	624	7/09/69	14.0	
Embarrass River	623	7/09/69	12.0	
Pensaukee River	618	7/08/69	<10.0	

APPENDIX III, TABLE 1

PESTICIDES IN BIOLOGICAL SAMPLES
continued
(concentrations in ppb)

Source	Lab No.	Date Collected	DDT Complex	Dieldrin
SHEBOYGAN COUNTY				
Clams				
Black Creek	313	5/27/69	13.1	
Black Creek	512	7/16/69	<2.0	
Black Creek	568	9/20/69		7.2
Pigeon River	510	7/15/69	24.0	
Pigeon River	566	9/20/69	24.0	
Seven Mile Creek	311	5/27/69	4.2	
Seven Mile Creek	509	7/15/69	7.0	
Sheboygan River	13097	8/01/68	<2.0	
Sheboygan River	13098	8/01/68	<2.0	
Sheboygan River	511	5/06/69		1.3
Sheboygan River	312	5/27/69	99.9	
Sheboygan River	567	9/20/69	1080.0	
Invertebrates				
Mullet River	244A1	4/10/69	3300.0	
Onion River	94A2	11/19/68		
Sheboygan River	96A	11/19/68	4390.0	
Sheboygan River	98A	11/19/68		
Sheboygan River	246A1	4/10/69		
WASHINGTON COUNTY				
Invertebrates				
Cedar Cr, No. Br	12111	5/08/68	10.0	
Menominee River	65A	5/24/68	51.0	1.0
Milwaukee River Br	12112	5/08/68	10.0	
Milwaukee River	12113	5/08/68	136.0	
Milwaukee River, No. Br	12114	5/08/68	10.0	
Milwaukee River, No. Br	12115	5/08/68	33.0	
WAUPACA COUNTY				
Invertebrates				
Crystal River	116A1	11/13/68	14.0	
Little Wolf River	117A1	11/13/68		
Maple Creek	122A1	11/14/68	8.0	6.0
Waupaca River	118	11/13/68		16.0

APPENDIX III, TABLE 2

PESTICIDES IN BIOLOGICAL* SAMPLES

MICHIGAN WATER RESOURCES COMMISSION
Michigan Drainage, 1970
(concentrations in ppb)**

River	Location	Placement	Removal	DDE	DDD	o,p-DDT	p,p'-DDT	Total DDT	Dieldrin
Black	U.S. 31 Bridge South Haven	6/11/70	10/23/70	10	11	13	28	62	4
White	S Channel Wall Whitehall	6/11/70	10/23/70	14	8	21	33	76	2
Pentwater	S Channel Wall Pentwater	6/11/70	10/23/70	13	7	23	36	78	4
Manistee	Maple St Bridge Manistee	6/10/70	10/23/70	9	7	9	19	44	2
Betsie	RR Crossing Frankfort	6/10/70	10/23/70	8	3	9	15	35	3
Crystal	Leelanau Public Schools	6/10/70	11/05/70	33	10	11	24	78	3
Leland	Below Dam Leland	6/10/70	11/05/70	17	8	9	25	59	2
Boardman	Above U.S. 31 Traverse City	6/10/70	11/05/70	10	15	14	39	83	1
Acme Cr	M-72 Bridge	6/10/70	11/05/70	15	7	15	31	67	2
Elk	Dam, Elk Rapids	6/10/70	11/05/70	7	4	13	27	51	3
Bear	McManus Dam Petoskey	6/09/70	11/05/70	7	2	9	18	35	3
Millecoquins Cr	U.S. 2, Bridge	8/05/70	11/09/70	5	2	7	15	29	6
Manistique	U.S. 2, Bridge Manistique	8/05/70	11/09/70	9	2	9	20	40	2

* Clams used as the biological monitor

** Mean of 2 samples. No extreme values were indicated; therefore, the means closely reflect the actual analysis values.

APPENDIX III, TABLE 2

PESTICIDES IN BIOLOGICAL SAMPLES
continued

River	Location	Placement	Removal	DDE	DDD	o,p-DDT	p,p'-DDT	Total DDT	Dieldrin
Sturgeon	Nahma	8/05/70	11/09/70	5	3	10	17	35	3
Whitefish	U.S. 2 Bridge	8/05/70	11/10/70	7	3	6	12	27	3
Escanaba	U.S. 2 - 41 Bridge	8/05/70	11/10/70	6	3	8	14	30	2
Ford	Above M-35 Bridge	8/05/70	11/10/70	6	3	7	16	32	2

APPENDIX III, PROCEDURE 3

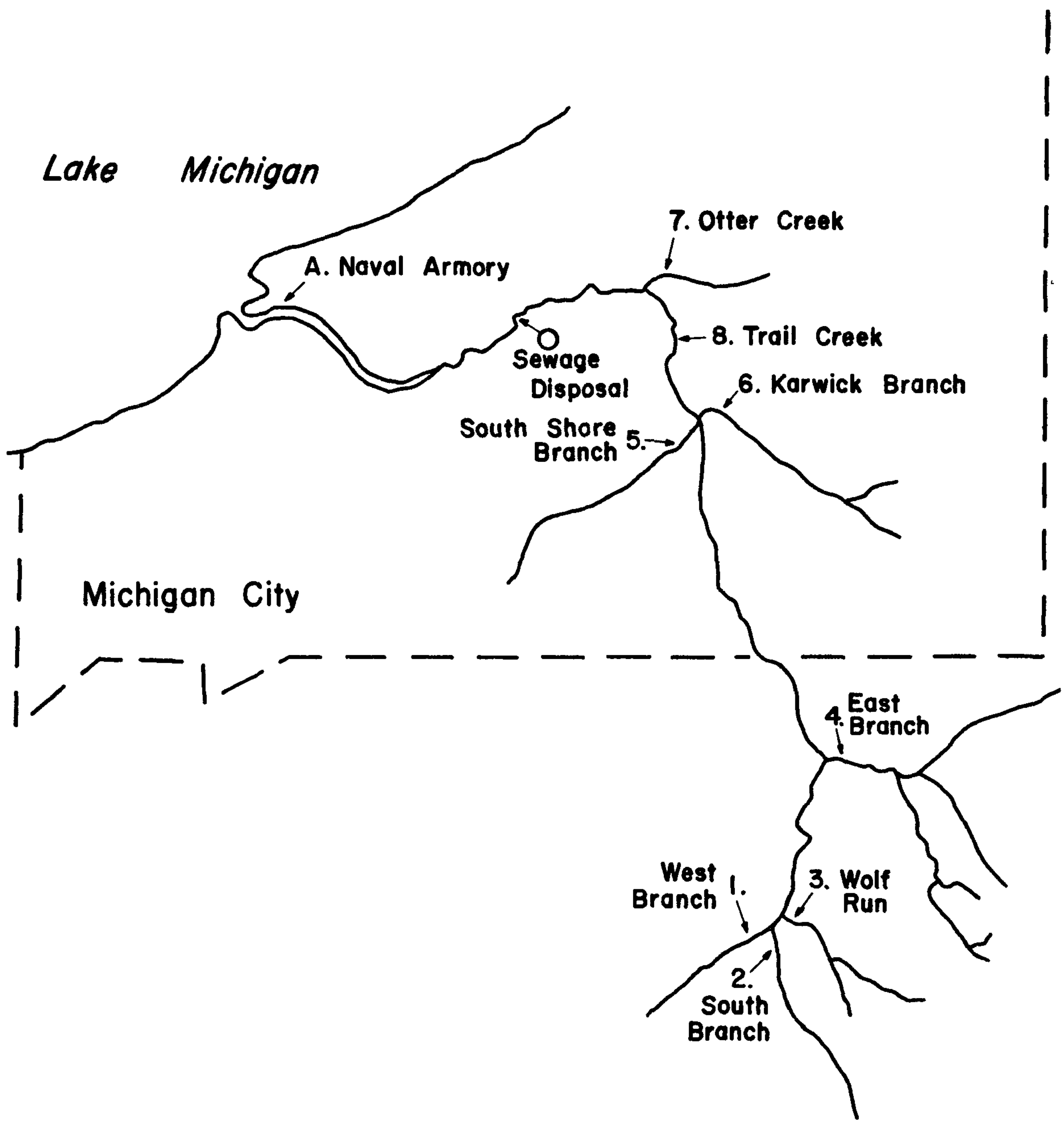
BIOLOGICAL COLLECTION AND ANALYTICAL PROCEDURE MICHIGAN WATER RESOURCES COMMISSION

Biological intake of chlordane and dieldrin was assessed by holding freshwater mussels in chrome-plated wire barbecue baskets at the six monitoring stations during open water periods. Mussels have been found to be good monitors of insecticides in lotic situations (Bedford, et al., 1968). These animals filter large volumes of water and concentrate insecticides in their tissues to levels many times greater than that in the water. Insecticide concentrations in the mussels reach equilibrium with their environment in about two weeks. Thus levels measured in these animals reflect the insecticide concentrations which existed in the environmental waters for about two weeks prior to sampling. Exposed mussels were retrieved prior to the insecticide applications of October 19-23, 1968, and at intervals thereafter. In most cases, three mussels were collected from each station on each collection date. The mussels were analyzed for pesticide content at the Michigan State University Pesticide Analytical Laboratory under the direction of Dr. Matthew Zabik.

Each mussel was removed from its shell, drained and weighed to the nearest mg and was then blended with 50 ml of acetonitrile in a Sorvall Omni-Mixer for three minutes at 10,000 rpms. The solvent mixture was decanted and the sample blended twice more with 50 ml aliquots of additional solvent. Fifty milliliters of n-hexane was added to the combined extract and the insecticides were partitioned into the hexane by removing the acetonitrile with ten percent sodium chloride solution. The hexane extract was concentrated to a volume of less than ten ml for introduction into a cleanup column.

Pyrex columns, 2 by 50 cm, fitted with a fritted-glass disk, were packed with 10 g of a 5:1 mixture of florisil to celite. The florisil, which was received activated at 649C, was deactivated with approximately five percent water. The mixture was calibrated before use to ensure conformation to the elution procedure used. Each sample was eluted with 300 ml of n-hexane and then procedures generally follow those recommended by Shell Development Company (1964) with several modifications.

A Beckman Gas Chromatograph 4 equipped with a discharge electron capture detector was used for the analyses. It was fitted with a six foot (1.83 m) by 1/15 inch (1.59 mm) pyrex column packed with 11 percent QF-1 and three percent DC 200 on Gas Chrom Q and was operated at a column temperature of 200° C and 30 ml per minute helium flow. Standards were injected at the beginning of each run, after every ten samples and at the end of the run. The identities of the pesticides found were confirmed using columns packed with 2.5 percent QF-1 on acid-base washed Chromsorb W and 2.5 percent S.E. 30 on Gas Chrom RP. Quantitations were based on peak height and the concentrations were based on the wet weight of the mussel.



APPENDIX III, FIGURE 1

INDIANA BIOLOGICAL PESTICIDE MONITORING STATIONS
INDIANA STATE BOARD OF HEALTH

APPENDIX III, TABLE 3

PESTICIDES IN BIOLOGICAL SAMPLES
INDIANA STATE BOARD OF HEALTH
Indiana Drainage, 1970
(concentrations in ppb)

River and Location	Date	Media	DDE	DDD	DDT	Total DDT	Dieldrin
Burns Ditch, Portage	5/14/70	Clams	*	*	*	*	*
Burns Ditch, Portage	6/11/70	Clams	*	*	*	*	*
Burns Ditch, Portage	7/03/70	Clams	*	*	48	48	*
Burns Ditch, Portage	6/11/70	Invert	25	*	39	64	28
Burns Ditch, Portage	7/03/70	Invert	*	*	*	*	*
Trail Creek, Michigan City	5/13/70	Clams	*	*	*	*	*
Trail Creek, Michigan City	6/11/70	Clams	*	16	12	28	*
Trail Creek, Michigan City	7/03/70	Clams	*	24	16	40	*
Trail Creek, Michigan City	6/11/70	Invert	100	168	150	418	123
Trail Creek, Michigan City	7/03/70	Invert	*	258	130	388	79
St. Joseph, South Bend	5/13/70	Clams	*	*	*	*	*
St. Joseph, South Bend	6/10/70	Clams	*	*	*	*	*
St. Joseph, South Bend	6/10/70	Invert	*	68	68	136	16
St. Joseph, Bristol	5/13/70	Clams	*	*	*	*	*
St. Joseph, Bristol	6/09/70	Clams	*	*	*	*	*
St. Joseph, Bristol	6/09/70	Invert	14	*	*	14	*
St. Joseph, Bristol	7/02/70	Invert	*	*	*	*	*
St. Joseph, Bristol	6/09/70	Algae	*	*	12	12	*
Trail Cr Trib 1**	8/25/70	Invert	*	*	24	24	*
Trail Cr Trib 2	8/25/70	Invert	*	*	27	27	*
Trail Cr Trib 3	8/25/70	Invert	*	*	*	*	*
Trail Cr Trib 4	8/25/70	Invert	*	*	13	13	*
Trail Cr Trib 6	8/26/70	Invert	*	10	17	27	*
Trail Cr Trib 7	8/26/70	Invert	19	26	14	59	*
Trail Cr Trib 8	8/26/70	Invert	*	*	37	37	*

* Less than 10 ppb
** Refer to Appendix III, Figure 1 for location.

APPENDIX IV

CHLORINATED HYDROCARBON INSECTICIDES IN LAKE MICHIGAN FISH

APPENDIX IV, TABLE 1

AVERAGE DDT (1965-1969) AND DIELDRIN (1967-1969)
CONCENTRATIONS (WHOLE FISH) FOR LAKE MICHIGAN FISHES*
March 1970

Species	DDT (DDT, DDE, DDD)			Dieldrin		
	No. of fish	No. of analyses	Concentration (ppm)	No. of fish	No. of analyses	Concentration (ppm)
Alewife	702	113	4.23	338	79	0.10
Bloater	591	116	9.33	301	85	0.21
Smelt	224	45	2.31	150	35	0.06
Yellow perch	224	36	3.16	77	21	0.07
Lake herring	8	7	6.71	8	7	0.20
Lake whitefish	7	6	2.12	7	5	0.14
Trout-perch	21	2	0.94	--	--	--
Kiyi	3	2	13.28	3	2	0.28
Carp	3	3	1.92	--	--	--
Sucker	13	4	0.29	--	--	--
Slimy sculpin	169	21	2.54	145	19	0.13
Lake trout						
2.0-5.9 inches	26	11	0.89	18	7	0.03
6.0-9.9 inches	95	34	2.24	77	33	0.12
10.0-15.9 inches	68	56	6.00	69	51	0.14
16.0-21.9 inches	63	57	8.00	57	57	0.21
22.0-26.9 inches	43	42	14.62	43	42	0.23
27.0-32.9 inches	3	3	19.23	3	3	0.26
Coho salmon						
9.0-10.9 inches						
2nd yr-fall	3	3	3.50	3	3	0.14
16.0-17.9 inches						
3rd yr-early spring	9	9	3.30	9	9	0.12
18.0-20.9 inches						
3rd yr-early summer	11	11	3.66	11	11	0.08
22.0-27.9 inches						
3rd yr-late summer	30	30	11.43	30	30	0.18

* Bureau of Commercial Fisheries

APPENDIX IV, TABLE 2

A COMPARISON BETWEEN DDT (DDT, DDE, DDD) AND DIELDRIN CONCENTRATIONS IN BLOATER CHUBS, COHO SALMON AND LAKE TROUT COLLECTED IN 1969 and 1970*

	1969			1970		
Species	No. fish	DDT	Dieldrin	No. fish	DDT	Dieldrin
Chubs	120	Min. 6.46	0.12	30	Min. 4.72	0.12
		Max. 15.29	0.49		Max. 19.65	0.27
		Ave. 9.93	0.27		Ave. 10.19	0.19
Coho	4	Min. 1.83	0.04	5	Min. 2.05	0.05
(Spring)		Max. 5.38	0.15		Max. 3.02	0.09
		Ave. 3.50	0.08		Ave. 2.82	0.07
Coho	12	Min. 9.24	0.14		Min. 9.03	0.05
(Fall)		Max. 17.07	0.29		Max. 16.66	0.18
		Ave. 12.73	0.22		Ave. 14.09	0.12
Lake trout	12	Min. 8.98	0.12	19	Min. 10.94	0.14
(22"-26")		Max. 24.75	0.39		Max. 28.06	0.45
		Ave. 17.98	0.26		Ave. 18.80	0.27

* Bureau of Commercial Fisheries data.

APPENDIX IV, TABLE 3

SUMMARY OF DDT AND DIELDRIN VALUES OF 120 SEPARATE ANALYSES OF LAKE MICHIGAN CHUBS (COREGONUS HOYI)
Fall, 1969[1]

Great Lakes Fishery Laboratory, Bureau of Commercial Fisheries

	Weight (grams)	Length (mm)	Percentage oil	DDE		o,p-DDT		DDD		p,p'-DDT		DDT total[2]	Dieldrin[2]
				ppm	%	ppm	%	ppm	%	ppm	%		
Minimum	155	260	13.2	1.66	21	0.61	5	0.00	0	2.16	23	6.46	0.12
Maximum	280	288	30.6	7.20	54	2.61	23	2.88	24	7.51	60	15.30	0.49
Average	208	270	22.1	3.75	38	1.31	13	1.10	11	3.78	38	9.93	0.27
Standard Deviation	27.2	6.9	3.50	106		0.43		0.56		.097		1.84	0.073

[1]All fish were taken from a single trawl haul at 40 fathons near Saugatuck, Michigan; all fish were females.

[2]All values based on analysis of whole fish.

APPENDIX IV, TABLE 4

MEAN PESTICIDE RESIDUES IN LAKE MICHIGAN FISH
1968*

Species No.	Species Name	Portion No.	Portion Type	Preparation No.	Preparation Type	% Water	% Fat	DDE	DDD	DDT	Total DDT	Dieldrin	No. of Samples
	Minnows	1	Whole	1	Raw	75.9	2.2	.48	.05	.04	.57	.001	1
01	Alewives	1	Whole	1	Raw	70.3	11.8	1.02	.33	.51	1.86	.121	5
06	Brook trout	1	Whole	1	Raw	73.6	5.8	1.25	.37	.61	2.09	.033	8
06	Brook trout	3	Dressed	1	Raw	69.0	9.8	1.75	.51	1.36	3.63	.225	4
09	Bullheads	1	Whole	1	Raw	77.1	2.7	.17	.11	.53	.81	.104	4
13	Carp	1	Whole	1	Raw	70.7	7.3	.53	.33	1.35	2.21	.257	7
16	Chubs, creek	1	Whole	1	Raw	73.0	4.7	3.32	.92	.53	4.76	.038	2
18	Chubs, human food	1	Whole	1	Raw	58.1	23.3	3.15	.80	2.11	6.06	.183	10
18	Chubs, human food	2	Drawn	1	Raw	58.8	24.2	2.98	.91	2.07	5.92	.223	17
18	Chubs, human food	3	Dressed	7	Smoked	63.4	15.8	2.22	.68	1.74	4.64	.119	4
24	Eels	1	Whole	1	Raw	72.7	7.3	1.95	.57	.93	3.45	.111	1
30	Goldfish	1	Whole	1	Raw	48.1	12.6	1.33	.84	.77	2.94	.132	2
33	Lake herring, human	2	Drawn	1	Raw	69.0	9.5	2.27	.74	1.71	4.72	.156	1
33	Lake herring, human	3	Dressed	1	Raw	63.4	14.2	2.13	.68	1.32	4.13	.172	1
35	Lake trout	1	Whole	1	Raw	60.2	20.1	3.84	.68	1.42	5.98	.127	12
35	Lake trout	2	Drawn	1	Raw	66.3	14.4	2.67	1.16	2.43	6.25	.247	8
35	Lake trout	3	Dressed	1	Raw	61.2	18.8	4.06	1.17	2.58	7.82	.160	45
35	Lake trout	7	Eggs	1	Raw	66.8	8.2	1.90	.35	.77	3.02	.058	9
43	Pike or pickerel					.0	.0	2.26	.52	.76	3.54	.065	1
43	Pike or pickerel	1	Whole	1	Raw	75.6	2.3	.95	.33	1.00	2.25	.097	9
43	Pike or pickerel	3	Dressed	1	Raw	72.1	4.1	1.61	.45	.65	2.71	.075	5
45	Brown trout	1	Whole	1	Raw	66.0	12.9	1.55	.59	1.09	3.23	.226	6
45	Brown trout	2	Drawn	1	Raw	69.4	10.6	5.05	.25	1.92	7.22	.253	1
45	Brown trout	3	Dressed	1	Raw	63.6	14.3	3.00	.78	1.92	5.63	.222	27
45	Brown trout	7	Eggs	1	Raw	65.3	3.2	1.13	.24	.46	1.83	.082	4
46	Rainbow trout	1	Whole	1	Raw	74.4	4.5	1.53	.37	.73	2.62	.074	18
46	Rainbow trout	2	Drawn	1	Raw	72.3	7.3	4.30	1.37	2.20	8.26	.236	28

* Data from the Wisconsin Department of Natural Resources

APPENDIX IV, TABLE 4

MEAN PESTICIDE RESIDUES IN LAKE MICHIGAN FISH
continued

Species No.	Species Name	Portion No.	Portion Type	Preparation No.	Preparation Type	% Water	% Fat	DDE	DDD	DDT	Total DDT	Dieldrin	No. of Samples
46	Rainbow trout	2	Drawn	7	Smoked	66.7	9.3	4.82	.86	1.76	7.43	.125	1
46	Rainbow trout	3	Dressed	1	Raw	72.1	6.7	2.56	.68	1.24	4.57	.119	19
46	Rainbow trout	6	Belly Fat	7	Smoked	67/0	7.2	2.90	.70	1.25	4.85	.086	2
46	Rainbow trout	7	Eggs	1	Raw	66.3	3.7	2.73	.80	1.52	5.05	.107	14
46	Rainbow trout	8	Defatted	7	Smoked	68.8	5.9	3.49	.70	1.19	5.38	.084	2
48	Salmon, chinook	3	Dressed	1	Raw	65.6	14.5	2.74	1.06	1.80	5.60	.253	2
49	Salmon, coho			1	Raw	81.1	1.1	1.29	.20	.46	1.96	.049	1
49	Salmon, coho			8	Offal	72.1	6.2	2.00	.59	1.48	4.07	.000	1
49	Salmon, coho			9	Gonads	76.1	.8	.04	.00	.00	.04	.000	1
49	Salmon, coho	1	Whole	1	Raw	73.9	3.5	3.18	.64	1.36	5.77	.210	17
49	Salmon, coho	2	Drawn	1	Raw	69.4	9.8	3.14	.96	1.46	5.56	.205	1
49	Salmon, coho	3	Dressed	1	Raw	72.0	6.5	2.33	.72	1.19	4.24	.111	40
49	Salmon, coho	6	Belly Fat	1	Raw	66.4	10.7	1.73	.67	1.46	3.86	.090	1
49	Salmon, coho	7	Eggs	1	Raw	63.0	4.7	2.73	.50	1.04	4.27	.113	11
49	Salmon, coho	9		1	Raw	73.4	4.8	1.46	.31	.97	2.75	.064	1
60	Smelt, human food	1	Whole	1	Raw	73.6	6.1	.82	.28	.44	1.54	.090	4
60	Smelt, human food	2	Drawn	1	Raw	76.5	3.5	.87	.37	.70	1.94	.057	1
64	Suckers	1	Whole	1	Raw	74.2	3.8	.67	.27	.55	1.49	.077	48
66	Sunfish	1	Whole	1	Raw	74.9	2.6	.18	.00	1.20	1.38	.156	1
67	Smallmouth bass	1	Whole	1	Raw	74.4	1.1	.11	.08	.06	.25	.000	1
67	Smallmouth bass	3	Dressed	1	Raw	73.6	5.9	2.77	.52	.95	4.24	.082	1
70	Whitefish, Comm	1	Whole	1	Raw	65.5	14.3	.81	.28	.54	1.63	.283	12
70	Whitefish, Comm	3	Dressed	1	Raw	63.1	16.2	1.09	.31	.64	2.03	.260	18
76	Yellow perch	1	Whole	1	Raw	74.0	2.1	.35	.11	.19	.65	.017	2
76	Yellow perch	2	Drawn	1	Raw	76.0	3.7	.60	.28	.76	1.64	.061	5
76	Yellow perch	3	Dressed	1	Raw	76.2	2.7	.39	.40	.31	1.10	.034	4
78	Yellow pike	1	Whole	1	Raw	80.5	.3	1.42	.48	1.15	3.05	.000	1
78	Yellow pike	3	Dressed	1	Raw	71.2	5.3	.96	.31	.51	1.78	.053	2

APPENDIX IV, TABLE 5

CONCENTRATIONS OF PESTICIDES FOUND IN FISH COLLECTED IN LAKE MICHIGAN IN ILLINOIS*

Sample Location	PPM (parts per million) pesticides in fish flesh							
	p,p'-DDT	TDE	o,p-DDT	o,p-DDE	p,p'-DDE	Dieldrin	Heptachlor Epoxide	Total DDT
I. Chicago (Yellow perch, 5F) 9.0-10.0 inches	.309	.162	.104	.063	.520	.072	.097	1.16
II. Chicago (Yellow perch, 5M) 8.5-10.0 inches	.490	.224	.138	.064	.554	.075	.081	1.47
III. Chicago (Yellow perch, 5F) 9.0-9.5 inches	.252	.139	.106	.045	.374	.060	.054	0.92
IV. Chicago (Yellow perch, 5M) 9.0-9.5 inches	.578	.233	.149	.075	.611	.069	.060	1.65
V. Waukegan (GLNTC) (Coho salmon, 4M) 24.5-31.0 inches	.561	.330	.152	.081	.973	.036	.027	2.10
VI. Waukegan (GLNTC) (Coho salmon, 4M) 28.0-29.0 inches	.420	.225	.151	.060	.865	.032	.021	1.72
VII. Waukegan (GLNTC) (Coho salmon, 3F) 26.0-27.5 inches	.33	.21	.12	.06	.76	.029	.018	1.48
VIII. Chicago (Div Hbr) (Coho salmon, 2F) 25.0-27.5 inches	.47	.24	.12	.09	.91	.026	.023	1.83

* Data from the Illinois Environmental Protection Agency
Chubs collected in December, 1970; all others collected November, 1970

APPENDIX IV, TABLE 5

CONCENTRATIONS OF PESTICIDES FOUND IN FISH COLLECTED
IN LAKE MICHIGAN IN ILLINOIS
continued

Sample Location	PPM (parts per million) pesticides in fish flesh							
	p,p'-DDT	TDE	o,p-DDT	o,p-DDE	p,p'-DDE	Dieldrin	Heptachlor Epoxide	Total DDT
IX. Waukegan (Chubs, 5M & F) 10.5-11.5 inches	1.08	.35	.43	.29	1.30	.056	.080	3.45
X. Waukegan (Chubs, 5M & F) 10.5-11.5 inches	.96	.26	.34	.27	1.17	.092	.101	3.00
XI. Chicago (Div Hbr) (Brown trout, 3F) 17.5-20.5 inches	.78	.53	.31	.15	1.26	.041	.016	3.04

APPENDIX IV, TABLE 6

PCB - PESTICIDE RESIDUES IN LAKE TROUT FROM LAKE MICHIGAN - 1971

		Residue (ug/g)[1]		Residue, ug/g[2]					
Sample	No.	DDE	Total	DDE	DDD	DDT	Total	PCBs	PCB/"DDT"
Fish	1	7.8	11.3	3.1	0.8	2.4	6.3	10.0	1.6
	2	8.4	13.0	4.8	0.8	3.5	9.1	9.6	1.0
	3	17.2	26.3	5.5	1.0	4.3	10.8	21.0	2.0

[1] Data from Great Lakes Fishery Laboratory. No PCB separations were made prior to analysis.

[2] Data from Fish-Pesticide Research Laboratory. PCB separated from pesticides with silicic acid column chromatography.

APPENDIX IV, TABLE 7

RELATIVE PCB - PESTICIDE RESIDUES IN LAKE TROUT FRY AND EGGS FROM LAKE MICHIGAN - 1971

		DDE[1]	Residue, ug (in sample)[2]					
Sample	No.	(ug/g)	DDE	DDD	DDT	Total	PCBs	PCB/"DDT"
Eggs	1	2.0	0.3	0.0	0.1	0.4	0.7	1.7
	2	3.9	1.0	0.2	0.6	1.8	2.6	1.4
	3	2.0	0.7	0.1	0.3	1.1	2.9	2.6
Fry	1	1.5	0.9	0.1	0.5	1.5	3.3	2.3
	2	1.3	1.0	0.1	0.4	1.5	2.7	1.8
	3	1.8	1.0	0.0	0.4	1.4	1.4	1.0

[1] Data from Great Lakes Fishery Laboratory. No PCB separations were made prior to analysis.

[2] Data from Fish-Pesticide Research Laboratory. PCBs were separated with silicic acid column chromatography. Sample size was not available, thus residues are expressed as amount in sample.

APPENDIX IV, TABLE 8

PCB - DDT RESIDUES IN FISH FROM THE GREAT LAKES REGION
1970
(concentrations in ppm)

No.	Species/Location	o,p' isomers			p,p isomers				PCBs					PCB/
		DDE	DDD	DDT	DDE	DDD	DDT	Total	1232	1248	1254	1260	Total	"DDT"
7*	Bloater Lake Michigan Sheboygan, Wis	0.29	0.01	0.55	2.09	0.14	2.15	5.23	1.2	1.9	3.2	1.5	8	1.7
34*	Carp Lake Huron Bay Port, Mich	0.01	0.10	0.02	0.18	0.38	0.02	0.71	7.8	2.5	0.6	-	11	15.5
35*	White perch Lake Ontario Port Ontario, NY	0.05	0.10	0.05	0.28	0.48	0.61	1.57	12.9	-	4.6	1.2	19	11.9
1*	Coho salmon Lake Michigan Manistee, Mich	0.4	0.5	-	4.3	0.8	2.3	8.3	-	6.7	6.7	-	13	1.6
2**	Lake trout Lake Michigan Little Bay de Noc, Mich	0.9	1.8	-	13.0	1.8	5.2	22.7	-	12.0	16.0	-	28	5.4

* 1970 National Pesticide Monitoring Program - Cross-check analyses.
** Samples from Great Lakes Fishery Laboratories

APPENDIX V

CHLORINATED HYDROCARBON INSECTICIDES IN MUNICIPAL WASTEWATER EFFLUENTS

APPENDIX V, TABLE 1

SEWAGE TREATMENT PLANTS*(ppt)
(Final Effluent, Unless Otherwise Indicated)

Municipality	Lab. No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Other Products	Remarks
BROWN COUNTY							
DePere	441	7/09/69	10	none	none		5 hour (composite)
Green Bay	600	8/18/69	10	none	none	Strong peak at Aldrin	24 hour (composite)
CALUMET COUNTY							
Chilton	603	9/10/69				PCB interference	6 hours, composite
New Holstein	585	9/10/69	10	33		Strong peak at Aldrin - PCB's	Grab
COLUMBIA COUNTY							
Portage	176	2/05-06/69				PCB's	24 hour, raw
Portage	177	2/05-06/69				PCB's	24 hour, primary effluent
Portage	178	2/05-06/69				PCB's	24 hour, filter effluent
Portage	179	2/05-06/69				PCB's	24 hours
Portage	180	2/05/69				Interference	Grab
Portage	181	2/05/69				Interference	Grab
Portage	182	2/05/69				PCB's	Grab
Portage	183	2/06/69				PCB's	Grab
DOOR COUNTY							
Forestville	601	8/19/69	10	none	none	Strong peak at Aldrin and Lindane	Grab
Sturgeon Bay	607	8/19/69	5	none	none		5 hour, composite
FOND DU LAC COUNTY							
Brandon	597	8/13/69	10	none	none	Strong peak at Aldrin and Lindane	4 hour, composite
Fond du Lac	440	7/07/69	10	none	none	Strong peak at Aldrin and Lindane	5 hour, composite
Ripon	596	8/13/69	10	none	none	Strong peak at Aldrin and Lindane	4 hour, composite
GREEN LAKE COUNTY							
Berlin	471	6/25/69	20	none	none		4 hour, composite
Green Lake	469	6/25/69	5	15	5.8		6 hour, composite
KENOSHA COUNTY							
Kenosha	272	5/02/69	5	42	17		6 hour, composite
Kenosha	690	1/29/70	10	124	none		Grab
Somers	799	6/23/70	10	50	none		Grab

* Data from the Wisconsin Department of Natural Resources

APPENDIX V, TABLE 1

SEWAGE TREATMENT PLANT*(ppt)
(Final Effluent, Unless Otherwise Indicated)
CONTINUED

Municipality	Lab. No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Other Products	Remarks
KEWAUNEE COUNTY							
Algoma	586	8/22/69	10	180	none		24 hour, composite
Kewaunee	579	8/22/69	10	1,180	none	Strong peak at Aldrin	24 hour, composite
MANITOWOC COUNTY							
Kiel	604	9/10/69	5	15	none		5 hour, composite
Manitowoc	595	8/05/69	20	none	none	Strong peaks at Lindane and Heptachlor Epoxide	4 hour, composite
Two Rivers	591	8/05/69	10	none	none		4 hour, composite
Valders	582	8/05/69	10	100	30	Strong peak at Aldrin	4 hour, composite
MARINETTE COUNTY							
Coleman	860	6/25/70	5	none	none	PCB's	Grab
Marinette	589	8/20/69	10	211	none		6 hour, composite
Peshtigo	588	9/21/69	10	none	none	Strong peak of Aldrin	6 hour, composite
Pound	858	6/25/70	5	none	none		Grab
MILWAUKEE COUNTY							
Milwaukee (Jones Is.)	269	4/29/69	5	42	none		2 hour, composite
Milwaukee (Jones Is.)	718	2/01-06/70	10	none	none		Composite
Milwaukee (Jones Is.)	719	2/08-14/70	10	none	none		Composite
Milwaukee (Jones Is.)	722	2/15-19/70	10	none	none		Composite
Milwaukee (Jones Is.)	721	2/22-28/70	none				Contaminated
Milwaukee (Jones Is.)	725	3/01-07/70	10	26	none	PCB's present	Composite
Milwaukee (Jones Is.)	724	3/15-21/70	10	32	none	PCB's present	Composite
Milwaukee (Jones Is.)	723	3/22-28/70	10	none	68		
Milwaukee (Jones Is.)	720	3/29- 4/04/70	none				Contaminated
Milwaukee (Jones Is.)	715	4/05-11/70	5	none	none	PCB's	Composite
Milwaukee (Jones Is.)	717	4/12-18/70	10	none	none	Unstable base line	Composite
Milwaukee (Jones Is.)	773	4/17-23/70	2	none	none		Composite
Milwaukee (Jones Is.)	774	4/19-25/70	10	102	none		Composite
Milwaukee (Jones Is.)	771	4/26- 5/02/70	10	112	none		Composite
Milwaukee (Jones Is.)	769	5/03-09/70	10	110	none		Composite
Milwaukee (Jones Is.)	770	5/10-16/70	10	29	none		Composite
Milwaukee (Jones Is.)	772	5/24-30/70	10	85	none		Composite
Milwaukee (Jones Is.)	775	5/31- 6/05/70	10	98	none		Composite
Milwaukee (Jones Is.)	821	6/07-13/70	20	none	none		Composite
Milwaukee (South Sh.)	268	4/28/69	-	-	Interference		6 hours
South Milwaukee	270	4/29/69		139	Fading base line		2 hours
South Milwaukee	688	1/28/70	25	none	none		Grab

APPENDIX V, TABLE 1

SEWAGE TREATMENT PLANTS*(ppt)
(Final Effluent, Unless Otherwise Indicated)
CONTINUED

Municipality	Lab. No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Other Products	Remarks
OCONTO COUNTY							
Gillette	592	8/28/69	10	45	none		6 hours
Oconto	581	8/28/69	10	none	none		6 hours
Oconto Falls	599	8/27/69	10	180		Strong peak at Aldrin	17 hours
OUTAGAMIE COUNTY							
Appleton	443	7/08/69	10	none	none	Peak at Lindane	7 hours
Kaukauna	593	8/18/69	2	7	none	Strong peak at Aldrin	6 hours
Kimberly	444	7/08/69	10	none	none		5 hours
Little Chute	442	7/08/69	10	none	none		5 hours
Seymour	583	8/29/69	10	120	none		7 hours
OZAUKEE COUNTY							
Cedarburg	260	4/23/69	10	none	36	Peak at Heptachlor Epoxide	
Grafton	28	8/28/68	10	none	740		Grab, raw
Grafton	40	8/28/68	10	none	415		Grab, final
Grafton	25	10/21/68	10	1,000	1,545		Grab, raw
Grafton	26	10/21/68	10	none	1,180		Grab, final
Grafton	169	1/29-30/69	10	none	400	Fading base line	24 hour, raw
Grafton	170	1/29-30/69	10	350	440	Fading base line	24 hour, primary effluent
Grafton	171	1/29-30/69	10	none	200	Fading base line	24 hour, final effluent
Grafton	172	1/29/69	20	none	none	Fading base line	Grab, final
Grafton	173	1/29/69	10	357	457	Fading base line	Grab, final
Grafton	174	1/29/69	10	none	530	Fading base line	Grab, final
Grafton	175	1/30/69	10	none	324		Grab, final
Grafton	729	4/24/69	10	none	none		
Grafton	731	4/22/70				Interference	
Port Washington	267	4/25/69				PCB's	3 hours
Port Washington	689	1/28/70				PCB's	Grab
Saukville	729	4/22/70	10	none	none		Grab

APPENDIX V, TABLE 1

SEWAGE TREATMENT PLANTS*(ppt)
(Final Effluent, Unless Otherwise Indicated)
CONTINUED

Municipality	Lab. No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Other Products	Remarks
RACINE COUNTY							
Racine	271	5/01/69	10	69	13,300		6 hours
Racine	470	6/29/69	10	70.4	184		Grab
Racine	424	7/01/69	10	none	625		6 hours
Racine	474	7/24/69	10	none	900		6 hours
Racine	697	2/04/70	50		1,100		24 hours
Racine	698	2/12/70	50	100	1,200		24 hours
Racine	699	2/20/70	50	200	1,600		24 hours
Racine	696	2/24-25/70	50	50	800		24 hours
Racine	700	3/01/70	50	200	1,400		24 hours
Racine	701	3/18/70	10	none	200		24 hours
Racine	702	3/18/70	50	none	1,750		24 hours
Racine	811	4/02/70	20	none	180		24 hours
Racine	814	4/10/70	10	none	850	)	24 hours
Racine	810	4/18/70	10	none	145	)	24 hours
Racine	813	4/19/70	10	none	270	)	24 hours
Racine	812	4/27/70	10	none	190	)	24 hours
Racine	809	5/05/70	10	none	710	)	24 hours
Racine	820	5/13/70	10	none	280	) Aldrin	24 hours
Racine	817	5/21/70	10	none	450	)	24 hours
Racine	816	5/29/70	10	none	410	)	24 hours
Racine	819	6/01/70	10	none	180	)	24 hours
Racine	818	6/09/70	10	none	330	)	24 hours
Racine	815	6/17/70	10	none	300	)	24 hours
Racine	800	6/23/70	10	none	320	PCB's	24 hours
SHAWANO COUNTY							
Shawano	584	8/27/69	10	none	none	PCB's	19 hours
SHEBOYGAN COUNTY							
Plymouth	594	8/06/69	10	1,850		PCB's	6 hours
Sheboygan Falls	598	8/06/69	10	2,700		PCB's	5 hours
WASHINGTON COUNTY							
Jackson	730	4/22/70	10	none	none		Grab
West Bend	587	7/28/69	10	88	none		4 hours
WAUPACA COUNTY							
Clintonville	590	9/09/69	10	70			20 hours
Waupaca	602	9/09/69	10	380		PCB's	Grab

APPENDIX V, TABLE 1

SEWAGE TREATMENT PLANTS*(ppt)
(Final Effluent, Unless Otherwise Indicated)
CONTINUED

Municipality	Lab. No.	Date Collected	Limit of Detectability	DDT Complex	Dieldrin	Other Products	Remarks
WINNEBAGO COUNTY							
Neenah-Menasha	445	7/07/69	50	none	none	PCB's	6 hours
Oshkosh	446	7/07/69	10	none	none		5 hours
Oshkosh	713	2/03-04/70	10	130	none		24 hours
Oshkosh	714	2/11-12/70	10	none	none	PCB's	24 hours
Oshkosh	712	2/16-17/70	10	none	none	PCB's	24 hours
Oshkosh	708	2/23-24/70	10	380	none	PCB's	24 hours
Oshkosh	710	3/03-04/70	10	360	none	PCB's	24 hours
Oshkosh	709	3/10-11/70	10	390	none	PCB's	24 hours
Oshkosh	711	3/16-17/70	10	none	none	PCB's	24 hours
Oshkosh	743	3/26-27/70	10	none	none	PCB's	24 hours
Oshkosh	742	3/31- 4/01/70	10	none	none	PCB's	24 hours
Oshkosh	739	4/08-09/70	10	none	none	PCB's	24 hours
Oshkosh	741	4/16-17/70	10	none	none	PCB's	24 hours
Oshkosh	740	4/21-22/70	10	none	none	PCB's	24 hours

APPENDIX V, TABLE 2

CONCENTRATIONS OF PESTICIDES FOUND IN SEWAGE TREATMENT PLANTS TRIBUTARY TO LAKE MICHIGAN IN ILLINOIS*
(concentrations in ppt)

Sample Location	p,p'-DDT	p,p'-TDE	o,p-DDT	p,p'-DDE	Total DDT	Heptachlor Epoxide	Dieldrin
SEWAGE TREATMENT PLANT**							
Waukegan	4.90	0.37	0.77	5.12	11.16	0.72	2.36
North Chicago	3.72	0.30	1.83	1.72	7.57	0.60	2.51
Lake Bluff	1.22	0.93	0.10	0.26	2.51	0.02	1.48
Lake Forest	1.20	0.35	0.45	1.49	3.49	0.07	2.16
Highland Park-Park Avenue	1.15	0.77	0.44	0.90	3.22	0.05	1.60
Highland Park-Ravine Drive	3.86	1.52	0.27	3.42	9.07	0.10	2.33
Highland Park-Cary Avenue	1.15	0.25	0.53	0.67	2.60	0.09	0.61

* Final effluent to Lake Michigan. Samples collected 10/23 and 11/02/70 by the Illinois Environmental Protection Agency.

** North Shore Sanitary District system

APPENDIX VI

INDUSTRIAL WASTEWATER EVALUATION OF PCBs IN LAKE MICHIGAN

APPENDIX VI

DEPARTMENT OF NATURAL RESOURCES
Box 450
Madison, Wisconsin 53701

(PCB Form Letter)

Dear Sir:

The nature of your business leads us to suspect you may have losses of polychlorinated biphenyls (PCB's) to the environment. As you probably know, current research in many parts of the world indicates that PCB's may be important in the environment as a toxicant causing significant physiological imbalances, especially in reproductive processes. Like DDT, PCB's contain chlorine, hydrogen, and carbon (chlorinated hydrocarbons), are virtually insoluble in water but soluble in fat, are extremely persistent, accumulate through food chains in fish and birds, and are found worldwide.

PCB's have a wide variety of uses because of their unique properties such as low volatility, adhesion, and resistance to fire, chemicals, oxidation, and hydrolysis. They are included in many products and formulations such as electrical insulation, fire-resistant heat transfer and hydraulic fluids, lubricants for use at high temperatures and pressures, sealants and expansion media, synthetic rubber, floor tile, printer's ink, coatings for paper and fabrics, paints, varnishes, waxes, asphalt, adhesives, resins, elastomers, and pigments.

Brand names of products containing polychlorinated biphenyls are:

American Made:		Foreign Made:
Arochlor	1100 series	Clophen
	1200 series	Fenchlor
	4000 series	Kannechlor
Chlorextol		Pyralene
Dykanol		Sovol
Interteen		
Noflamol		
Pyranol		
Pydraul		
Therminal	FR series	

While you may not be using any of the above products directly, you may be using products containing them as additives.

PCB's have been found in Lake Michigan water, sediments, fish and birds. The Federal-Interstate Conferees on Pollution of Lake Michigan and its Tributary Basin recognized the importance of each State inventoring the use of and possible losses of PCB's in the Lake Michigan Basin and have asked us to initiate the following questionnaire survey. Your responses by mail will save the necessity of having a staff member call on you for an onsite investigation. It is not our intent to ban the use of these materials, but we must become knowledgeable of possible sources to the environment.

Please answer the attached questions. Thank you for your anticipated cooperation in this matter.

Very truly yours,
Division of Environmental Protection

Thomas G. Frangos
Administrator

Attach.

Name of Business ______________________________

Address __________ ______________________

Name of Person Filling Out Questionnaire ______________________

Telephone ______________________________

QUESTIONNAIRE

1. Are you currently using any of the afore-mentioned brand named products in your products or operations?

2. Have you used any of these products in the last three years? (If no, refer to question No. 7)

3. How do you use these compounds?

Product	Pounds Per Year	Use of Product

4. Estimate your disposal/or losses of these products to the environment in pounds per year.

   A. Atmosphere
   B. Soils
   C. Sewers and Drains
   D. Dumps
   E. Incinerators
   F. Industrial Waste Haulers
   G. Other Disposal Procedures

5. Comment on disposal techniques or loss characteristics.

6. What action are you taking to reduce your losses to the environment?

7. The following products do or may contain PCB's. Do you manufacture (M), formulate (F), incorporate (I), or use (U) any of these products in your operations?

PROBABLE SOURCES

Product	PCB Component	MFI and/or U	Trade Name	Disposal/or Loss to Environment-# Per Year
Adhesives, Glues and Pastes	Additive			
Air Conditioning Systems, Units and Accessory	Capacitors, Condensors & Transformers			
Capacitors and Condensors	Fluids			
Compressors	Fluids			
Cutting Machines and Tools	Oils			
Die Casting	Oils			
Electrical Wire and Cable	Coatings			
Food and Kindred Products	Heat Transfer Fluid			
Furniture and Fixtures	Coatings			
Ink	Additives			
Lighting Fixtures & Equipment	Balasts			
Molded Rubber Products (Synthetic)	Additives			
"O" Rings	Additives			
Oils (Cutting-Hydraulic and Industrial)	Additives			
Paints and Allied Products	Additives			

Product	PCB Component	MFI and/or U	Trade Name	Disposal/or Loss to Environment-# Per Year
Plastic Molding Compounds	Additives			
Printing Chemicals	Additives			
Resins	Additives			
Rubber Lined Products	Synthetics			
Rubber Packing	Adhesives			
Rubber Specialities	Additives			
Rubber-Synthetic				
Rust Inhibitors and Removers				
Sealants and Sealers	Adhesives			
Seals	Adhesives			
Shoe Finishes and Polishes	Additives			
Sponge Rubber				
Transformers	Oils			
Vinyl	Additives			
Waxes and Polishes	Additives			

POSSIBLE SOURCES

Agricultural Chemicals and Fertilizers	Dedusters			
Asbestos and Fire Resistant Curtains	Fireproofing			
Batting	Fireproofing			
Candles	Extenders			
Canvas Products and Specialities	Fireproofing			

Product	PCB Component	MFI and/or U	Trade Name	Disposal/or Loss to Environment-# Per Year
Castings	Oils			
Cloth and Burlap	Fireproofing			
Cosmetics and Toilet Preparations	Dedusters			
Cushions	Fireproofing			
Detergents and Soaps	Dedusters			
Draperies and Curtains	Fireproofing			
Drawing Compounds				
Foundry Machinery - Equipment and Supplies	Hydraulic Fluid			
Gaskets	Additives & Adhesives			
Gummed Tape	Adhesive			
Heating Equipment and Parts	Fluids			
Hydraulic Cylinders	Fluids			
Hydraulic Drives	Fluids			
Hydraulic Presses	Fluid			
Industrial Curtains	Fireproofing			
Labels and Seals	Adhesives			
Laminated Wood Products	Adhesives			
Lubricators, Lubrication Systems and Components	Additives			
Motors (Hydraulic)	Fluids			
Paints (Strippers and Primers)	Additives			
Particle Board	Adhesives			

Product	PCB Component	MFI and/or U	Trade Name	Disposal/or Loss to Environment-# Per Year
Pesticides (Insecticides)	Carriers			
Petroleum Products	Additives			
Plasticizers	Additives			
Plastisols	Additives			
Plastic Coated Clothing	Vinyls & Plastics			
Plastic Coated Gloves	Vinyls & Plastics			
Plywood	Glues			
Pressure Sensitive Tape	Adhesive			
Printed Circuit Boards	Coatings			
Reinforced Tape	Adhesive			
Rubber Cement	Additives			
Rubber Coating (Syn)	Additives			
Rubber-Metal Bonding	Adhesives			
Rugs and Carpets	Fireproofing			
Solvents	Additives			
Stains	Additives			
Textile Specialities	Fireproofing			
Upholstery	Fireproofing			
Vacuum Pumps and Platers	Capacitors, Transformers			
Varnishes	Additives			

Product	PCB Component	MFI and/or U	Trade Name	Disposal/or Loss to Environment-# Per Year
Veneer	Adhesives			
Waxed Paper	Coatings			
Wood Fiber and Products	Adhesives			

APPENDIX VII

CHLORINATED HYDROCARBON INSECTICIDES IN STREAM SEDIMENTS

APPENDIX VII, PROCEDURE 1

PESTICIDE ANALYSIS OF SEDIMENT SAMPLES
WISCONSIN ALUMNI RESEARCH FOUNDATION

The samples were mixed and two 25 gram samples were weighed into two 150 ml beakers. One beaker was placed in an air oven at 100° C and dried for two to three days and the moisture was determined. The other sample was transferred to a Waring blender jar (one quart) and blended for two minutes with 200 ml of acetonitrile. The acetonitrile was filtered through a plug of glass wool into a one liter separatory funnel containing about 500 ml of tap water. The sample was then blended for about one-half minute with an additional 50 ml of acetonitrile and then filtered into the separatory funnel. Two hundred milliliters of petroleum ether was added to the separatory funnel and shaken for two minutes. The layers were allowed to separate and the bottom layer was drawn off. The petroleum ether extract was washed two more times with about 600 ml of tap water, discarding the water both times. Ten grams of sodium sulphate was added to the petroleum ether extract and the sample was filtered into a 300 ml erlenmeyer flask (rinse separatory funnel with about 70 ml of petroleum ether). The sample was then taken down to about five ml on a steam bath. The sample was then run through a florisil column using 20 grams of florisil and 150 ml of five percent ether in petroleum ether and 250 ml of 15 percent ether in petroleum ether. The column elutions were made up to 25 ml with hexane. Ten microliters or less of the cleaned-up extract was injected into a gas chromatograph.

APPENDIX VII, TABLE 1

PESTICIDES IN STREAM SEDIMENTS*
July, 1969
Data in mg/l

Sample No.	Location	Total DDT	Dieldrin	Est PCB
1	East River	1.07	.001	0.50
2	Big Suamico River	.001	.001	0.01
3	Little Suamico River	.006	.001	0.02
4	Pensaukee River	.023	.001	0.05
5	Oconto River	.002	.001	0.01
6	Peshtigo River	.002	.001	0.01
7	Menominee River	.001	.001	0.01
8	Mud Lake Creek	.001	.001	0.01
9	Clark Lake Creek	.011		.028
10	N Jacksonsport Creek	.003	.001	0.01
11	Kangaroo Lake Creek	.015	.001	0.01
13	Stony Creek	.019	.001	0.03
14	Ahnapee River	.102	.001	1.10
15	Kewaunee River	.033	.001	.035
16	East Twin River	.079	.001	.21
17	West Twin River	.035	.001	.052
18	Manitowoc River	.037	.001	.12
19	Silver Creek	.016		.01
20	Calvin Creek	.082	.001	.01
21	Pine Creek	.008		.033
22	Point Creek	.026	.001	.015
23	Fisher Creek	.042	.001	.021
25	Seven Mile Creek	.067	.001	
26	Pigeon River	.053		.036
27	Sheboygan River	.173	.001	7.2
28	Black River	.011		.052
29	Sauk Creek	.067	.001	.065
30	Milwaukee	.082	.040	3.2
31	Menominee River	.114	.040	4.4
33	Root Creek	.069	.004	.075
34	Pike River	.137	.002	.20
35	Barnes Creek	.010		.013
36	Calumet River at Calumet City	.063	.004	1.25
37	Burns Ditch	.017	.001	.021
38	Trail Creek	.143	.002	
39	Galien River	.024	.002	.060
40	Drain at Sawyer	.009		.037
41	St. Joseph River	.029	.001	.032
42	Paw Paw River	.035	.001	.08
43	Black River	.044	.005	.11
44	Kalamazoo River	.053	.001	.043
46	Pigeon River	.03	.001	.018

* Data from the Wisconsin Alumni Research Foundation

APPENDIX VII, TABLE 1
continued
Data in mg/1

Sample No.	Location	Total DDT	Dieldrin	Est PCB
47	Grand River	.061	.002	.17
48	Muskegon River at mouth into Muskegon Lake	.006	.001	.01
49	White River	.008	.003	.02
50	Pentwater River	.001	.001	.01
51	Pere Marquette River	.007	.001	.01
52	Manistee River	.001	.001	.01
53	Betsie River	.012	.001	.01
54	Platte River	.011	.001	.01
56	Leelanan Lake	.005	.001	.01
57	Boardman River	.008	.001	.01
59	Lake Charlevoix	.008	.001	.01
60	Bear River, Petoskey	.006	.001	.01
61	Millecoquins Creek	.002	.001	.01
62	Manistique River	.114	.001	.80
63	Sturgeon River	.003	.001	.01
64	Whitefish River	.007		.04
65	Escanaba River	.069	.001	1.46
66	Ford River	.007	.001	.03

APPENDIX VIII

FIVE STATE PESTICIDE LEGISLATION

APPENDIX VIII, TABLE 1

STATUS OF LEGISLATION ACCEPTING PESTICIDE USAGE
IN THE LAKE MICHIGAN BASIN

Compiled by the Governor's Interdisciplinary Committee on Pesticides

INDIANA

Agency Responsible for Registration, Labelling - State Chemist

Body Responsible for Regulations, Rules - State Chemist and Pesticide Review Board

Composed of: One Representative State Board of Health
One Representative Department of Natural Resources
One Representative Purdue University Agricultural Experiment Station
One Representative Indiana Cooperative Extension Service - Voting Members
State Toxicologist
State Veterinarian
A Terrestrial Ecologist
An Aquatic Ecologist
One Public Representative
One Pesticide Industry Representative
Two Public Representatives from Conservation Organization - Members

Restricted Pesticides Use by Permit Only - Yes

Commercial Applicators Licensed or Approved
- Aerial - Yes - Approval for private applicators only for restricted pesticides
- Aquatic - Yes - Approval for private applicators only for restricted pesticides
- Brush Control & Soil Sterilent - Yes - Approval for private applicators only for restricted pesticides
- Mosquitoes - Yes - Approval for private applicators only for restricted pesticides
- Space Fumigation - Yes - Approval for private applicators only for restricted pesticides
- Structural Pest - Yes - Approval for private applicators only for restricted pesticides
- Vertebrate Control - Yes - Approval for private applicators only for restricted pesticides
- Pests of Animals - No
- Field Crops - Yes - Approval for private applicators only for restricted pesticides
- Fruit Crops - Yes - Approval for private applicators only for restricted pesticides

APPENDIX VIII, TABLE 1

STATUS OF LEGISLATION ACCEPTING PESTICIDE USAGE
IN THE LAKE MICHIGAN BASIN
continued

INDIANA CONTINUED

Lawn, Garden & Ornamental - Yes - Approval for private applicators only for restricted pesticides
Forest & Shade Tree - Yes - Approval for private applicators only for restricted pesticides

Agency Regulating Commercial Applicators - State Chemist

Regulation of Local Government Units Applying Pesticides - No

Licensing of Dealers Handling Restricted Materials -

Notice of Intent to Use Pesticides-Required -

Disposal
Agency Having Authority for Regulation - Pesticide Review Board
Disposal Sites Approved by State -
Adequate Incineration - No
Guidelines Developed - No

Basic Memorandum of Agreement Signed with USDA re Toxic Pesticides - Yes

Supplemental Memorandum of Agreement Signed with USDA re Ethyl Parathion - Yes

Agency Testing for Pesticide Residues in Food - Public Health

APPENDIX VIII, TABLE 2

STATUS OF LEGISLATION ACCEPTING PESTICIDE USAGE IN THE LAKE MICHIGAN BASIN

Compiled by the Governor's Interdisciplinary Committee on Pesticides

ILLINOIS

Agency Responsible for Registration, Labelling - Agriculture

Body Responsible for Regulations, Rules - Agriculture & Public Health
Interagency Committee must advise and recommend.
Interagency Committee Composed of: Director, Dept of Agriculture
Director, Dept of Conservation
Director, Dept of Public Health
Director, Dept of Public Works and Buildings
Director, Environmental Protection Agency
Chief, Illinois Natural History Survey
Dean, College of Agriculture

Restricted Pesticides Use by Permit Only - Yes - DDT Only

Commercial Applicators Licensed or Approved
- Aerial - Yes
- Aquatic - Yes
- Brush Control & Soil Sterilent - Yes
- Mosquitoes - No
- Space Fumigation - No
- Structural Pest - No
- Vertebrate Control - No
- Pests of Animals - No
- Field Crops - Yes
- Fruit Crops - Yes
- Lawn, Garden & Ornamental - Yes
- Forest & Shade Tree - Yes

Agency Regulating Commercial Applicators - Agriculture

Regulation of Local Government Units Applying Pesticides - No

Licensing of Dealers Handling Restricted Materials -

Notice of Intent to Use Pesticides-Required -

Disposal
- Agency Having Authority for Regulation - Agriculture and Public Health
- Disposal Sites Approved by State - Yes
- Adequate Incineration - No
- Guidelines Developed - Yes

APPENDIX VIII, TABLE 2

STATUS OF LEGISLATION ACCEPTING PESTICIDE USAGE
IN THE LAKE MICHIGAN BASIN
continued

ILLINOIS CONTINUED

Basic Memorandum of Agreement Signed with USDA re Toxic Pesticides - Yes

Supplemental Memorandum of Agreement Signed with USDA re Ethyl Parathion - Yes

Agency Testing for Pesticide Residues in Food - Agriculture and Public Health

APPENDIX VIII, TABLE 3

STATUS OF LEGISLATION ACCEPTING PESTICIDE USAGE
IN THE LAKE MICHIGAN BASIN

Compiled by the Governor's Interdisciplinary Committee on Pesticides

MICHIGAN

Agency Responsible for Registration, Labelling - Agriculture

Body Responsible for Regulations, Rules - Agriculture

Restricted Pesticides Use by Permit Only - Yes - DDT Only

Commercial Applicators Licensed or Approved
- Aerial - Yes
- Aquatic - Yes
- Brush Control & Soil Sterilent - Yes
- Mosquitoes - Yes
- Space Fumigation - Yes
- Structural Pest - Yes
- Vertebrate Control - Yes
- Pests of Animals - Yes
- Field Crops - Yes
- Fruit Crops - Yes
- Lawn, Garden and Ornamental - Yes
- Forest and Shade Tree - Yes

Agency Regulating Commercial Applicators - Agriculture

Regulation of Local Government Units Applying Pesticides - No

Licensing of Dealers Handling Restricted Materials - Yes - Statutory Authority for Licensing of dealers; currently being implemented.

Notice of Intent to Use Pesticides-Required -

Disposal
- Agency Having Authority for Regulation -
- Disposal Sites Approved by State -
- Adequate Incineration - Limited private facilities available
- Guidelines Developed - Yes

Basic Memorandum of Agreement Signed with USDA re Toxic Pesticides -

Supplemental Memorandum of Agreement Signed with USDA re Ethyl Parathion -

Agency Testing for Pesticide Residues in Food - Agriculture

APPENDIX VIII, TABLE 4

STATUS OF LEGISLATION ACCEPTING PESTICIDE USAGE
IN THE LAKE MICHIGAN BASIN

Compiled by the Governor's Interdisciplinary Committee on Pesticides

MINNESOTA

Agency Responsible for Registration, Labelling - Agriculture

Body Responsible for Regulation, Rules - Agriculture and Department of Natural Resources Admin Order

Restricted Pesticides Use by Permit Only - Yes

Commercial Applicators Licensed or Approved
- Aerial - Yes
- Aquatic - Yes
- Brush Control & Soil Sterilent - Yes
- Mosquitoes - Yes
- Space Fumigation - Yes
- Structural Pest - Yes
- Vertebrate Control - Yes
- Pests of Animals - Yes
- Field Crops - Yes
- Fruit Crops - Yes
- Lawn, Garden & Ornamental - Yes
- Forest and Shade Tree - Yes

Agency Regulating Commercial Applicators - Agriculture

Regulation of Local Government Units Applying Pesticides - Yes

Licensing of Dealers Handling Restricted Materials - 1/1/72

Notice of Intent to Use Pesticides-Required -

Disposal
- Agency Having Authority for Regulation - Agriculture and Pollution Control Agency
- Disposal Sites Approved by State -
- Adequate Incineration - No
- Guidelines Developed - Yes

Basic Memorandum of Agreement Signed with USDA re Toxic Pesticides - Yes

Supplemental Memorandum of Agreement Signed with USDA re Ethyl Parathion - Yes

Agency Testing for Pesticide Residues in Food - Agriculture

APPENDIX VIII, TABLE 5

STATUS OF LEGISLATION ACCEPTING PESTICIDE USAGE

IN THE LAKE MICHIGAN BASIN

Compiled by the Governor's Interdisciplinary Committee on Pesticides

WISCONSIN

Agency Responsible for Registration, Labelling - Agriculture

Body Responsible for Regulations, Rules - Agriculture, Department of Natural Resources and Public Health -
Pesticide Review Board Concurs on Regulations to be Adopted.
Pesticide Review Board Composed of: Heads of three agencies listed.
Technical Council is advisory to Pesticide Review Board.
Technical Council composed of: One Representative From Agriculture, Natural Resources and Public Health
Three Representatives from the University of Wisconsin (one each from College of Agriculture and Life Sciences, Water Resources Center, and School of Natural Resources)
Three Citizen Members (one representing each the Pesticide Industry, the Agricultural Industry, and Conservation interests)

Restricted Pesticides Use by Permit Only - Yes

Commercial Applicators Licensed or Approved
- Aerial - No
- Aquatic - No - Commercial Applicators are not licensed but are required by law to do all work under the immediate supervision of a representative of the Department of Natural Resources
- Brush Control & Soil Sterilent - No
- Mosquitoes - No
- Space Fumigation - No
- Structural Pest - No
- Vertebrate Control - No
- Pests of Animals - No
- Field Crops - No
- Fruit Crops - No
- Lawn, Garden & Ornamental - No
- Forest and Shade Tree - No

Agency Regulating Commercial Applicators - By Administrative Code the Department of Agriculture requires commercial applicators of pesticides to register annually with the Department and submit information of the amounts and kinds of pesticides used or sold.

Regulation of Local Government Units Applying Pesticides - No

Licensing of Dealers Handling Restricted Materials - Dealers are not licensed by the Administrative Code are required to register with the Department of Agriculture to be eligible to sell restricted-use pesticides and they must report amounts and kinds of such pesticides sold during the preceding calendar year.

Notice of Intent to Use Pesticides-Required - Yes

Disposal
- Agency Having Authority for Regulation - Department of Natural Resources
- Disposal Sites Approved by State -
- Adequate Incineration - No
- Guidelines Developed - Yes

Basic Memorandum of Agreement Signed with USDA re Toxic Pesticides - Yes

Supplemental Memorandum of Agreement Signed with USDA re Ethyl Parathion - Yes

Agency Testing for Pesticide Residues in Food - Agriculture

1 Accession Number	2 Subject Field & Group	**SELECTED WATER RESOURCES ABSTRACTS** INPUT TRANSACTION FORM
W		

5 *Organization*

Wisconsin Department of Natural Resources
Illinois Environmental Protection Agency
Michigan Water Resources Commission and Indiana Nat. Res. Department

6 *Title*

An Evaluation of DDT and Dieldrin in Lake Michigan

10 *Author(s)*

Lloyd A. Lueschow

16 *Project Designation* Environmental Protection Agency Grant 16050 EYV, ESP, EPV, and EYS.

21 *Note*

22 *Citation*

Environmental Protection Agency report number EPA-R3-72-003, August 1972.

23 *Descriptors (Starred First)*

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25 *Identifiers (Starred First)*

Pesticide-Monitoring, Tributaries of Lake Michigan in Wisconsin, Illinois, Indiana, Michigan

27 *Abstract*

The presence of pesticides and particularly the chlorinated hydrocarbon insecticides in Lake Michigan water is responsible for biological accumulations that affect a wide variety of legitimate uses. The data collected from waters, wastewaters, invertebrate organisms and fish all suggest that DDT plus analogs and dieldrin are observed consistently at levels that warrant concern from both a public health and wildlife preservation standpoint. The sources of these chlorinated hydrocarbon insecticides include not only industrial and wastewater effluents but also diffuse sources such as from agricultural activities and municipal pest control programs.

The evaluation of the chlorinated hydrocarbon insecticides in both wastewater and biological specimens is complicated by the presence of products such as polychlorinated biphenyls and phthalates. These products interfere with the analysis for the target insecticide and indeed, have biological implications of their own.

This report is submitted in fulfillment of four cooperative grants to the Lake Michigan Enforcement Conference participating states under the sponsorship of the Environmental Protection Agency and include grant numbers 16050 EYV, 16050 EYS, 16050 EPV, and 16050 ESP.

Abstractor	Institution
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