

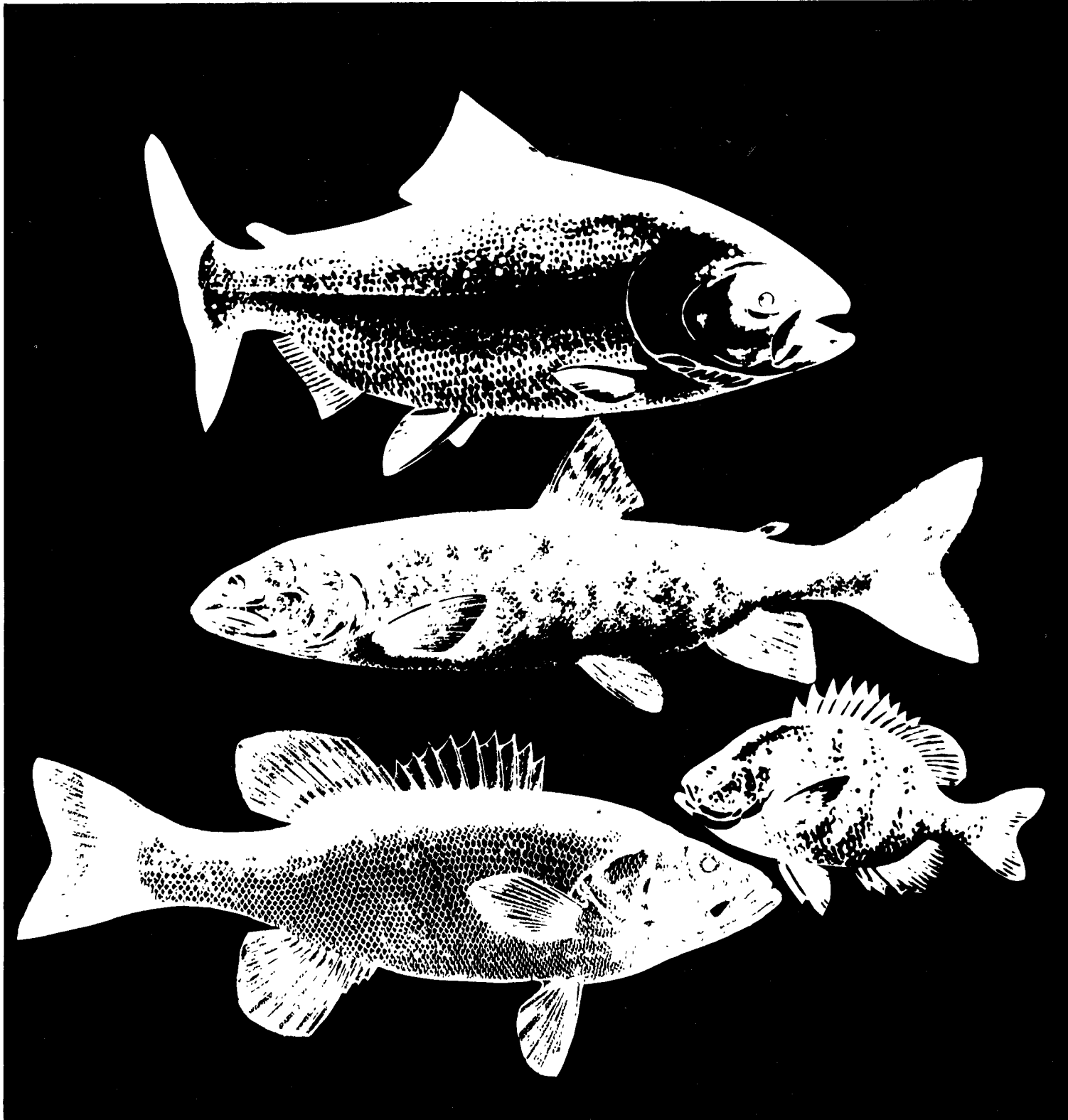
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Great Lakes National
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Contaminants in Fish From Great Lakes Harbors and Tributary Mouths 1980-81



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Contaminants in Fish From Great Lakes
Harbors and Tributary Mouths 1980-81

by

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FOREWORD

The Great Lakes National Program Office (GLNPO) of the U.S. Environmental Protection Agency was established in Region V, Chicago to focus attention on the significant and complex natural resource represented by the Great Lakes.

GLNPO implements a multi-media environmental management program drawing on a wide range of expertise represented by universities, private firms, State, Federal and Canadian governmental agencies and the International Joint Commission. The goal of the GLNPO program is to develop programs, practices and technology necessary for a better understanding of the Great Lakes system and to eliminate or reduce to the maximum extent practicable the discharge of pollutants into the Great Lakes system. The GLNPO also coordinates U.S. actions in fulfillment of the Agreement between Canada and the United States of America on Great Lakes Water Quality of 1978.

This study was carried out under a cooperative agreement between GLNPO, and the States of Ohio, and Wisconsin. The samples were collected by state personnel and analyzed by USEPAs Central Regional Laboratory data analysis and program coordination was provided by GLNPO.

ABSTRACT

Composite fish samples collected from Great Lakes Harbors and Tributaries between 1980 and 1981 were analyzed by gas chromatography-electron capture detector and gas chromatographic-mass spectrometry for a wide range of pesticides and priority pollutants. Severe PCB contamination was observed in Sheboygan River fish with moderate to severe PCB contamination in samples from the Milwaukee, Kinnickinnic, Fox, and Ashtabula Rivers. The Ashtabula River samples also contained several chlorinated aromatic and aliphatic hydrocarbons. Polynuclear aromatic hydrocarbons were detected in fish from the Black, Kinnickinnic and Menominee Rivers, while a number of benzene derivatives were observed in samples from the Fox and Wolf Rivers.

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INTRODUCTION

The Great Lakes Fish Monitoring Program (GLFMP) is a cooperative program between the U.S. Environmental Protection Agency, Great Lakes National Program Office (GLNPO), U.S. Fish and Wildlife Service (USFWS), U.S. Food and Drug Administration (USFDA) and the eight Great Lakes states. It is designed to provide a coordinated approach to monitoring contaminants in Great Lakes fish. The GLFMP consists of 3 elements to: (1) monitor temporal and spacial trends in contaminants known to be a problem in Great Lakes fish, (2) evaluate the potential exposure of the fish consuming public to hazardous contaminants, (3) locate source areas of PCB and other known contaminants in the Great Lakes and to detect emerging problems and previously unknown contaminants before the entire lake ecosystem is affected.

This report presents data from a limited number of analysis performed under element 3 of this program. Samples from Astabula River (Ohio), Black River (Ohio), Sheboygan River (Wisconsin), Memonimee River (Wisconsin), Kinnickinic River (Wisconsin), Fox River (Wisconsin), Wolf River (Wisconsin) and Chequamegon Bay (Lake Superior, Wisconsin) were analyzed for PCB and common pesticides by gas- liquid chromatography electron capture detection (GC/EC) as well as scanned for over 100 priority pollutants using gas chromatography - mass spectrometry (GC/MS).

METHODS

State personnel collected indigenous fish from harbor and tributary mouth sites in the Great Lakes basin using gillnets, trap nets, electro-shock and other conventional methods. Individual fish were weighed, measured for length and wrapped in solvent rinsed aluminum foil in the field. Fish were then frozen and shipped to the US Environmental Protection Agency's (USEPA) Central Regional Laboratory (CRL) in Chicago for compositing and analysis.

Table 1 gives the mean size, weight and collection date of the composite samples. After composite groupings were formed, each fish was chopped into 2 to 3 inch cubes with a meat cleaver or butcher saw and ground twice in a solvent washed Hobart meat grinder. The ground fish was then thoroughly mixed and stored in glass until analysis (EPA 1979a). Some samples were composited and ground by state personnel, using similar procedures, prior to shipment to CRL.

In CRL the samples were dried with anhydrous Na_2SO_4 and Soxhlet extracted with 1:1 acetone/hexane for 16 hours. The extract was then concentrated to 10 ml in a Kuderna-Danish concentrator. Two mls of the concentrate was transferred to a pre-tared aluminum pan and the solvent evaporated for lipid determination. Lipids were removed from the remaining extract by gel permeation chromatography using 100% ethyl acetate (EPA 1979a). The elutriate from the gel permeation unit was divided into 2 aliquots, 1 for GC/MS analysis for priority pollutants and 1 for GC/EC analysis for PCBs and pesticides.

TABLE 1
SAMPLE COLLECTION DATA

Sample Number	Site Location	Collection Date	Species	# Fish/ Sample	Mean Length (Range)(MM)	Mean Weight (Range) (G)	% Lipid
1S82	Black River, Ohio	10/21/81	carp	3	464.0 (422-493)	1391.7 (1025-1700)	10.0
1S88	Ashtabula River, Ohio	10/28/81	northern pike	1	520.0 (NA)	1724.0 (NA)	6.7
1S90	Ashtabula River, Ohio	10/28/81	blue gill	3	148.0 (144-154)	53.0 (41-60)	4.4
1S95	Ashtabula River, Ohio	10/28/81	brown bullhead	3	262.0 (232-286)	267.7 (170-325)	6.5
1S97	Ashtabula River, Ohio	10/28/81	yellow bullhead	1	152.0 (NA)	130.0 (NA)	1.9
1S02	Sheboygan River, Wis.	9/30/80	carp	1	640.1 (NA)	3950.0 (NA)	8.0
1S01	Sheboygan River, Wis.	9/30/80	carp	3	408.9 (NA)	1430.0 (NA)	8.7
0S99	Sheboygan River, Wis.	9/30/80	northern pike	2	708.7 (NA)	2750.0 (NA)	10.1
2S09	Milwaukee River, Wis.	7/15/81	red Horse Sucker	15	243.8 (NA)	200.0 (NA)	2.2
2S10	Milwaukee River, Wis.	7/15/81	black Crappie	3	182.9 (NA)	200 (NA)	3.7
2S04	Menominee River, Wis.	8/15/81	carp	5	639.6 (604-704)	4170.0 (3600-5400)	33.2
1S99	Menominee River, Wis.	8/15/81	bullhead	5	283.4 (254-300)	350.0 (300-450)	2.2
1S98	Kinnickinic River, Wis.	7/15/81	carp	3	559.0 (508-599)	12433.0 (12200-12800)	22.8
1S11	Wolf River, New London Wis.	9/15/80	carp	5	566.4 (NA)	2100.0 (NA)	9.6
1S09	Wolf River, New London Wis.	9/15/80	walleye	3	442.0 (NA)	800.0 (NA)	6.2
1S14	Fox River above DePere, Wis.	10/10/80	carp	5	406.0 (NA)	900.0 (NA)	3.1
2S14	Fox River, at Mouth	11/15/81	carp	5	427.0 (410-445)	1090.0 (900-1250)	8.3

1S12	Fox River, above Depere, Wis.	10/15/80	rock bass	5	177.8 (NA)	160.0 (NA)	3.2
1S07	Fox River, below DePere, Wis.	10/15/80	carp	5	452.0 (NA)	1400.0 (NA)	10.9
1S06	Fox River, below DePere, Wis.	10/15/80	walleye	5	383.5 (NA)	400.0 (NA)	10.7
1S16	Chequamegan Bay Ashland, Wis.	8/15/80	white sucker	5	463.0 (NA)	960.0 (NA)	4.3
1S15	Chequanegan Bay, Ashland, Wis.	8/15/80	Walleye	5	462.3 (NA)	1000.0 (NA)	8.3

The GC/MS portion of the extract was screened by a Varian 2700 gas chromatograph equipped with a flame photometric detector to determine the sample volume adjustments required for GC/MS analysis as well as what, if any, additional cleanup was required (EPA 1979a). This was then analyzed by a Hewlett-Packard 5985 automated gas chromatograph/mass spectrometer using the following operating conditions (EPA 1979b):

Column: 30m x 0.2mm SE-54 fused silica capillary
Carrier Gas: Helium at 25 cm/sec.
Mass Range: 45-450 AMU
Electron voltage: 70 EV
Temperature Program: T₁ = 50°C for 1 min.
T₂ = 300° for 20 min.
rate: 100°C to 300°C by 10°C/min.

Priority pollutants were identified and quantified by the Hewlett-Packard 5985 Quantid program. This program uses the response factor for the internal standard (D10-phenanthrene) and the external standard in the base/neutral or acidic standard mixture. Unknown peaks which were 10 percent above baseline noise were identified by computer or manual search of the NBS and Wiley mass spectral libraries. Identification required a match of at least 5 major ion peaks. Compounds identified in this process are indicated as tentative (T) in Table 4 as they were not compared with authentic standards. Quantitation of tentative compounds was estimated on the basis of a 1 point internal standard calibration procedure (EPA 1979b). Table 2 lists those compounds for which authentic standards were used.

The second aliquot from the gel permeation unit was separated into a mixed and a pesticide fraction on a activated Florisil column by eluting first with 6% diethyl ether in hexane and, secondly, with 50% diethyl ether in hexane. The second fraction was refrigerated for later pesticide analysis. The first fraction was further separated into a PCB and a pesticide fraction on silica gel by eluting first with hexane (PCB fraction) and secondly with

TABLE 2
Compounds Scanned by GC/MS

Bis (2-Chloroethyl) Ether	2-Chlorophenol	*Triflan(Trifluralin)
1,3-Dichlorobenzene	*2,4-Dimethylphenol	*2,4,D-Isopropyl Ester
1,4-Dichlorobenzene	2-Nitrophenol	Alpha BHC (A-BHC)
1,2-Dichlorobenzene	2,4-Dichlorophenol	*Beta-BHC (B-BHC)
Nitrobenzene	P-T-Butylphenol	*Gama-BHC (G-BHC)
Hexachloroethane	P-Chloro-M-Cresol	Heptachlor
N-Nitrosodipropylamine	2,4,6-Trichlorophenol	*Aldrin
Isophorone	4-Nitrophe	*Dieldrin
Bis(2-Chloroethoxy) Methane	4,6-Dinitro-Ortho Cresol	*DCPA (Dacthal)
1,2,4-Trichlorobenzene	Pentachlorophenol	*Isodrin
Naphthalene	Hexachlorobutadiene	*Heptachlor Epoxide
2-Chloronaphthalene	Acenaphthene	*Oxychlorane
Dimethylphthalate	2,4-Dinitrotoluene	*Gama Chlordane
Acenaphthylene	2,6-Dinitrotoluene	*O,P DDE
Fluorene	Diethylphthalate	*P,P DDE
N-Nitrosodiphenylamine	1,2-Diphenylhydrazine	*O,P, DDD
4-Bromophenylphenyl Ether	Hexachlorobenzene	*Endrin
*Phenanthrene/Anthracene	Di-N-Octylphthalate	*Chlorobenzilate
Di-N-Butylphthalate	Dibromobiphenyl	*Endosulfan-II
Fluoranthene	Pyrene	*O,P-DDT P,P-DDD
ButylBenzylphthalate	Chrysene/Benz(A)Anthracene	*P,P DDT
Bis(2-Ethylhexyl)Phthalate	*Benzo(B)Fluoranthene	Benzo(G,H,I)Perylene
*Benzo(A)Pyrene	*Indeno(1,2,3-C,D)Pyrene	*Kepone(Chlordecone)
*Perylene	Phenol	
*Methoxychlor	*Tetradifon	

*Computer match only. Standards are not run. All others matched and quantified with authentic standards.

20% diethyl ether in benzene (pesticides). All fractions were concentrated to the appropriate volumes and analyzed on a Perkin-Elmer (PE-3920B) dual column gas chromatograph with electron capture detectors using the following operating conditions (EPA 1979b):

Channel 1:

Column: 3% SP-2100 Supelcoport
Length, Diameter: 2.4m, 3.175mm (ID)
Injection Column: 5 ul Injection Temperature: 270°C
Column Temperature: 200°C Detector Temperature: 325°C
Carrier Gas: 95% Argon/Methane (5%)
Flow Rate: 25 ml/min
Standing Current: 1

Channel 2:

Column: 1.5% SP-2250/1.9% SP-2401 on Supelcoport
Length, Diameter: 2.4m, 3.175mm (ID)
Standing Current: 1
Flow Rate: 25 ml/min

All compound analyzed by GC/EC (Table 3) were compared to Authenic Standards. The data are reported as mg/kg wet weight and are not corrected for extraction efficiency.

RESULTS

GC/EC

GC/EC analysis identified 19 pesticides and industrial compounds in the 22 composite samples analyzed (Table 3). These include compounds currently in use in the Great Lakes basin and those whose use has been banned, such as PCB and DDT, or severely restricted such as chlordane and heptachlor.

PCB's were the most predominant contaminant found, occurring in all samples at concentrations ranging from 0.175 mg/kg to 98.44 mg/kg. The highest PCB concentrations occurred in fish from the Sheboygan River with concentrations ranging from 38.60 mg/kg to 98.44 mg/kg. Elevated PCB concentrations also occurred in samples from the Fox River (2.01 mg/kg to 20.89 mg/kg), the Ashtabula River (1.72 mg/kg to 10.68 mg/kg), the Kinnickinnic River (17.73 mg/kg) and the Milwaukee River (6.63 mg/kg to 15.54 mg/kg). All samples exceeded the International Joint Commission's (IJC) objective of 0.1 mg/kg total PCB for whole fish (IJC 1978). The contribution of the individual Aroclor mixtures to the total PCB varied from site to site but was consistent between samples at each site. With the exception of carp from the Kinnickinnic River, those samples with total PCB concentrations ranging from 1.72 mg/kg to 98.44 mg/kg were dominated by Aroclor 1248. Those samples with lower total PCB concentrations were dominated by the more highly chlorinated, more persistent (Mieure et al. 1975, Sloan et al. 1983) Aroclors 1254 and 1260.

DDT and metabolites occurred in all samples with total DDT ranging from 0.023 mg/kg in bullheads from the Ashtabula River to 1.93 mg/kg in Northern pike from the Sheboygan River. Total DDT was below the IJC objective of

Table 3 cont'd
Gas Chromatographic Results for Harbor and Tributary
Mouth Fish (mg/kg)

Sample#	Menominee River		Kinnickinnic River	Wolf River		Fox River above DePere			Fox River below DePere		Chequamegon Bay	
	2S04	1S99	1S98	1S11	1S09	1S14	2S14	1S12	1S07	1S06	1S16	1S15
Aroclor 1248	2.75	0.06	5.76	<0.05	<0.05	4.81	4.72	1.29	12.90	5.58	<0.05	<0.05
Aroclor 1254	0.42	0.33	8.25	0.09	0.49	4.10	2.15	0.57	7.03	2.57	0.28	0.24
Aroclor 1260	<0.05	0.36	3.72	0.06	0.32	0.62	0.35	0.15	0.96	0.46	0.35	0.14
Total PCB	3.195	0.75	17.73	0.175	0.835	9.53	7.22	2.01	20.89	8.61	0.655	0.40
P,P-DDT	<0.002	0.01	0.06	0.08	0.02	<0.002	<0.002	0.004	<0.002	0.02	0.05	<0.002
O,P-DDT	0.16	0.03	0.17	0.07	0.02	0.05	0.02	0.003	0.02	0.05	0.01	0.06
P,P-DDE	1.10	0.14	0.85	0.05	0.08	0.31	0.04	0.02	0.17	0.22	0.11	0.05
O,P-DDE	0.26	0.07	0.36	0.01	0.01	0.13	0.02	0.04	0.07	0.32	0.05	0.05
P,P-DDD	<0.005	<0.005	<0.005	<0.005	<0.00	<0.005	<0.005	<0.005	<0.005	<0.005	0.04	<0.005
O,P-DDD	0.18	0.01	0.14	<0.005	<0.005	<0.005	0.03	0.01	<0.005	0.04	<0.005	0.04
Total DDT	1.703	0.262	1.582	0.215	0.135	0.496	0.113	0.079	0.266	0.652	0.262	0.203
G-Chlordane	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Oxychlordane	0.03	<0.002	<0.002	<0.002	0.004	0.15	0.04	0.02	0.15	0.13	0.02	0.01
Heptachlor	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Heptachlor-epoxide	0.005	0.023	0.08	0.003	0.004	0.09	0.01	0.01	0.20	0.13	0.05	0.01
B-BHC	<0.002	0.04	0.03	<0.002	0.002	0.09	0.04	0.01	0.90	<0.002	<0.002	0.01
G-BHC(Lindane)	<0.002	0.01	0.01	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002
Hexachlorobenzene	0.02	0.005	0.05	0.004	0.004	0.02	0.01	0.003	0.01	0.013	0.004	0.004
Aldrin	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Dieldrin	0.02	0.01	0.15	0.01	0.01	0.09	0.02	<0.002	0.02	0.03	0.01	<0.002
Endrin	<0.002	0.01	0.01	<0.002	<0.002	0.01	<0.002	<0.002	0.005	<0.002	<0.002	<0.002
Methoxychlor	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.12
Endosulfan II	0.02	0.03	0.01	0.03	0.01	0.02	0.02	0.02	0.01	0.04	0.01	0.03
Dacthal	0.12	0.01	0.12	0.01	0.002	0.003	0.01	<0.002	0.01	0.005	0.002	<0.002
Trifluralin	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

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1.0 mg/kg in all but 4 samples from the Sheboygan, Menominee, and Kinnickinnic Rivers. The ratio of DDE to the parent compounds varied from sample to sample, however, DDE was predominant in all but sample #1S11 (Wolf River).

One interesting result was the high proportion of O,P-DDT and O,P-DDE to the corresponding P,P isomers. The predominance of the O,P-isomer has also been observed in sediment samples from several Great Lakes location (GLNPO 1981). Several hypothesis including differential degradation rates and the possible environmental impact of O,P-DDT and O,P-DDE contaminated kelthane are under investigation.

Hexachlorobenzene was detected at low (0.003 mg/kg to 0.13 mg/kg) concentrations at all sites except the Ashtabula River where high (0.71 mg/kg to 3.47 mg/kg) concentrations occurred. Methoxychlor was detected in samples from the Sheboygan River, Fox River, and Chequamegon Bay at low (0.01 mg/kg to 0.17 mg/kg) concentrations. The pesticides aldrin/dieldrin, endosulfan, chlordane, heptachlor and BHC occurred at low levels in most samples.

The herbicides dacthal was detected in 73 percent of the samples. Concentrations of dacthal were low ranging from 0.002 mg/kg to 0.12 mg/kg. The herbicide trifluralin was detected in one sample from the Black River 0.007 mg/kg.

GC/MS Scans

In addition to providing confirmation of PCB, DDT, hexachlorobenzene and some others of the above pesticides and industrial compounds, GC/MS scans revealed the presence of several additional compounds of environmental concern (Table 4).

Chlorinated aliphatic and aromatic hydrocarbons were detected in samples from the Ashtabula River. These included dichlorobenzaldehyde, pentachlorobenzene, hexachlorobenzene, pentachlorobutadiene, hexachloroethane, hexachlorobutene and hexachlorobutadiene.

Polynuclear aromatic hydrocarbons (PAHs) were detected in samples from several sites. Chrysene or benz(a)anthracene was found in samples from the Kinnickinnic and Black Rivers at 0.10 mg/kg and 10.5 mg/kg respectively. Phenanthrene or anthracene was found in Menominee and Black River samples. Fluorene was also detected in Black River samples.

Benzene derivatives were found in a number of the Fox and Wolf River samples while pentyl furan and pentachlorophenol were detected in the Menominee River.

Table 4

Results of GC/MS Scans of Harbor and Tributary Mouth Fish (mg/kg)

	Menominee River		Kinnickinnic River	Wolf River		Fox River above DePere			Fox River below DePere		Chequamegon Bay	
	2S04	1S99	1S98	1S11	1S09	1S14	2S14	1S12	1S07	1S06	1S15	1S16
<u>Chlorinated Aromatics</u>												
Dichlorobenzaldehyde												
Pentachlorobenzene												
Hexachlorobenzene	<0.3	<0.2	<0.2	<0.06	<0.06	<0.04	<0.28	<0.04	<0.04	<0.04	<0.04	<0.20
<u>Chlorinated Aliphatic Hydrocarbons</u>												
Pentachlorobutadiene												
Hexachloroethane												
Hexachlorobutene												
Hexachlorobutadiene												
<u>Polynuclear Aromatic Hydrocarbons</u>												
Chrysene/Benz(a)anthracene	<0.60	<0.50	0.46	<0.04	<0.04	<0.02	<0.64	<0.02	<0.04	<0.03	<0.04	<0.20
Fluorene	<0.10	<0.10	<0.10	<0.02	<0.02	<0.02	<0.12	<0.02	<0.02	<0.10	<0.02	<0.10
Phenanthrene/anthracene	0.10	<0.04	<0.12	<0.02	<0.02	<0.02	<0.08	<0.02	<0.02	<0.20	<0.02	<0.02
<u>Phenols</u>												
Pentachlorophenol	4.52	<2.30	<0.40	<0.12	<0.12	<0.12	<2.84	<0.08	<0.08	<0.80	<0.08	<0.40
<u>Heterocyclic Compound</u>												
Pentyl Furan												
<u>Napthalenes</u>												
Napthalene												

T = Compounds identified by computer library search or manual spectral interpretation. These compounds were quantified using the internal standard (quantifications are therefore only approximate) and were not compared to authentic standards. As manual interpretation was impacted by time constraints detection limits have not been estimated.

Table 4 cont'd

Results of GC/MS Scans of Harbor and Tributary Mouth Fish (mg/kg)

Sample#	Menominee River		Kinnickinnic River	Wolf River		Fox River above DePere			Fox River below DePere		Chequamegon Bay	
	2S04	1S99	1S98	1S11	1S09	1S14	2S14	1S12	1S07	1S06	1S15	1S16
<u>Monocyclic Aromatics</u>												
Butylhexyl benzene									0.4 T			
Dimethy/(phenylmethyl) benzene						0.4 T			2.4 T	1.2 T		
Dimethyl/(Methylpropyl) Benzene Thiol				2.4 T	2.3 T	1.6 T		0.4 T	4.0 T			
Propylheptyl benzene									0.1 T			
<u>Phthalates</u>												
Bis(2-Ethylhexyl)phthalate	32.10	<0.80	4.30	1.80	0.30	0.50	0.05	0.60	1.5	3.4	0.12	<0.20
Di-N-Butylphthalate	15.64	35.0	<0.04	<0.02	<0.02	<0.02	<0.16	<0.02	<0.02	<0.10	<0.02	<0.10
Diethylphthalate	<0.20	<0.02	<0.08	<0.04	<0.04	<0.02	<0.24	<0.02	<0.02	<0.30	<0.04	<0.20
<u>Ketones and Aldehydes</u>												
Benzaldehyde							0.6 T					

T = Compounds identified by computer library search or manual spectral interpretation. These compounds were quantified using the internal standard (quantifications are therefore only approximate) and were not compared to authentic standards. As manual interpretation was impacted by time constraints detection limits have not been estimated.

Table 4 cont'd

Results of GC/MS Scans of Harbor and Tributary Mouth Fish (mg/kg)

Sample #	Black River	Ashtabula River			Sheboygan River			Milwaukee River		
	1S82	1S88	1S90	1S95	1S97	1S02	1S01	0S99	2S09	2S10
<u>Chlorinated Aromatics</u>										
Dichlorobenzaldehyde				2.4 T						
Pentachlorobenzene		3.8 T	3.1 T							
Hexachlorobenzene		5.14	4.8	0.80	0.40	<0.04	<0.04	<0.04	<0.03	<0.03
<u>Chlorinated Aliphatic Hydrocarbons</u>										
Pentachlorobutadiene		4.8 T								
Hexachloroethane		0.1 T								
Hexachlorobutene		6.3 T								
Hexachlorobutadine		2.8 T								
<u>Polynuclear Aromatic Hydrocarbons</u>										
Chrysene/Benz(a)anthracene	10.5	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.60	<0.60
Fluorene	0.05	<0.02	<0.04	<0.04	<0.04	<0.02	<0.02	<0.02	<0.20	<0.20
Phenanthrene/Anthracene	0.17	<0.02	<0.04	<0.04	<0.04	<0.02	<0.04	<0.04	<0.10	<0.10
<u>Phenols</u>										
Pentachlorophenol	<0.20	<0.20	<0.24	<0.20	<0.20	<0.10	<0.10	<0.10	<3.0	<3.0
<u>Heterocyclic Compound</u>										
Pentyl Furan		10.0 T								
<u>Napthalenes</u>										
Napthalene							0.008T			

T = Compounds identified by computer library search or manual spectral interpretation. These compounds were quantified using the internal standard (quantifications are therefore only approximate) and were not compared to authentic standards. As manual interpretation was impacted by time constraints detection limits have not been estimated.

TABLE 4 cont'd

Results of GC/MS Scans of Harbor and Tributary Mouth Fish (mg/kg)

Sample #	Black River	Ashtabula River				Sheboygan River			Milwaukee River	
	1S82	1S88	1S90	1S95	1S97	1S02	1S01	0S99	2S09	2S10
<u>Monocyclic Aromatics</u>										
Butylhexyl benzene										
Dimethyl/penylmethyl benzene										
Methyl/(Methylpropyl)										
Benzene Thiol										
Propylheptyl benzene										
16 <u>Phthalates</u>										
Bis(2-Ethylhexyl)phthalate	0.25	0.76	<0.04	<0.04	0.24	<0.04	0.36	2.00	<1.0	<1.0
Di-N-Butylphthalate	1.08	<0.02	2.2	6.9	4.36	<0.02	<0.02	<0.02	19.80	28.60
Diethylphthalate	<0.04	<0.04	<0.08	<0.08	<0.08	<0.04	<0.04	0.12	<0.30	<0.30
<u>Ketones and Aldehydes</u>										
Benzaldehyde		5.0 T								

T = Compounds identified by computer library search or manual spectral interpretation. These compounds were quantified using the internal standard (quantifications are therefore only approximate) and were not compared to authentic standards. As manual interpretation was impacted by time constraints detection limits have not been estimated.

Discussion

These data illustrate the environmental persistence and continued existence of sources to the Great Lakes of industrial contaminants and pesticides whose use has been banned or restricted. These include PCB, chlordane, heptachlor and DDT. The presence of herbicides presently in use in the basin is also demonstrated. Dacthal was above detection limits in samples from most sites. Dacthal has been reported in fish samples from the Pike and Root Rivers (Wisconsin) (St. Amant et al. 1983), coho salmon from Lakes Michigan, Huron and Erie (DeVault and Weishaar 1983, Clark et al. 1984) and in water from the Imperial Valley (California) (Picker et al. 1979).

Several sites exhibited specific contaminant problems with severe fish contamination identified in the Sheboygan, Black and Ashtabula Rivers. Somewhat less severe problems occurred in the Milwaukee, Kinnickinnic, and Fox Rivers.

The Sheboygan River samples contained extremely high PCB concentrations reflecting the continued existence of PCB contamination in the lower reaches of that River. Composite fish samples analyzed in 1978 ranged from 10.0 mg/kg to 750 mg/kg total PCB. At that time both fish and sediment indicated severe contamination in the Sheboygan River from below the Sheboygan Falls Dam to Lake Michigan. Studies conducted in 1979 indicated that PCB had migrated into the underlying soil stratum (DOA 1980). Fish analyzed in 1980 and 1981 by the Wisconsin Department of Natural Resources (WDNR) ranged from 34.0 mg/kg to 79.0 mg/kg total PCB (St. Amant et al. 1983),

in general agreement with the present study. While PCB concentrations in Sheboygan River fish appear to have declined since 1978 the fishery remains severely impacted with WDNR continuing to advise against consumption.

Elevated PCB concentrations were also found in samples from the Kinnickinnic and Milwaukee Rivers. St. Amant et al. (1983) reported PCB concentrations ranging from 5.0 mg/kg to 49.0 mg/kg and from 2.70 mg/kg to 34.0 mg/kg in fish from the Kinnickinnic and Milwaukee Rivers respectively, in general agreement with this study. These authors also reported the presence of a number of polynuclear aromatic hydrocarbons (PAHs) including naphthalenes, biphenyls, anthracene/phenanthrene, fluoranthrene and pyrene in Milwaukee and Kinnickinnic River samples. These were not identified in our samples possibly due to our higher detection limits. Their PAH detection limits ranged from .05 mg/kg to 0.10 mg/kg while ours ranged from 0.10 mg/kg to 0.60 mg/kg. The present study quantified chrysene/benz(a)anthracene, a carcinogenic PAH (USPHS 1983, IJC 1983) that had not been previously identified.

The composite sample from the Black River contained relatively low levels of PCB and common pesticides. However, 3 and 4 ring Polynuclear Aromatic Hydrocarbons (PAHs) which are known or suspected carcinogens were detected (EPA 1980, IJC 1983). Vieth et al. (1981) also reported several PAHs in a composite of 5 channel catfish and 1 fresh water drum. These included, among others, methylnaphthalene, phenanthrene, fluoranthene, pyrene, fluorene and acenaphthalene. One of the most intensive PAH

analysis of Black River samples was conducted by Baumann et al. (1983). They quantified 18 PAHs in brown bullheads and 24 PAHs in sediments. They also found that PAH concentrations were correlated with a high incidence of tumors in fish. While there are distinct differences between the 3 studies in both the compounds identified and concentrations reported, these are to be expected as a result of the more intensive analytical methodologies employed in the Vieth et al. (1981) and Baumann et al. (1982) studies, as well differences in habits of the species analyzed.

The high concentrations of known and potential carcinogens in fish and sediments from the Black River has resulted in the Ohio Department of Health (ODOH) advising the public against swimming, wadding or consuming fish from the lower 8.0 km of the river.

High concentrations of PCB and hexachlorobenzene and the presence of several other chlorinated hydrocarbons characterized the Ashtabula River samples. Studies by Veith et al. (1979), Veith et al. (1981) and Kuehl et al. (1981) have compiled a lengthy list of contaminants in fish from the Ashtabula River. Compounds which have been identified include chlorinated benzenes (tri, tetra, penta, hexa), chlorinated styrenes (hexa, hepta, octa), chlorinated butadienes (tetra, penta, hexa), tetrachlorobutadiene, pentachlorobutadiene, tetrachloropropene, pentachloropropane, pentachloronorborene, pentachloroanisole, as well as PCB. This study confirms the presence of several of the above compounds and has added dichlorobenzaldehyde, hexachloroethane, hexachlorbutene and pentyfuran to this list. While quantitative comparisons are not possible due to the differing species composition and

compositing schemes used in the different studies, this data is in general agreement with the earlier data. The contaminant problem in the Ashtabula River has resulted in the Ohio Department of Health (ODOH) and the Ohio Environmental Protection Agency (OEPA) advising against consumption of fish from the lower 3.2 km of the river.

Elevated PCB concentrations and the presence of several benzene derivatives characterized the Fox River samples. Veith et al. (1981) reported 10.0 mg/kg total PCB for a composite sample of carp, sucker and channel catfish taken below the DePere Dam in 1978, within our range of 8.61 mg/kg to 20.89 mg/kg in the same area. St. Amant et al. (1983) reported mean PCB concentration of 16.0 mg/kg and 6.0 mg/kg in 1980 and 1981 respectively for fish in the lower (below DePere) Fox River. They also detected PCB substitutes such as isopropyl biphenyl, di-isopropyl biphenyl and santasols (C₁₅ H₁₆) which were not detected in this study.

Sediment analysis conducted by USEPA in 1981 support the fish data as well as add additional parameters of concern. Sediment PCB concentrations in the Fox River ranged from 25.9 mg/kg below DePere to 1.2 mg/kg at the mouth. Several benzene derivatives including monochlorobenzene, dichlorobenzene, trichlorobenzene, methylbenzene and dimethylbenzene were also detected in the sediments as were PAHs including phenanthrene/anthracene, fluoranthene, fluorene, pyrene, acenaphthene and chrysene/benz(a)anthracene (GLNPO 1981). That the PAHs found in the Fox River sediments were not detected in fish is not surprising. Fish are capable of oxidizing PAH via the mixed function oxidase system. Therefore the accumulation of PAHs above instrument detection limit requires continued high level exposure, as is illustrated by the study by Baumann et al. (1983) discussed earlier. They quantified

fluoranthene at 22 mg/kg in Black River sediments. However brown bullheads, a bottom dwelling species ranged from 0.558 mg/kg to 1.938 mg/kg. In the Fox River sediments all PAH concentrations were below 2.1 mg/kg (GLNPO 1981). This illustrates the need to utilize mechanisms other than fish tissue to monitor the potential exposure to PAH of both animal and human populations.

Chequamegon Bay (Lake Superior) differed from the other sites in the relative absence of typical organic contaminants found by both GC/EC and GC/MS. This data supports the low levels of PCB and pesticides reported by Sheffy and St. Amant (1980).

The data produced by this element of the GLFMP is in general agreement with that of other studies and proves the feasibility of using GC/MS scans and limited GC/EC analysis to screen areas for additional work. The data does not allow quantitative intersite comparison nor rigorous trend analysis. These goals will be addressed with second level programs using species of consistent size, age and lipid content at all sites.

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16. ABSTRACT Composite fish samples collected from Great Lakes Harbors and Tributaries between 1980 and 1981 were analyzed by gas chromatography-electron capture detector and gas chromatographic-mass spectrometry for a wide range of pesticides and priority pollutants. Severe PCB contamination was observed in Sheboygan River fish with moderate to severe PCB contamination in sampled from the Milwaukee, Kinnickinnic, Fox, and Ashtabula Rivers. The Ashtabula River samples also contained several chlorinated aromatic and aliphatic hydrocarbons. Polynuclear aromatic hydrocarbons were detected in fish from the Black, Kinnickinnic and Menominee Rivers, while a number of benzene derivatives were observed in samples from the Fox and Wolf Rivers.		
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