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Harbors and Tributary Mouths 1980-81

by

David S. DeVault, III Surveillance and Research Staff Great Lakes National Program Office

United States Environmental Protection Agency 536 South Clark Street Chicago, Illinois 60605

## DISCLAIMER

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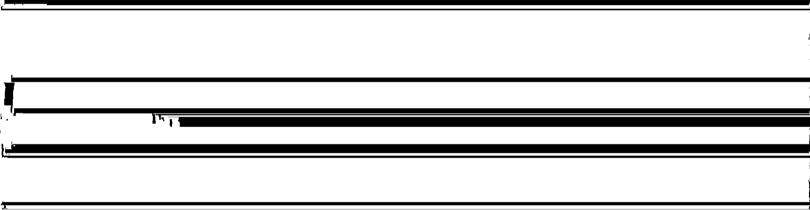
#### FOREWORD

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 \_\_Eederal\_and\_Canadian governmental agencies and the International

## **ABSTRACT**

Composite fish samples collected from Great Lakes Harbors and Tribu-
taries 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
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# TABLES

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#### <u>Acknowledgements</u>

I thank the many people in the Fisheries and Natural Resources\_Departments

of the States of Wisconsin and Ohio for collecting the samples and providing valuable site information. I also thank Dr. James Clark, (USEPA, Environmental Research Laboratory, Gulf Breeze, Florida), Mr. David Rockwell (USEPA, Great Lakes National Program Office) for reviewing and commenting on the report. I also wish to thank Mary Martin and

## INTRODUCTION

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	between the U.S. Environmental Protection Agency, Great Lakes National
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	Program Office (GLNPO), U.S. Fish and Wildlife Service (USFWS), U.S. Food
j <b>a</b>	and Brua Administration (USFRA) and the eight Great lakes states. It is
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#### **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. Ind	ividual 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

### TABLE 1 SAMPLE COLLECTION DATA

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	The GC/MS portion of the extract was screened by a Varian 2700 gas chromato-
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	adiustments required for GC/MS analysis as well as what, if any, additional
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	cleanup was required (EPA 1979a). This was then analyzed by a Hewlett-Packard
	5985 automated gas chromatograph/mass spectrometer using the following oper-

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:  $T_1 = 50^{\circ}\text{C}$  for 1 min.  $T_2 = 300^{\circ}$  for 20 min.

ating conditions (EPA 1979b):

Bis (2-Chloroethyl) Ether 1,3-Dichlorobenzene 1,4-Dichlorobenzene

2-Chlorophenol
\*2,4-Dimethylphenol
2-Nitrophenol

\*Triflan(Trifluralin)
\*2,4,D-Isopropyl Ester
Alpha BHC (A-BHC)

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)

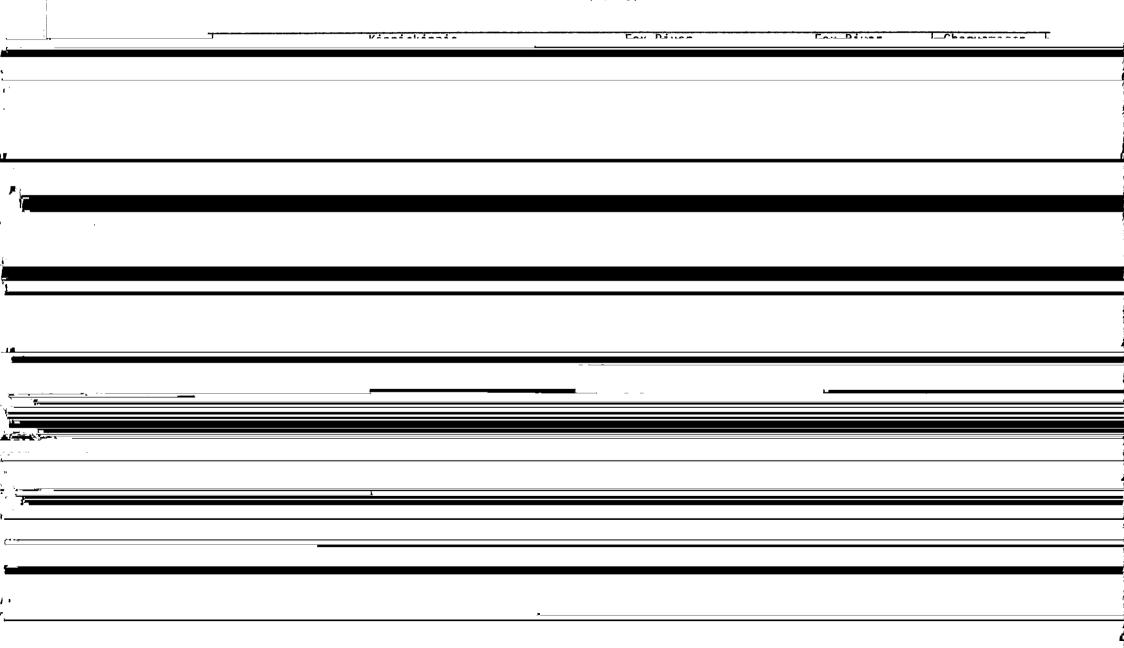
J<u>njection Column: 5 ul Injection Temperature: 270°C</u>

	GC/EC
-	CC_FC = -1 main identified. 10 nonticides and industrial compounds in the
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	22 composite samples analyzed (Table 3). These include compounds currently
•	in was in the Prest lates basin and those whose was has been banned such
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	PCP - m.d BPT - m - country post-riched such as ablandance and bootschlan

Table 3
Gas Chromatographic Results for Harbor and Tributary

	Black River		Ashtabul	a River			Sheboygan	River	Milwaul	kee River
Sample #	1582	1588	1\$90	1595	1S97	1502	1801	0\$99	2509	2S10
Aroclor 1248	0.42	4.17	8.81	2.01	0.88	21.30	51.37	31.3	3.27	7.36
Aroclor 1254	0.57	2.39	1.85	0.79	0.62	15.79	42.37	29.25	2.16	5.32
Aroclor 1260	0.29	<0.05	<0.05	<0.05	0.22	1.51	4.70	2.55	1.20	2.86

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



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	Rivers. The ratio of DDE to the parent compounds varied from sample to
1	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
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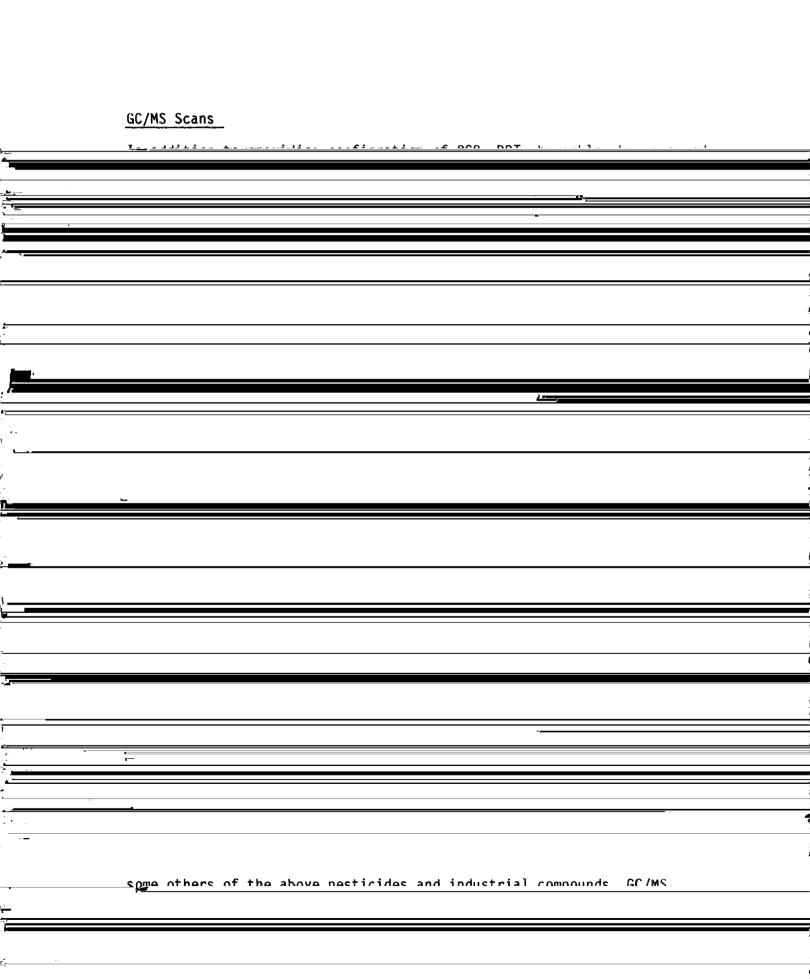


Table 4 Results of GC/MS Scans of Harbor and Tributary Mouth Fish (mg/kg)

Table 4 cont'd

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

l		Kir	nnickinnic	Fox River	Fox River
		Menominee River	River   Wolf River	above DePere	below DePere Chequamegon
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 $\label{thm:cont'd} Table~4~cont'd$  Results of GC/MS Scans of Harbor and Tributary Mouth Fish (mg/kg)

	B1-3 a <sub>7</sub> .	Nahtahula	Chohouaan	Milwankaa
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TABLE 4 cont'd

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

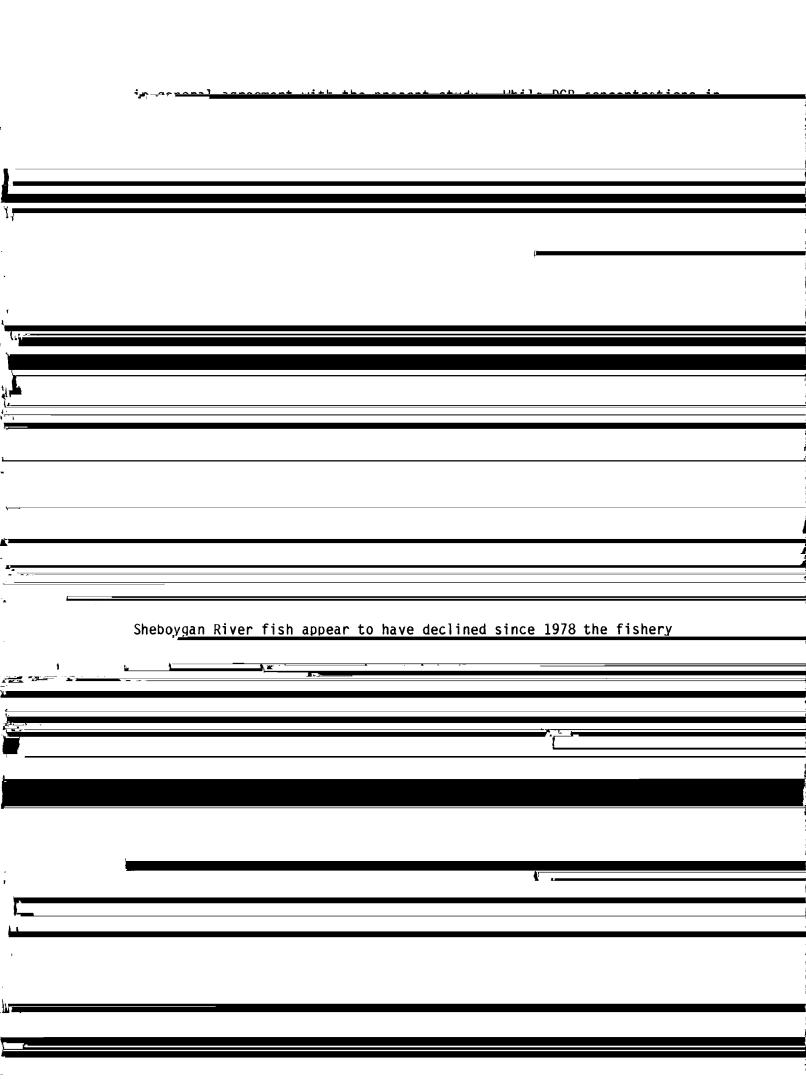
	Black River	Ashtabula River	
Sample #	1582	1588 1590 1595 1597	1802 1801 0899 2809 2810
Monocyclic Aromatics			
<u>Rutylhexyl Menzene</u>		<u>i i i l</u>	<u>i i i i i i</u>



#### Discussion

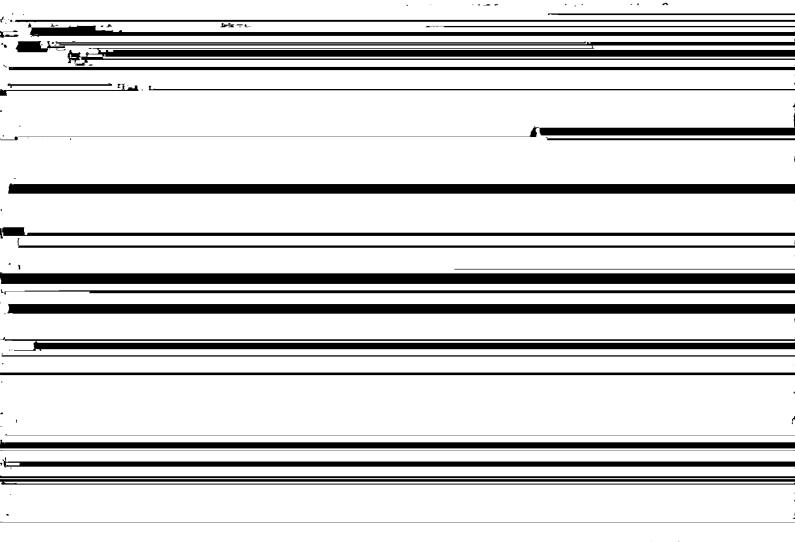
	These data illustrate the environmental persistance and continued existence
	of sources to the Great Lakes of industrial contaminants and pesticides
	whose use has been hanned or restricted. These include DCR chlordane
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basin is also demonstrated. Dacthal was above detection limits in samples



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



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.

	compositing schemes used in the different studies, this data is	; in general
T	gaggamanhidh a <u>ha sanlian daka. Tha sankaminank umaklam in kh</u>	
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-	fluoranthene at 22 mg/kg in Rlack River sediments.	However brown bullheads.
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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.

## REFERENCES

	Baumann, P.C., Smith, W.D., and M. Ribick. 1982. Hepatic tumor rates and $polynuclear$ aromatic hydrocarbon levels in two nonulations of brown bull-
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