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Contaminants in Fish From Great Lakes

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Harbors and Tributary Mouths 1980-81

by

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DISCLAIMER

This report has been reviewed by the Great Lakes National Program Office,  
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products constitute endorsement or recommendation for use.

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

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 Chubbuck River fish with residues to

1981

severe PCB contamination in samples from the Milwaukee Kinnickinnic

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## INTRODUCTION

The Great Lakes Fish Monitoring Program (GLEMP) 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

## 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



1812

(Fox River above

11/15/90

1 week back

1.5

1.37-0

100%

100%

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: T<sub>1</sub> = 50°C for 1 min.  
T<sub>2</sub> = 300° for 20 min.  
Rate: 100°C to 200°C by 10°C/min

TABLE 2

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)

Injection Volume: 5  $\mu$ l

Injection Temperature: 270°C

## 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

DDE and DDT are severely restricted such as chlordane and heptachlor



Table 3  
Gas Chromatographic Results for Harbor and Tributary

| Sample #     | Black River | Ashtabula River |       |       |      | Sheboygan River |       |       | Milwaukee River |       |
|--------------|-------------|-----------------|-------|-------|------|-----------------|-------|-------|-----------------|-------|
|              | 1S82        | 1S88            | 1S90  | 1S95  | 1S97 | 1S02            | 1S01  | 0S99  | 2S09            | 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  |
| Total PCBs   | 1.28        | 6.50            | 10.60 | 2.80  | 1.70 | 38.60           | 98.44 | 63.10 | 6.63            | 15.54 |







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)

| Menominee River | Kinnickinnic River | Wolf River  | Fox River above DePere | Fox River below DePere | Chequamegon Bay |
|-----------------|--------------------|-------------|------------------------|------------------------|-----------------|
| 1994   1999     | 1999               | 1911   1999 | 1914   1914   1919     | 1907   1906            | 1915   1916     |

Table 4 cont'd

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

|  | Black | Ashtabula | Shobougan | Milwaukee |
|--|-------|-----------|-----------|-----------|
|--|-------|-----------|-----------|-----------|





## 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

basin is also demonstrated. Dacthal was above detection limits in samples

in general agreement with the present study. While DCD concentrations in

Sheboygan River fish appear to have declined since 1978 the fishery

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

in agreement with the earlier data. The contaminant problem in the Ahtahkapi

Dixon has resulted in the Ohio Department of Health (1991) and the Ohio

fluoranthene at 22 mg/kg in Black River sediments. However brown bullheads,

bottom dwelling species ranged from 0.558 mg/kg to 1.028 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.

REFERENCES

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



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