ORGANOCHLORINE AND HEAVY METALS RESIDUES IN THE NEARSHORE BIOTA OF THE CANADIAN LOWER GREAT LAKES

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International Joint Commission

by

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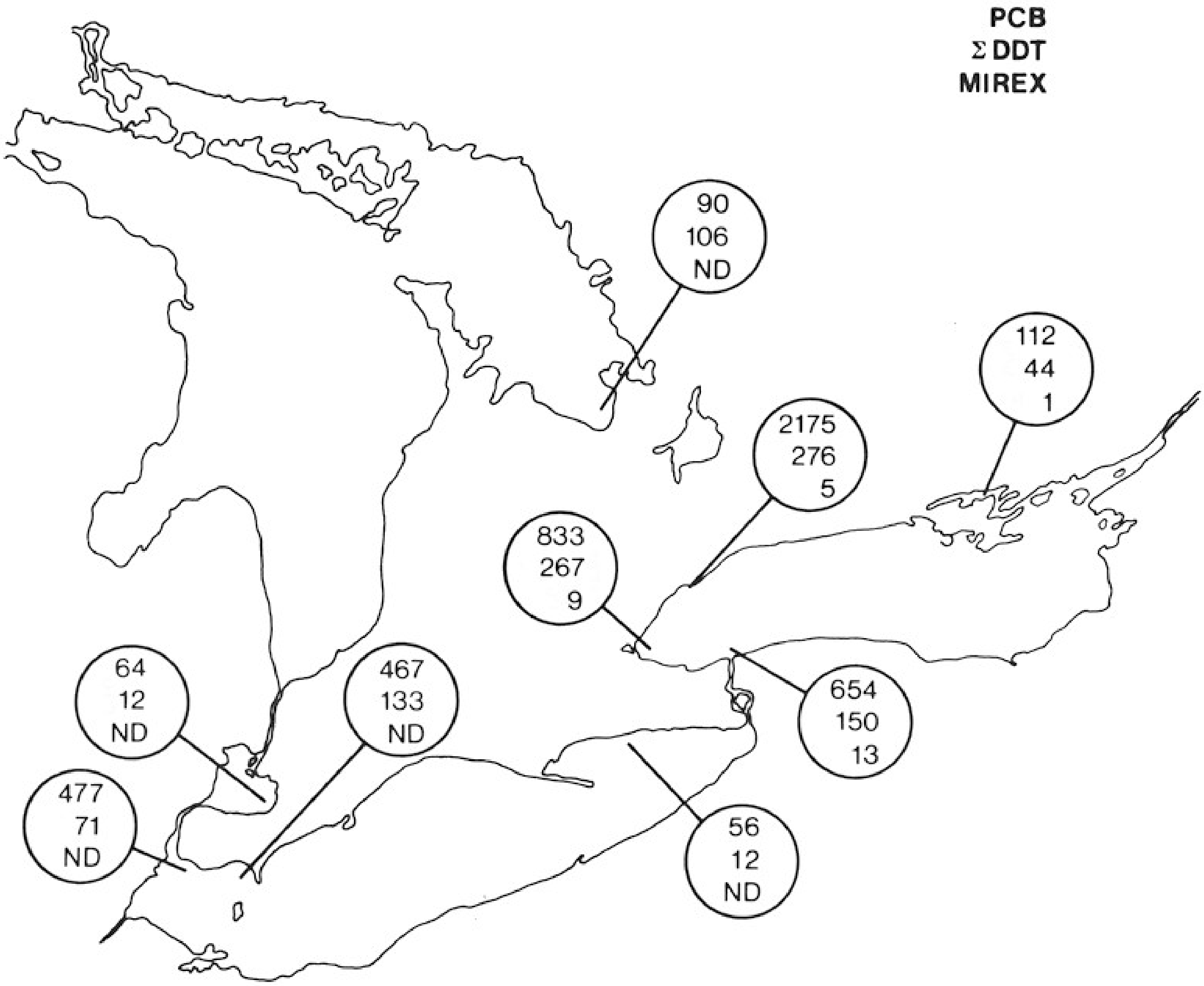
PCB
Σ DDT
MIREX
90
106
ND
112
44
1
2175
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5
833
267
9
64
12
ND
467
133
ND
654
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477
71
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12
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SUMMARY

1976 - Oakville Creek and Grand River Studies

Dissolved organochlorine residue levels in the river waters were not significantly different when comparing Oakville Creek and Grand River water samples.

Body-burden levels of polychlorinated biphenyls (PCB's), hexachlorobenzene (HCB), total 1,1,1-trichloro-2, 2-bis (p-chlorophenyl ethane) ($\sum$DDT) and Mirex were significantly higher in emerald shiners from the Oakville Creek estuary, than shiners from the Grand River.

PCB residues in adult emerald shiners at both stations exceeded the proposed I.J.C. guideline criteria for protection of wildlife.

Mirex and HCB residues were found only in the Oakville Creek estuary shiners.

1977 Study

PCB's, DDT and chlordane were the contaminants most frequently found in spottail shiners collected.

Of the nine sites sampled, six exceeded the PCB body-burden criteria for wildlife protection.

PCB levels in spottail shiners at Point Pelee had decreased significantly since 1975.

DDT levels in Niagara River spottail shiners had decreased significantly since 1975.

Chlordane, not detected in the 1975 fish collections, exceeded recommended guideline levels at the Niagara River in 1977. Chlordane residues in spottail shiners from primarily agricultural watersheds were relatively low.

Mirex, detected only in Lake Ontario fish showed a distinct geographic distribution. Highest Mirex residue levels were found in the Niagara spottails with progressively decreasing residue concentrations eastward.

Mercury residues in young spottails ranged from 0.0101 µg/g to 0.10 µg/g. Highest levels were found in the Detroit River fish, although guideline recommendations were not exceeded.

Results from the 1976-1977 studies indicate that organochlorine contaminants present in the biota of the Lower Great Lakes can be largely attributed to industrial sources rather than agricultural practices.

INTRODUCTION

In order to determine the impairment of water quality and assess the effects of contaminants on the biota, field surveys of selected areas of the boundary waters in Ontario were undertaken by the Canadian Task D, Subactivity-3 of the International Joint Commission, Pollution from Land Use Activities Reference Group (Lower Great Lakes).

The primary purpose of this study was to determine the levels of persistent contaminants in the biota of estuaries of the drainage basins chosen, as well as to interpret the results in terms of biological significance by utilizing the available information in literature.

It has long been recognized that several persistent contaminants do bioaccumulate in the Great Lakes, as a result of point source, diffuse and atmospheric loadings. Numerous studies have dealt with chlorinated hydrocarbon residues in the Great Lakes fish (Hickery *et al* 1966; Reinert 1970; Reinke *et al* 1972; Frank *et al* 1974a, 1974b; Kelso and Frank 1974; Veith 1975 and Parejko *et al* 1975. Similarly, Lucas and Edgerington 1970; Uthe and Bligh 1971; Henderson *et al* 1972; Hesse and Evans 1972; and Kelly *et al* 1975 have investigated metal residues.

While the majority of these studies have interpreted the residue levels in the fish in terms of their relevance to human health aspects only, a few have provided some insight into the biological significance of contaminant bioaccumulations. Reinert (1970) suggested that DDT and dieldrin in Lake Michigan coho salmon eggs were close to the level that could adversely affect reproduction (Burdick *et al* 1964; Macek 1968).

A subsequent investigation (Reinert and Bergman 1974) also found that levels of DDT in eggs of Lake Michigan lake trout and coho salmon were such as to be affecting reproduction in these species. Furthermore, it has been shown that bio-accumulation of contaminants in the Great Lakes fish have had an effect on the fish eating birds of the area (Keith 1966; Anderson 1968; Gilbertson and Reynolds 1972; and Gilbertson 1974).

Bioaccumulation in Great Lakes food chains was the outstanding criteria in selecting the contaminants studies. However, analytical capabilities restricted the types of contaminants analyzed and, therefore, the study does not include all contaminants considered to be present and persistent in the Great Lakes (G.L.W.Q.B., 1976).

The ability to biomonitor a localized area was the major criterion in selecting the organisms studied. In addition their importance as fish food organisms was considered.

Plankton has been utilized widely in the marine environment for monitoring chlorinated hydrocarbon pollution (Cox 1970; Jensen *et al* 1972; Risebrough *et al* 1972; Harvey *et al* 1974), but generally has not been used extensively in the Great Lakes (Gilbertson, 1971; Le Feuvre 1972; Hartung 1975; Haile *et al* 1975). Hence its role in the movement of contaminants is unclear at the present time.

Amphipods have been used extensively to monitor chlorinated hydrocarbon pollution in streams (Sodergren *et al* 1972) and lakes (Hickey *et al* 1966; Haile *et al* 1975). Amphipods, represent a substantial base to the food web leading to numerous economically important fishes in the Great Lakes. It was hoped that the detrivorous food habit of amphipods would give some insight into the significance of sediment adsorbed contaminants.

The emerald shiner (*Notropis atherinoides*) and the spottail shiner (*Notropis hudsonius*) are abundant forage species and therefore of considerable importance to the Great Lakes Fishery (Scott and Crossman, 1973). Suns and Rees (1975) used spottail shiners successfully to monitor localized contamination of chlorinated hydrocarbons.

The 1976 study involved an intensive look at the Grand River and Oakville Creek. The Grand River located on Lake Erie carries a relatively high suspended load; suspended solids are known to ameliorate the direct effects of pesticides on the biota by adsorption and subsequent deposition in the profundal zones. Oakville Creek on Lake Ontario represents a situation opposite to that of the Grand River. Therefore, it was interesting to see what role a relatively low suspended load had on the accumulation of contaminants in the biota. In turn there was the possibility that a relationship existed between 'particulate' and 'soluble' phases of contaminants and contaminants in the various trophic levels examined.

The 1977 study represented a surveillance of some Great Lakes watersheds draining agricultural, grazing and highly industrialized areas. The purpose was to determine contaminants present in fish and denote any trends related to land use activities.

AREAS OF STUDY

Grand River

The Grand River watershed has the largest catchment area (6770 km^2) of streams in southwestern Ontario, originating less than twenty miles south of Nottawasaga Bay. The main stream runs a 290 km course, dropping a total of 526m before reaching Port Maitland on Lake Erie.

Land use is quite variable in the watershed. The main industrial centres are Guelph, Galt, Kitchener, Waterloo and Brantford. The upper and lower thirds of the basin are largely rural, the latter supporting the bulk of the agricultural activity. Usage of agricultural chemicals in the basin is considerable (Appendix 1). All the Grand River water samples were taken above the weir at Dunnville approximately 7 km from the river mouth.

Oakville Creek

This comparatively small watershed of 361 km^2 is divided into two sectors by the Niagara Escarpment with 26% of the basin lying above the escarpment.

The basin is largely rural, but extensive suburban and industrial development is occurring at Oakville and at Milton on the main branch.

Agriculture is carried on throughout the basin but use of agricultural chemicals is minimal (Appendix 2).

Oakville Creek samples were taken below the bridge on Highway #2 in Oakville, approximately ½ km from Lake Ontario.

Other Watersheds

Areas of study for 1977 included the mouth of the Nottawasaga River on Georgian Bay draining a total of 167,300 hectares; the mouth of the Saugeen River on Lake Huron draining 391,140 hectares; the mouth of the Thames River near Tremblay Creek on Lake St. Clair draining 594,340 hectares; the Detroit River as it enters Lake Erie; the mouth of Sturgeon Creek near Point Pelee; the mouth of the Grand River draining 656,810 hectares; the Niagara River at Niagara-on-the-Lake in Lake Ontario; Burlington Beach, at the entrance to Hamilton Harbour; the mouth of the Humber River draining 99,890 hectares and flowing through the west end of

Metropolitan Toronto; and the mouth of the Salmon River draining 109,676 hectares and flowing into the Bay of Quinte on Lake Ontario (Fig. 1).

SAMPLING METHODS AND PROCEDURES

Analytical techniques are described in the "Handbook of Analytical Methods for Environmental Samples", Laboratory Services Branch, Ministry of the Environment, with modifications as indicated.

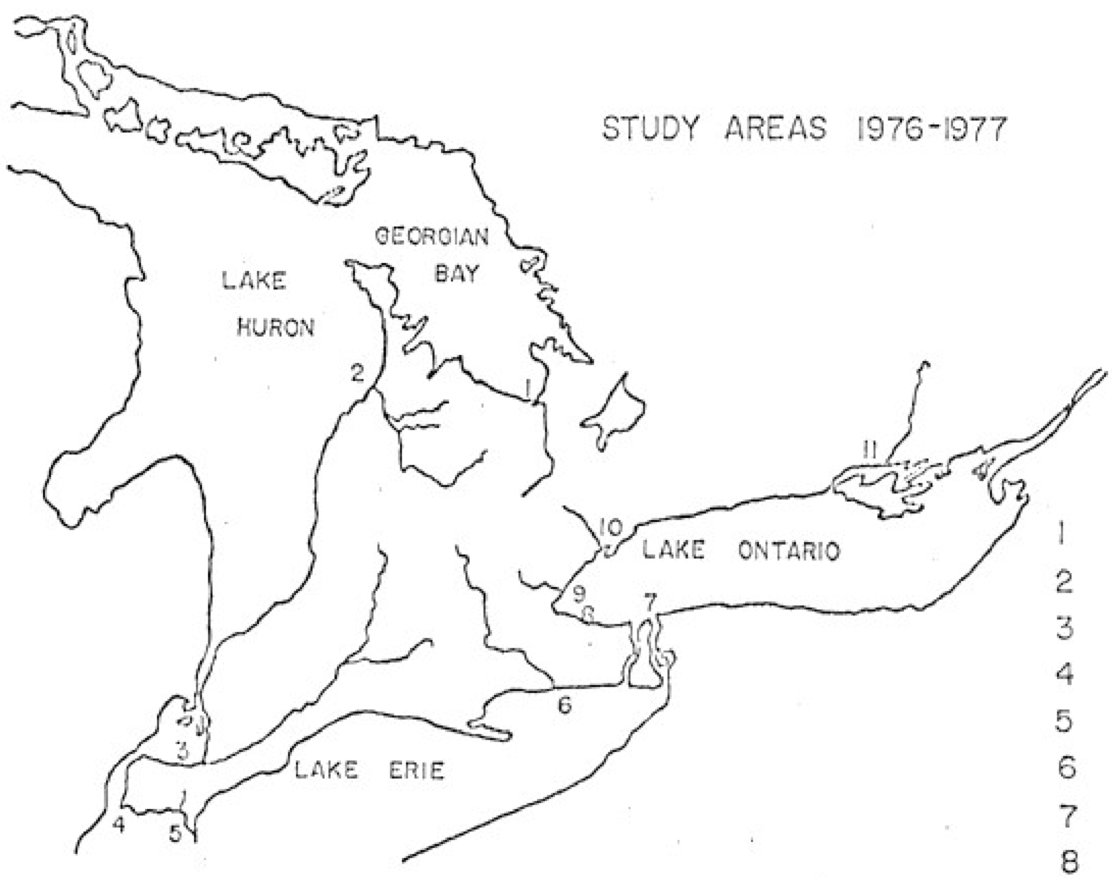
Water

Samples for soluble organochlorine analyses were taken at the surface approximately one meter from the river bank with a benzene-acetone pre-rinsed metal pail. A total of forty-eight litres of water were collected and stored in glass carboys which had been washed once with chromic acid solution (10%), rinsed several times with tap water and rinsed once with benzene and twice with acetone. The carboys were sealed with hexane rinsed aluminum foil-lined tops. They were delivered to the Canada Centre for Inland Waters (Burlington) within two hours of sampling where they were centrifuged on a continuous-flow gravity fed Westphalia Separator centrifuge at 9400 rpm. Hardware of the centrifuge was primarily of glass or stainless steel with a minimal amount of aged plastic. Samples were returned to the Ministry of the Environment (Rexdale) after centrifugation and refrigeration at 4°C until they were analyzed for organochlorine compounds (Appendix 3).These samples were not pre-extracted.

Samples for soluble metals analysis were taken from the centrifugate of bulk water samples (≈1000 L) collected for particulate metal and organochlorine determinations. A 250 ml. sample was taken for mercury analysis while a 1L sample was collected for the other metal species (Appendix 4). The former was preserved with nitric acid (Baker) and potassium permanganate while the latter was preserved with nitric acid only. All samples were refrigerated (4°C) until time of analysis.

Suspended Solids

To provide sufficient solids for particulate metal and organochlorine analyses ≈2000 L of water was taken from each of the sampling sites near the surface, 1 m from the river bank. This



1 NOTTAWASAGA RIVER
2 SAUGEEN RIVER
3 THAMES RIVER (Tremblay Creek)
4 DETROIT RIVER
5 STURGEON CREEK (Pt. Pelee)
6 GRAND RIVER
7 NIAGARA RIVER
8 BURLINGTON BEACH
9 OAKVILLE CREEK
10 HUMBER RIVER
11 SALMON RIVER

was accomplished with a submersible pump (Little Giant), which fed into plastic carboys (Nalgene). The samples were centrifuged at C.C.I.W. (Burlington) in a continuous flow pump-fed Westphalia Separator centrifuge at 9400 rpm. Subsamples (≈10 gm) taken for the two types of analysis were stored in glass jars and refrigerated (40°C). The sample for metal analysis was subsequently air-dried prior to analysis, while the sample for organochlorine analysis was frozen (-20°C) prior to analysis.

Sampling times and locations were the same as those for water samples.

Plankton

Plankton samples were taken within the plume areas of both Oakville Creek and the Grand River.

A small Wisconsin plankton net (80 µ) previously rinsed with hexane was used. The plankton straining bucket made of brass and nitrex had also been hexane rinsed.

The net was held away from the side of the boat, but well ahead of the motor to eliminate possible contamination from exhaust. Horizontal surface tows were of approximately five minutes duration in Oakville Creek and the Grand River.

Plankton for organic trace contaminant analyses were stored in hexane washed glass jars with hexane washed foil lined lids. Samples were washed onto pre-soaked benzene extracted glass-fibre filters (Gelman) wrapped in cleaned foil and weighed. Polytron extraction of pesticides and PCB's was followed by gas chromatographic analysis.

Plankton sampling schedule is shown in Appendix 5.

Benthos

A preliminary survey of the benthic community at the mouth of the Grand River and Oakville Creek with an Eckman grab (15 x 15 cm) revealed a paucity of organisms.

The virtual absence of benthos in the sediments meant that samples had to be taken from the *Cladophora* mats found on rocks in the vicinity of the stream confluence.

Since *Gammarus* spp. were the most consistently abundant organisms, they were sampled for contaminant analyses (Appendix 3). Approximately ten grams were collected for analyses at both sites. Samples were refrigerated in order to maintain the organisms for purposes of clearing their guts of detritus, a factor found to influence contaminant levels (Elwood *et al.* 1976). They were then strained, placed in a small quantity of tap water and frozen (-20°C) in hexane washed glass jars. Before analysis the samples were thawed, towel dried, subdivided into five aliquots and weighed.

Samples were collected during the month of September.

Fish

The species selected for contaminant analysis for 1976 was the emerald shiner *(Notropis atherinoides*) a known zooplanktonovore (Gray 1942). The spottail shiner (*Notropis hudsonius*), a forage species of considerable importance to sport fish (Scott and Crossman, 1973), was chosen for collection for 1977. Spottail shiners were collected in all locations in 1977 but the Saugeen River where the emerald shiners provided an alternative species. Additional collections of emerald shiners, common shiners and golden shiners were made at some locations (Appendix 5).

Fish were collected using a 20 meter beach seine with an 0.6 cm mesh within the river plumes.

Young-of-the-year and yearling emerald shiners were taken at the Grand River, while only yearlings could be seined at the Oakville Creek location. Fish composites of ten were collected of yearling shiners at both sites in 1976 while eight composites of fifteen young-of-the-year fish were collected at the Grand River.

Ten fish composites of ten shiners each were collected at each site for the 1977 study. Individual fish lengths were recorded and ten fish composites were wrapped in hexane-washed aluminum foil and frozen (-20°C). Fish were homogenized and each sample split for the two types of analysis.

Analytical procedure for pesticide and PCB determinations after soxhlet extraction with hexane involved Florisil clean-up and gas chromatographic analyses as outlined in the handbook cited earlier.

RESULTS AND DISCUSSIONS

1976 Survey

Water

Dissolved organochlorine contaminant residue levels in river water were not significantly ($p < 0.05$) different when comparing the Grand River and Oakville Creek collections (Table 1). However, there were significant concentration fluctuations between the July and September collections at both sampling sites ($p < 0.05$).

Dissolved metals residue levels in the Grand River and Oakville Creek waters were comparable (Table 2).

Suspended Solids

The following organochlorine contaminants were not detected in the suspended sediments load: HCB; heptachlor epoxide; thiodan; dieldrin; endrin and mirex (Table 3). It should be noted, however, that insufficient sample bulk in some collections may have unfavourably influenced detection limits for certain contaminants analyzed.

Metals residues associated with the suspended solids are summarized in Table 4. With the exception of arsenic, no significant concentration differences were found in the metals analyzed ($p < 0.05$).

Plankton

Organochlorine contaminant residues were generally lower in plankton than fish and amphipods. Some of the chemicals detected in the other biological samples (HCB; BHC; mirex) were totally absent in the plankton samples analyzed (Table 5). Perhaps as a result of low biomagnification, plankton residue concentration differences were less pronounced when comparing the two watersheds, with only PCB's being significantly ($p < 0.05$) different (Table 5). Plankton

TABLE 1: Dissolved Organochlorine Contaminant Residues in Oakville Creek and Grand River Waters, July and September 1976 (ng/L). ($\bar{X}$ and 95% Confidence Limits).

Chemical	# of Analyses	Oakville Creek	Grand River
PCB	9	3.5 ± 1.2	2.6 ± 0.65
HCB	9	0.04 ± 0.03	0.02 ± 0.02
χ - BHC	9	2.24 ± 1.14	1.91 ± 0.97
LINDANE	9	1.55 ± 0.8	0.67 ± 0.16
β -BHC	9	ND	ND
HEPTACHLOR	9	ND	ND
ALDRIN	9	ND	ND
HEPTACHLOR EPOXIDE	9	0.22 ± 0.13	0.42 ± 0.20
THIODAN I	9	ND	ND
THIODAN II	9	ND	ND
DIELDRIN	9	0.36 ± 0.14	0.32 ± 0.05
ENDRIN	9	0.19 ± 0.13	0.12 ± 0.10
∑ - DDT	9	0.55 ± 0.35	0.36 ± 0.13
χ - CHLORDANE	9	0.21 ± 0.03	0.13 ± 0.02
γ - CHLORDANE	9	0.14 ± 0.03	0.10 ± 0.02
MIREX	5	0.07 ± 0.04	0.08 ± 0.04*

* September values only

ND - non detectable

TABLE 2: Metals in Grand River and Oakville Creek Waters - Dissolved Phase 1976 (µg/L)

	Sampled	Grand River			Oakville Creek		
		No. of Analyses	Range Min.	Range Max.	No. of Analyses	Range Min.	Range Max.
Mercury	July	5	<0.05	<0.06	5	<0.05	<0.06
	Sept.	4	<0.03	0.15	5	<0.02	0.11
Copper	July	5	2	4	5	1	5
	Sept.	4	2	3	5	3	4
Lead	July	5	<2	8	5	<2	6-
	Sept.	4	<2	2	5	<2	7
Chromium	July	5	<2	4	5	<2	<2
	Sept.	4	<2	4	5	<2	2
Cadmium	July	5	<1	<1	5	<1	1
	Sept.	4	<1	<1	5	<1	<1
Arsenic	July	5	<1	2	5	2	3
	Sept	4	<1	2	5	1	1
Zinc	July	5	<1	10	5	2	9
	Sept.	4	9	20	5	12	110

TABLE 3: Organochlorine Residues Associated With Suspended Solids in Oakville Creek and Grand River Waters (Dry Weight ng/g). ($\bar{X}$ and 95% Confidence Limits).

	July		September	
July	Oakville Creek	Grand River	Oakville Creek	Grand River
# of Analyses	5	4	5	4
PCB	76 ± 60	55 ± 43	384 ± 377	49 ± 41
HCB	ND	ND	ND	ND
χ - BHC	TR	1.6 ± 2	9 ± 11	ND
LINDANE	TR	0.4 ± 0.5	7 ± 10	TR
β - BHC	ND	ND	ND	ND
HEPTACHLOR	ND	ND	ND	ND
ALDRIN	ND	ND	ND	ND
HEPTACHLOR EPOXIDE	ND	ND	ND	ND
THIODAN I	ND	ND	ND	ND
THIODAN II	ND	ND	ND	ND
DIELDRIN	ND	0.4 ± 0.90	1 ± 1	TR
ENDRIN	ND	ND	ND	ND
∑-DDT	16.4 ± 8	3.4 ± 4.2	15 ± 21	TR
χ - CHLORDANE	3.0 ± 1	3.4 ± 2.3	9 ± 5	2 ± 2
γ - CHLORDANE	3.2 ± 2	2.2 ± 1.8	8 ± 9	2 ± 2
MIREX	Not Analyzed		ND	ND

TABLE 4: Heavy Metal Residues Associated with Suspended Solids in Oakville Creek and the Grand River, 1976 (µg/g). ($\bar{X}$ and 95% Confidence Limits).

Metal	Number of Analyses	Oakville Creek	Grand River
Mercury	9	0.9 ± 0	0.9 ± 0
Copper	9	66 ± 8	40 ± 3.3
Zinc	9	518 ± 417	259 ± 31
Arsenic	9	7.7 ± 0.5	4.1 ± 0.3
Lead	9	221 ± 145	49 ± 5
Cadmium	9	2.6 ± 0.9	1.2 ± 0.2
Chromium	9	41 ± 4	53 ± 4

TABLE 5: Organochlorine Contaminant Residues in Net Plankton From Oakville Creek and the Grand River, 1976 (Wet Weight ng/g). ($\bar{X}$ and 96% Confidence Limits).

Chemical	# of Analyses	Oakville Creek	Grand River
PCB	5	21 ± 6	2 ± 4
HCB	5	TR	ND
χ - BHC	5	ND	—
LINDANE	5	ND	—
β -BHC	5	ND	ND
HEPTACHLOR	5	ND	ND
ALDRIN	5	ND	ND
HEPTACHLOR EPOXIDE	5	TR	TR
THIODAN I	5	ND	ND
THIODAN II	5	ND	ND
DIELDRIN	5	1 ± 1	2 ± 1
ENDRIN	5	2 ± 2	—
p,p' DDE	5	3 ± 1	—
o,p' DDT	5	TR	ND
p,p' DDD	5	2 ± 2	1 ± 2
p,p' DDT	5	—	—
χ - CHLORDANE	5	—	2 ± 2
γ - CHLORDANE	5	3 ± 5	3 ± 3
MIREX	5	ND	ND

ND - non detectable

TR - trace

— - less than 1

TABLE 6: Organochlorine Contaminant Residues in Amphipods From Oakville Creek and the Grand River, 1976 (Wet Weight ng/g). ($\bar{X}$ and 95% Confidence Limits)

Chemical	# of Analyses	Oakville Creek	Grand River
PCB	4	40 ± 8	5 ± 6
HCB	4	5 ± 4	ND
χ - BHC	4	7 ± 1	6 ± 3
LINDANE	4	2 ± 1	1
β -BHC	4	2 ± 0	ND
HEPTACHLOR	4	ND	ND
ALDRIN	4	ND	ND
HEPTACHLOR EPOXIDE	4	ND	ND
THIODAN I	4	ND	ND
THIODAN II	4	ND	ND
DIELDRIN	4	6 ± 1	3 ± 1
ENDRIN	4	ND	ND
p,p' DDE	4	25 ± 4	9 ± 2
o,p' DDT	4	1 ± 1	—
p,p' DDD	4	2 ± 1	—
p,p' DDT	4	2 ± 1	ND
χ - CHLORDANE	4	2 ± 1	—
γ - CHLORDANE	4	2 ± 1	1 ± 1
MIREX	4	16 ± 5	14 ± 5

ND - non detectable

— - less than 1

composition was similar at both stations, consisting of approximately 99% of phytoplankton and 1% of zooplankton. The diatoms were dominant in the phytoplankton and rotifers in the zooplankton fractions.

Plankton samples were found to be contaminated in the filtering process, therefore no metals analyses were attempted.

Benthos

Mirex was found in amphipod samples analyzed from both watersheds (Table 6). Similarly mirex residues were present in the dissolved phase of both river waters analyzed, whereas only the Oakville fish sample contained mirex residues. These results suggest that amphipods are more representative indicators of specific watershed discharges due to their sedentary life-style, as opposed to localized fish species whose home range, while restricted, is likely to be influenced also by the contaminants regime of the lake proper. Significant residue level differences between the Grand and Oakville samples were noted for PCB; ∑DDT and dieldrin (Table 6).

Metals residue levels for amphipods were not determined.

Fish

Of all the components analyzed, fish contained the highest levels of organochlorine contaminants (Table 7, Appendix 9). PCB levels in adult emerald shiners from both sampling sites exceeded the residue concentration (100 ng/g) recommended for protection of wildlife (IJC 1977). DDT and its metabolites ranked second highest of all the organochlorine contaminants analyzed. Mirex and HCB were only present in samples from Oakville Creek (Lake Ontario). Since mirex was found in amphipods from the Grand River but not in fish it appears that body-burden levels cannot be solely identified with land-use activities in the watershed studied. Contaminant imports from the lake proper must be considered as well. Significant fish residue differences between the two watersheds were noted for PCB; HCB; DDT and mirex ($p < 0.05$). Levels of organochlorine contaminants in the young-of-the-year fish from the Grand were found to be significantly lower than residues in the adult emeralds ($p < 0.05$).

Frank *et al.* (1974) found mean total DDT and dieldrin residue concentrations in emerald shiners from the Holland River to be 386 ng/g and 22 ng/g respectively. Reinert (1970) reported

TABLE 7: ORGANOCHLORINE CONTAMINANT RESIDUES FOUND IN EMERALD SHINERS IN OAKVILLE CREEK AND THE GRAND RIVER, 1976 (ng/g). ($\bar{X}$ and 95% confidence limits).

LOCATION	No. Samples	Total Length (mm)	% Lipid	PCB	HCB	χ BHC	Lindane	β BHC	Heptachlor	Aldrin
LAKE ONTARIO										
Oakville Creek	10	82 ± 3	3.9 ± 0.6	1402 ± 473	12±4	5 ± 4	2 ± 1	1 ± 1	ND	ND
LAKE ERIE										
Grand River	10	81 ± 1	4.3 ± 0.9	5541 ± 75	ND	5 ± 2	2 ± 1	ND	ND	ND
Grand River (young-of-the-year)	8	46 ± 0.1	2.6 ± 0.2	146 ± 8	ND	6 ± 2	3 ± 1	—	ND	ND

Continuation of above

LOCATION	Heptachlor Epoxide	Thiodan I & II	Dieldrin	Endrin	p,p' DDE	o,p' DDT	p,p' DDD	p,p' DDT	χ-Chlordane	γ-Chlordane	Mirex
LAKE ONTARIO											
Oakville Creek	2 ± 1	ND	7 ± 2	2 ± 1	182 ± 73	18 ± 7	28 ± 10	6 ± 3	20 ± 7	19 ± 3	39 ± 8
LAKE ERIE											
Grand River	2 ± 1	ND	14 ± 7	2 ± 1	72 ± 14	15 ± 7	24 ± 6	5 ± 2	11 ± 6	13 ± 6	ND
Grand River (young-of-the-year)	1 ± 0	ND	5 ± 2	—	24 ± 6	4 ± 1	11 ± 2	2 ± 1	3 ± 2	7 ± 2	ND

ND - non detectable

— - Less than 1

average concentrations of total DDT in Lake Erie emerald shiners to be 940 ng/g in 1968. Unfortunately Reinert's publication does not provide the necessary fish size information for comparisons with the results from this study.

The metals residues for the adult and young-of-the-year emeralds are summarized in Tables 8 and 9. With the exception of arsenic and copper, metals residue levels were found to be similar in the adult fish at both locations, and were similar to metals residues found in yellow perch from the Long Point Bay (Kelso and Frank, 1974). Arsenic levels in the Grand River adult emeralds were significantly higher when compared to Oakville collections. Young-of-the-year fish at the Grand contained higher arsenic residues than adults, whereas higher mercury concentrations were found in adult emeralds. Zinc and cadmium concentrations in the young-of-the-year emeralds were not significantly different from residues found in the adults ($p < 0.05$).

Although aging of individual fish was not done, mean lengths and lipid contents of the adult collections were similar. The size distributions of adult emeralds analyzed suggest that the majority of the collections consisted of 1+ age group (Table 7).

Interrelationships

No reference material is available at present to assess individually, or collectively the biological significance of the organochlorine contaminant residue loads in terms of the species survival or well-being.

However, it should be noted that PCB residue levels alone exceeded the acceptable guidelines for protection of wildlife, therefore the combined organochlorine contaminant residue loads should be cause for concern at the localities sampled.

The biological samples from the Oakville collections showed significantly higher concentrations of organochlorine contaminants for the following chemicals: PCB, dieldrin, mirex, HCB and DDT. Yet no significant differences in dissolved contaminant levels were found in river waters analyzed. Since the water sampling stations were located upstream from the river estuaries, the residue loads associated with river waters may not have accurately represented the contaminant regimes in river estuaries for body-burden level evaluations in the biota. It may be postulated that the quantitative and qualitative alterations occurring in river water quality between

TABLE 8: Heavy Metal Residues in Emerald Shiners, 1976 (µg/g). ($\bar{X}$ and 95% Confidence Limits).

METAL	# of Samples	ADULTS	
		Oakville Creek	Grand River
Mercury	10	0.06 ± 0.02	0.05 ± 0.01
Copper	10	1.3 ± 0.06	1.5 ± 0.12
Zinc	10	66.0 ± 3.00	65.0 ± 3.00
Arsenic	10	0.08 ± 0.01	0.19 ± 0.02

TABLE 9: Heavy Metal Residues in Adult Emerald Shiners Versus Young-of-the-year at the Grand River, 1976 (µg/g). ($\bar{X}$ and 95% Confidence Limits).

Metal	# of Samples	Adults (1+)	# of Samples	Young
Mercury	10	0.05 ± 0.01	8	0.02 ± 0.01
Copper	10	1.5 ± 0.12	8	1.7 ± 0.47
Zinc	10	65.0 ± 3.00	8	55.0 ± 1.00
Arsenic	10	0.19 ± 0.2	8	0.36 ± 0.01

the water sampling points and river estuaries may have had a significant effect on biological uptake of the contaminants. Of particular interest is the Grand River site, where seven kilometers of marshland separated the river water sampling stations from the river estuary.

The evaluation of contaminant partitioning in the components analyzed has identified biological materials to be more reliable indicators of contaminant presence than water samples. Furthermore, the results from the Grand River and Oakville Creek study suggest that biological materials that accumulate high levels of persistent contaminants provide the best base for comparative contaminant level investigations.

Considering the logistics involved with the need for large volume water samples, and the frequent sampling necessary to minimize seasonal contaminant level fluctuations, biological samples such as fish offer definite advantages. Perhaps most important of all, biological samples offer the integrated results of all physico-chemical and biological factors affecting biological uptake.

1977 Surveys

Organics

Spottail shiners were collected at nine of the ten study sites selected for the 1977 survey. With the exception of the Grand and Salmon River collections all samples consisted of comparable size young-of-the-year fish. Due to their small size the Grand River fish have to be considered belonging to a late-spawning population, while the Salmon River fish were composed of yearlings. Table 10 summarizes the organochlorine residue data obtained from the spottail shiners analyses, and Appendix 10 depicts the geographic distribution of the major organochlorine contaminant groups found in this survey.

Of all the organochlorine contaminants identified, PCB and DDT residues were found most frequently, followed by chlordane. While the distribution patterns of other chemical groups were erratic, PCB and DDT residues were found at all sites sampled and mirex was limited to Lake Ontario.

Mean PCB residue levels in young-of-the-year spottail shiners ranged from 56 ng/g - 2175 ng/g and, of the nine stations sampled, six exceeded the recommended body-burden concentration

TABLE 10. Organochlorine Contaminant Residues Found in Spottail Shiners in Some Ontario Drainage Basins, 1977 (ng/g). ($\bar{X}$ and 95% confidence limits)

LOCATION	No. Samples	Total Length (mm)	% Lipid	PCB	∑DDT	Mirex	HCB	χBHC	Lindane
GEORGIAN BAY									
Nottawasaga River	10	58±2	8.0±0.1	90±7	106±7	ND	ND	4±1	ND
LAKE ST CLAIR									
Thames R. (Tremblay Creek)	10	58±2	1.5±0.2	64±11	12±4	ND	ND	ND	ND
LAKE ERIE									
Detroit River (Big Creek)	9	57±2	0.9±0.1	447±41	71±13	ND	ND	ND	ND
Sturgeon Creek (Pt. Pelee)	10	58±2	1.6±0.2	467±70	133±28	ND	ND	ND	ND
Grand River	10	45±2	1.5±0.1	56± 7	12± 1	ND	ND	ND	ND
LAKE ONTARIO									
Niagara River	10	51±3	2.9±0.1	654±105	150±20	13±2	25±7	8±3	11±5
Burlington Beach	9	55±3	5.3±0.5	833±69	267±24	9±1	4±2	7±1	3±1
Humber River	10	62±2	7.2±0.3	2175±155	276±36	5±1	5±1	38±4	3±1
Salmon River	10	78±2	3.8±0.2	112±20	44±7	1±1	ND	3±1	ND

Continuation of above

LOCATION	β-BHC	Heptachlor Epoxide	Dieldrin	Endrin	χChlordane	γChlordane	Heptachlor	Aldrin
GEORGIAN BAY	ND	3±1	6±3	2±1	8±3	3±2	ND	ND
Nottawasaga River								
LAKE ST. CLAIR	ND	ND	ND	ND	3±2	ND	ND	ND
Thames R. (Tremblay Creek)								
LAKE ERIE								
Detroit River (Big Creek)	ND	ND	ND	ND	ND	ND	ND	ND
Sturgeon Creek (Pt. Pelee)	ND	ND	ND	ND	13±3	11±2	ND	ND
Grand River	ND	ND	ND	ND	ND	ND	ND	ND
LAKE ONTARIO								
Niagara River	7±4	1±1	ND	ND	87±8	28±8	ND	ND
Burlington Beach	1±1	3±1	ND	ND	25±6	23±6	ND	ND
Humber River	ND	2±1	18±1	4±1	3±1	57±11	ND	ND
Salmon River	ND	ND	ND	ND	1±1	12±3	ND	ND

ND - non-detectable

level of 100 ng/g established for protection of wildlife (IJC 1977). High PCB residues were generally found in fish collected in watersheds associated with industrial activities. The highest fish residue levels were obtained from the western part of Lake Ontario, while relatively low residues were found in the predominately rural watersheds: Nottawasaga, Thames, Grand, Salmon. PCB residue levels in fish from Point Pelee have decreased significantly ($p < 0.05$) compared to those reported in 1975 (Suns and Rees, 1975). However, PCB residues in fish from Niagara-on-the Lake showed no decrease over the same period.

While DDT and metabolite residues were found in all of the samples analyzed, their body-burden levels did not exceed the acceptable wildlife standards of 1 µg/g (IJC 1977). Total DDT concentration levels in the fish analyzed ranged from 12 ng/g - 276 ng/g (Table 10). Total DDT residue levels for the young-of-the-year spottails from Niagara-on-the-Lake were found to have decreased significantly ($p < 0.05$) compared to those reported in 1975 (Suns and Rees, 1975). The ban on DDT usage in 1969 seems to be reflected in the decreased body-burden levels of the biota at this location. However, no significant decline was evident when comparing the same data base for the Point Pelee collections. Assuming that low DDE/DDT ratios represent recent inputs of DDT, distinct distributions were found when analyzing the residue data of this survey. Most of the low metabolite levels were found at Lake St. Clair and the Western Lake Erie stations: Thames River (0.15); Detroit River (0.10); Point Pelee (0.17), whereas increasingly larger proportions of the major metabolite were found at the Nottawasaga River (0.39) on Georgian Bay and the Eastern Lake Erie and Lake Ontario sampling sites: Grand River (0.53); Niagara River (0.47); Burlington Beach (0.60); Humber River (0.61) and the Salmon River (0.46). The above distribution pattern may be indicative of more recent DDT usage in the Lake St. Clair, Western Lake Erie basins, such as an extended usage on tobacco crops in that area.

With the exception of Detroit and Grand River sites, chlordane was found in all fish samples analyzed. The combined α and γ chlordane fraction residues at Niagara-on-the-Lake exceeded the established guideline limits of 100 ng/g for protection of wildlife (EPA, 1973). It should be noted that chlordane residues in fish from the Niagara-on-the-Lake and Point Pelee stations have increased since 1975. Whereas the 1975 Ontario Ministry of the Environment survey reported non-detectable concentrations in young- of-the-year spottails at both stations, residue levels in the present survey were found to be 115 ng/g and 24 ng/g respectively. Although chlordane has been used increasingly in corn production in Ontario (R. Frank pers. comm.), fish residues from the corn belt area of southwestern Ontario were relatively low. Therefore, sources other than agricultural applications are likely active in chlordane inputs in Lake Ontario.

Mirex residues in spottail shiners from nearshore waters of Lake Ontario indicated a definite trend in geographic distribution (Appendix 10). The highest residues in fish were found in the western parts of Lake Ontario (Niagara River), with progressively decreasing concentrations eastward. The above trend implicates the Niagara River as a source of mirex to Lake Ontario. Sediment plume analyses have similarly identified the Niagara River as a major point source of mirex (Van Hove, Holdrinet *et al.* unpublished data). In the absence of quantitative body-burden criteria for mirex and dechlorane, evaluations of its impact have to be limited to human health considerations in sport and commercial fishes.

Emerald shiners were collected from three sites to provide cross- reference material for the 1976 survey results and inter-species comparison. Table 11 summarizes organochlorine contaminant residues for the emerald collection only. Young-of-the-year spottail and emerald residue data from the Humber River collection were used to assess inter-species comparability of organochlorine contaminant uptake. While the data base was small and residue data represented a single locality only, the results suggested species-specific differences in organochlorine contaminant uptake.

Metals

Fish collections from all sites were analyzed for mercury, while copper, zinc and arsenic analyses were also completed on Detroit, Niagara and Humber River collections (Table 12). Mercury levels in the young-of- the year spottails ranged from 0.01 µg/g - 0.10 µg/g. Highest mercury concentrations were found in the fish from the Detroit River, followed by the Niagara-on-the-Lake and Thames River sites.

No significant differences in copper concentrations were found when comparing residue levels from the Detroit, Niagara and Humber River collections ($p < 0.05$). Arsenic residues in the spottails analyzed were found to be significantly different at all stations sampled. None of the metals body-burden levels obtained from this survey exceeded the adopted limits for protection of wildlife.

TABLE 11: Organochlorine Contaminant Residues in Adult Emerald Shiners From Oakville Creek and Grand River (1976) Compared to Adult Emerald Shiners From Nottawasaga and Saugeen Rivers (1977), (ng/g). ($\bar{X}$ and 95% confidence limits).

LOCATION	No. of Analyses	Total Length (mm)	% Lipid	PCB	∑DDT	Mirex	HCB	χBHC	Lindane
Oakville Creek	10	82±3	3.9±0.6	1402±473	235±124	39±8	12±4	5±4	2±1
Grand River	10	81±1	4.3±0.9	554±75	116±20	ND	ND	ND	2±1
Nottawasaga River	10	83±3	10±1	241±72	160±9	ND	ND	7±1	1±1
Saugeen River	10	81±3	6±1	188±23	100±18	ND	ND	2±1	2±2

Continuation of above

LOCATION	β-BHC	Heptachlor	Heptachlor Epoxide	Aldrin	Dieldrin	Endrin	χChlordane	γChlordane
Oakville Creek	1±1	ND	2±1	ND	7±2	2±1	20±7	19±3
Grand River	ND	ND	2±1	ND	14±7	2±1	11±6	13±6
Nottawasaga River	ND	ND	3±1	ND	12±5	4±2	3±1	14±2
Saugeen River	ND	ND	1±1	ND	ND	ND	16±5	ND

ND - non-detectable

TABLE 12: Heavy Metal Residues in Spottail Shiners, 1977 (µg/g) (Means and 95% Confidence Limits)

SITE LOCATION	Sample No	T.L. (mm)	% Lipid	Hg	Cu	Zn	Pb	As
GEORGIAN BAY								
Nottawasaga River	10	58 ±2	8 ±0.1	0.035 ±0.003	_*	_*	_*	_*
LAKE ST. CLAIR								
Thames River (Tremblay Creek)	10	58 ±2	1.5 ±0.2	0.062 ±0.004	_*	-*	_*	-*
LAKE ERIE								
Detroit River (Big Creek)	9	57 ±2	0.9 ±0.1	0.093 ±0.010	1.57 ±0.3	29 ±2		0.13 ±0.008
Sturgeon Creek	10	58 ±2	1.6 ±0.2	0.056 ±0.004	_*		_*	-*
Grand River	10	45 ±2	1.5 ±0.1	0.037 ±0.010	_*	_*	_*	_*
LAKE ONTARIO								
Niagara River	10	51 ±3	2.9 ±0.1	0.074 ±0.008	1.27 ±0.3	32 ±4		0.21 ±0.020
Burlington Beach	9	55 ±3	5.3 ±0.5	0.039 ±0.006	_*	_*	_*	_*
Humber River	10	62 ±2	7.2 ±0.3	0.044 ±0.003	1.22 ±0.2	26 ±1		0.09 ±0.009
Salmon River	10	78 ±2	3.8 ±0.2	0.01 ± 0.004	_*	_*	_*	_*

* not analyzed for

CONCLUSIONS AND RECOMMENDATIONS

In the absence of more comprehensive toxicity data for fish and other components of the aquatic life, impact assessment of contaminant loads had to be restricted to wildlife guideline applications.

Evaluations of trace contaminant partitioning results from the Grand River and Oakville Creek study suggests that biological materials offer a more reliable base for environmental impact assessment than sediments or water. Components of the biota at higher trophic levels proved to be more useful for station-to-station body-burden comparisons.

Organochlorine pesticide concentrations found in the biota suggest that agricultural practices in the watersheds sampled have not contributed in a major way to trace contaminant loadings.

While some DDT and PCB residue declines in fish have been observed in parts of Lake Erie and Lake Ontario, chlordane concentrations in fish have increased substantially over a two year period ending in 1977. Since chlordane levels have remained relatively low in the corn-belt area of southwestern Ontario, the increasing agricultural usage of chlordane in corn production cannot be identified with the increased fish residue accumulations. On the contrary, the highest fish residue levels of PCB, DDT and chlordane were found in watersheds associated with industrial activities. Considering the observed trends in fish residues, there is a need for input source identification in Lake Ontario.

Mirex residues in young spottail shiners from the nearshore waters of Lake Ontario exhibited a definite geographic distribution. Highest fish residue concentrations were found in the Western part of Lake Ontario (Niagara River), with declining residues eastward. These results implicate the Niagara River as a major input source of Mirex to Lake Ontario.

None of the metals residues analyzed exceeded the body-burden criteria for protection of wildlife.

Although predator species of fishes have traditionally been preferred for contaminant impact evaluations, the forage species used in this study have shown to be sensitive indicators of trace contaminant uptake, and provided a good data base for geographic contaminant distribution evaluations.

Although body-burden criteria for the comon persistent contaminants are generally available from literature, these standards provide only general guidelines for protection of wildlife, and do not constitute a proper base for environmental significance assessment. Furthermore, the criteria are single-compound orientated without reference to the complex nature of contaminant loads encountered in the Great Lakes fish. It has to be recognized, therefore, that in the absence of quantitative uptake data for persistent contaminants and their effect on the biota, certain limitations are inevitable in environmental impact assessments.

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Appendix 1: Agricultural Chemical Usage in the Grand River Drainage Basin

Type	Agricultural Chemical	Annual Usage (kg)
	Lindane	77
	Endosulphan	1195
	Vorlex	73304
Organochlorine	Telon	15523
	Shell DD	44868
	Chlordane (+)	
	Methoxychlor	12
	Lorsban	2291
	Phosmel	1366
	Diazinon	256
	Dylox	371
Organophosphate	Malathion	264
	Phosdrin	4
	Parathion	4
	Dasanit	181
	Birlane	1407
	Thimet	733
	Sevin	1293
Carbamate	Furadan	1358
	Bladex	32151
	Lasso	21007
	Atrazine	121628
	Linuron	412
	Sutan	37348
	Outfox	126
	Amitrol-T	1630
	Kil-Mor	486
	2,4-D Amine	19318
	2,4-D Ester	256
	Tilan	2488
	Balan	3
Herbicide	Avadex BW	262
	Eptum	753
	Patoran	1030
	Treflan	120
	MCPA	15452
	MCPB	5013
	Gramoxone	27
	Embutox	5984
	Ekko	2087
	Carbyne	42
	Afesin-dinitro	
	Dipel	383
	Agrox N-M	20
Other	Vitaflow	44
	Polyram	4
	Bux	218
	Dyfonate	133

From OMAF and AC, 1975.

Appendix 2: Agricultural Chemical Usage in the Oakville Creek Drainage Basin

Type	Agricultural Chemical	Annual Usage Kg
Organochlorine	Lindane	1
Organophosphate	Diazinon	1
	2,4-D Amine	392
	Embutox	377
	Dalapon	139
	MCPA	157
Herbicides	Atrazine	1730
	Lasso	1002
	Bladex	528
	Ekko	501
	Linuron	2

From OMAF and AC, 1975

APPENDIX 3

Organic Chemicals Analyzed

	1976	1977	
PCB	DIELDRIN	PCB	p,p' DDE
HCB	ENDRIN	HCB	o,p' DDT
χ - BHC	p,p' DDE	χ - BHC	p,p' DDD
β - BHC	p,p' DDD	LINDANE	p,p' DDT
LINDANE	o,p' DDT	β - BHC	DIELDRIN
HEPTACHLOR EPOXIDE	p,p' DDT	HEPTACHLOR	ENDRIN
THIODAN I	χ - CHLORDANE	ALDRIN	χ - CHLORDANE
THIODAN II	β - CHLORDANE	HEPTACHLOR EPOXIDE	γ - CHLORDANE
	MIREX		MIREX

APPENDIX 4

Metal Species Analyzed

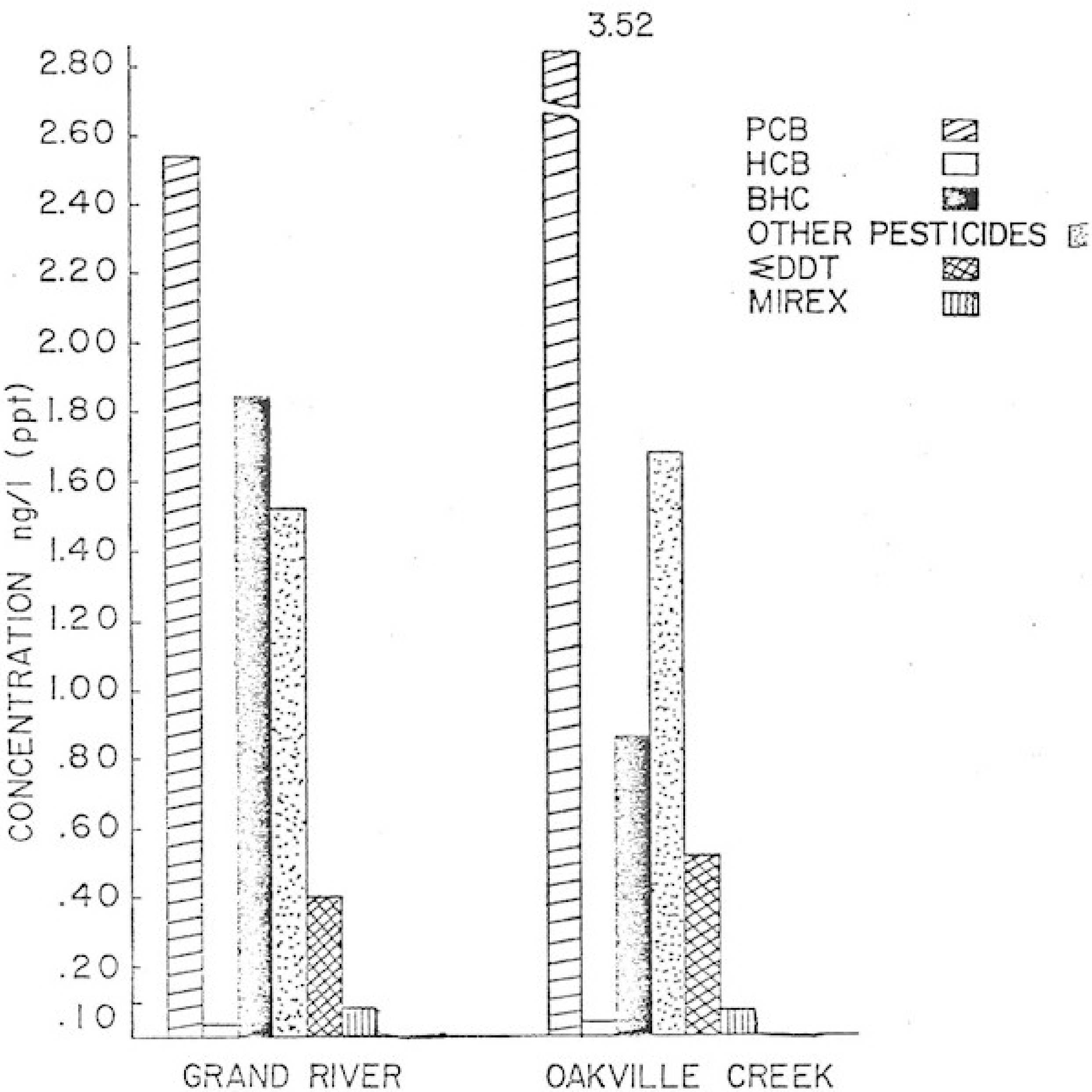
1976		1977	
COPPER	LEAD	COPPER	LEAD
CHROMIUM	MERCURY	ARSENIC	MERCURY
ARSENIC	CADMIUM	ZINC	
ZINC			

APPENDIX 5

SCHEDULE FOR COLLECTION OF CHEMICAL AND BIOLOGICAL SAMPLES, 1976 AND 1977

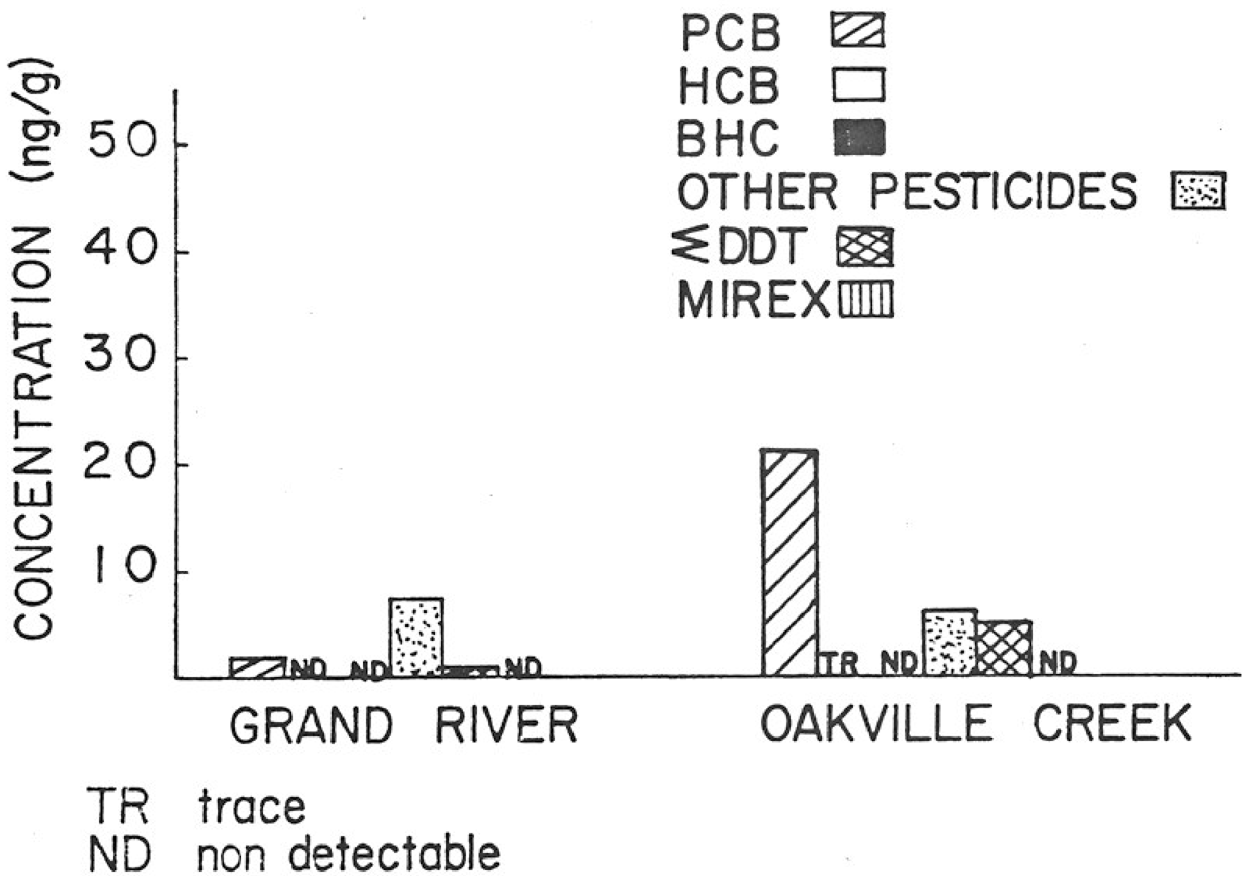
LOCATION	SAMPLE TYPE	SAMPLING DATE/PERIOD
1976		
Oakville Creek and	suspended solids	July 12-16; September 27-October 1
Grand River	water	July 12-16; September 27-October 1
	benthos	September
	plankton	July 12-16; September 27-October 1
	fish (emerald shiner)	September
1977		
Sturgeon Creek (Point Pelee)	fish (spottail shiners)	August 22
Detroit River	" " "	August 23
Thames River (Tremblay Creek)	" " "	August 24
Saugeen River	" (emerald shiners)	September 7
Saugeen River	" (common shiners)	September 7
Nottawasaga River	" (spottail shiners)	September 9
Nottawasaga River	" (emerald shiners)	September 9
Niagara River	" (spottail shiners)	September 14
Grand River	" (spottail shiners)	September 15
Salmon River	" (golden shiners)	October 6
Salmon River	" (spottail shiners)	October 6
Burlington Beach	" (spottail shiners)	October 11
Humber River	" (spottail shiners)	October 13
Humber River	" (emerald shiners)	October 13

Appendix 6: Concentrations Of Organic Residues Found In The Dissolved Phase Of Waters Of Grand River And Oakville Creek, 1976.

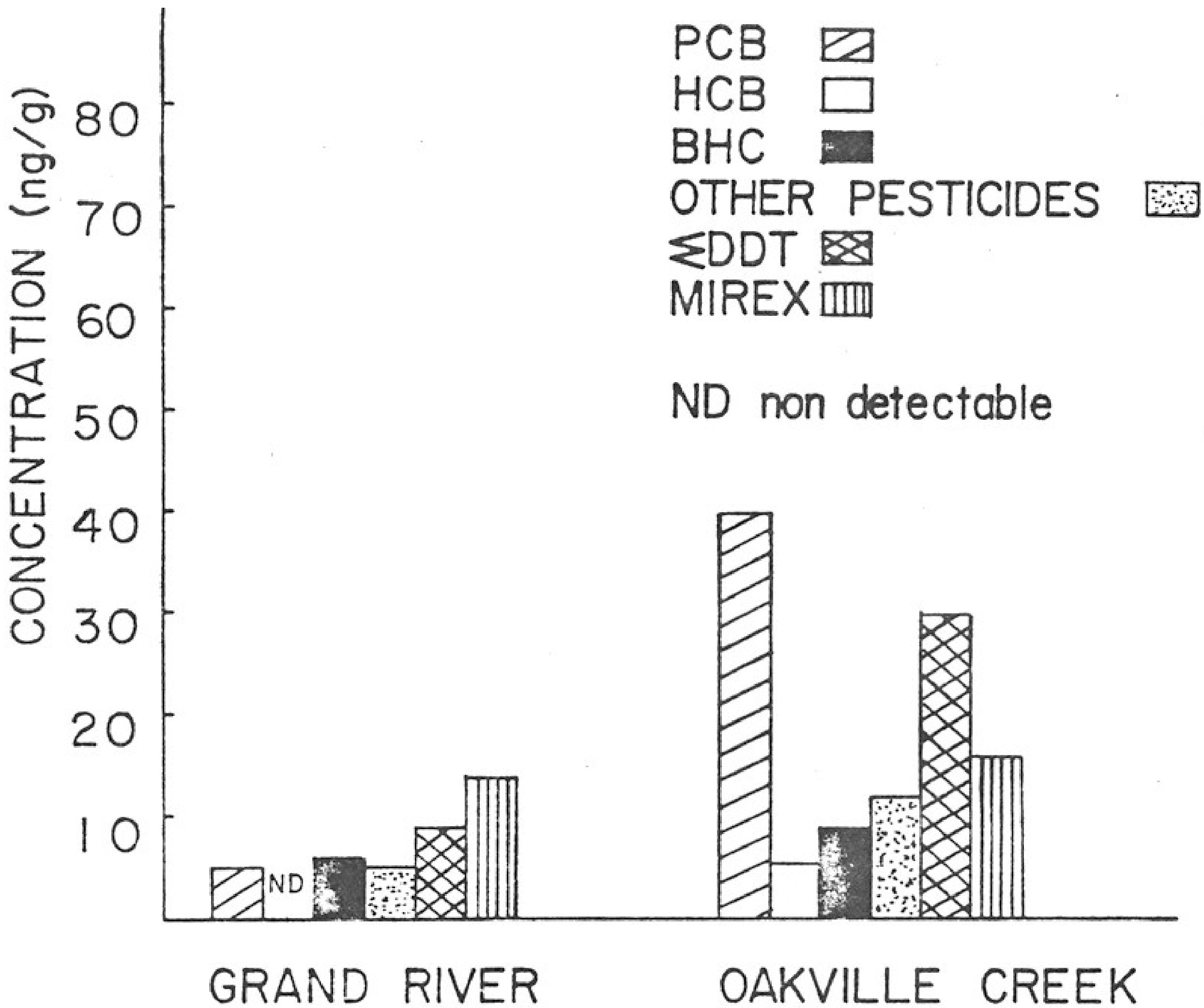


Note: Averages of July and September values.

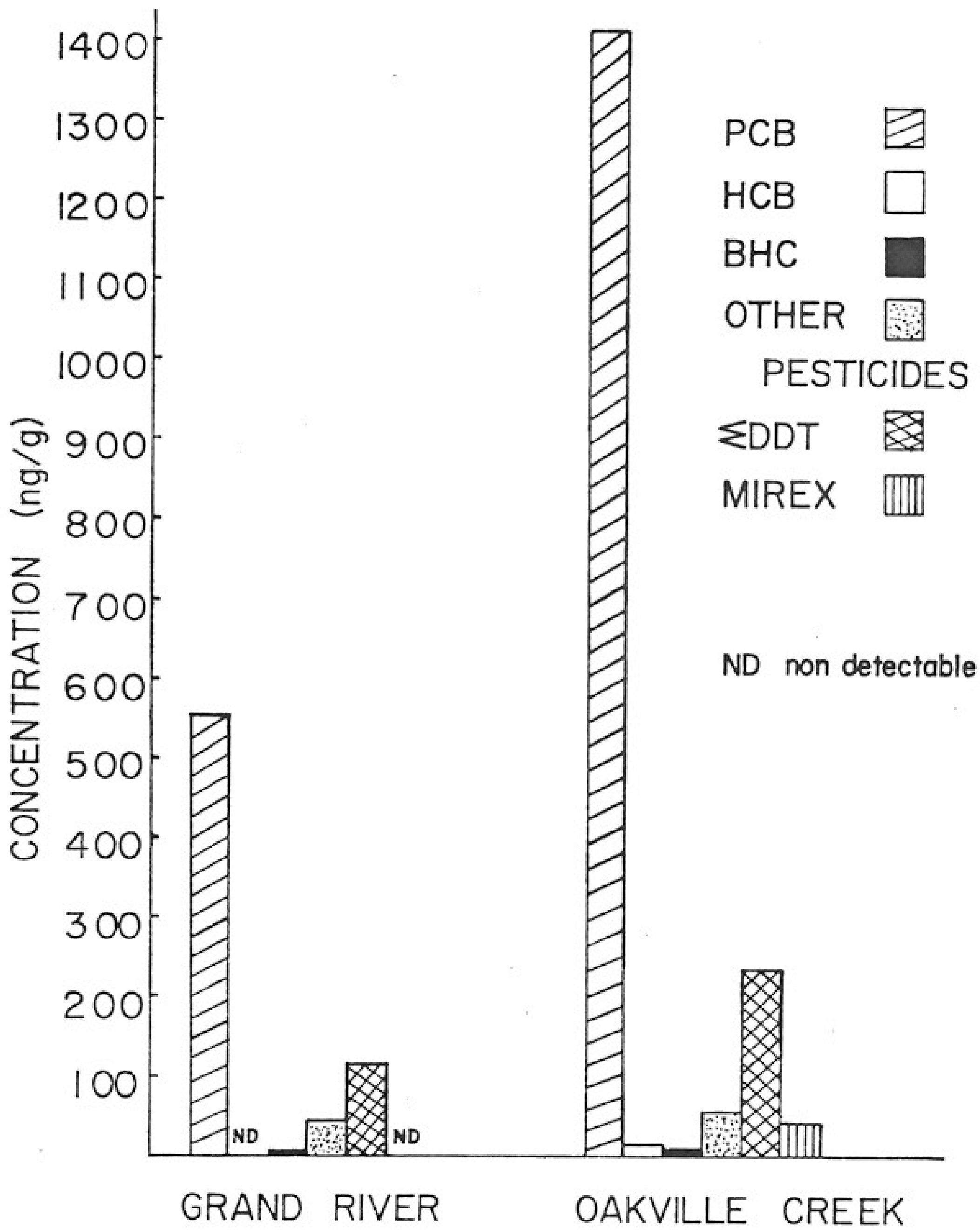
Appendix 7: Concentrations Of Organic Residues Found In Plankton In Grand River And Oakville Creek, 1976.



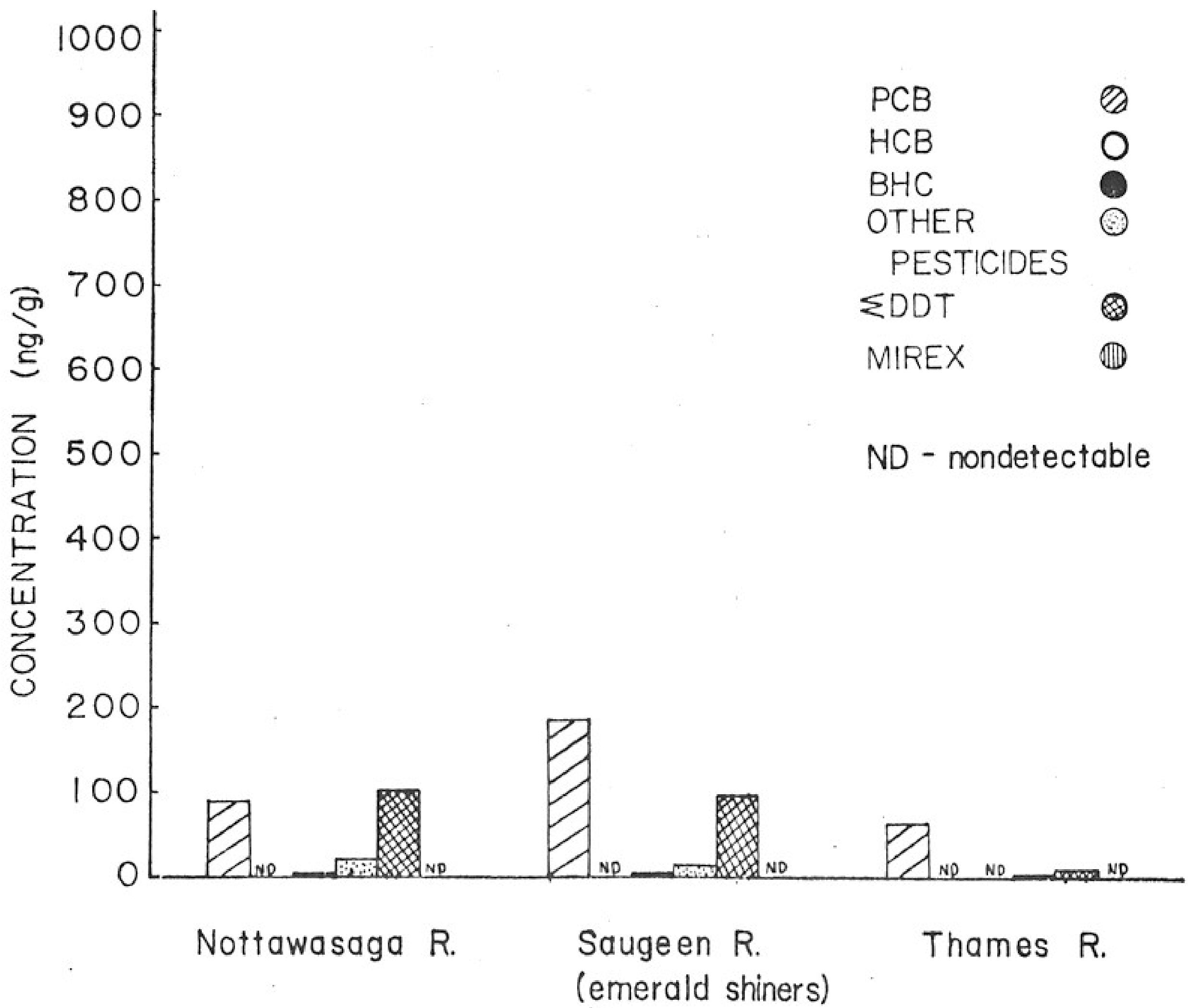
Appendix 8: Concentrations Of Organic Residues Found In Amphipods In Grand River And Oakville Creek, 1976.



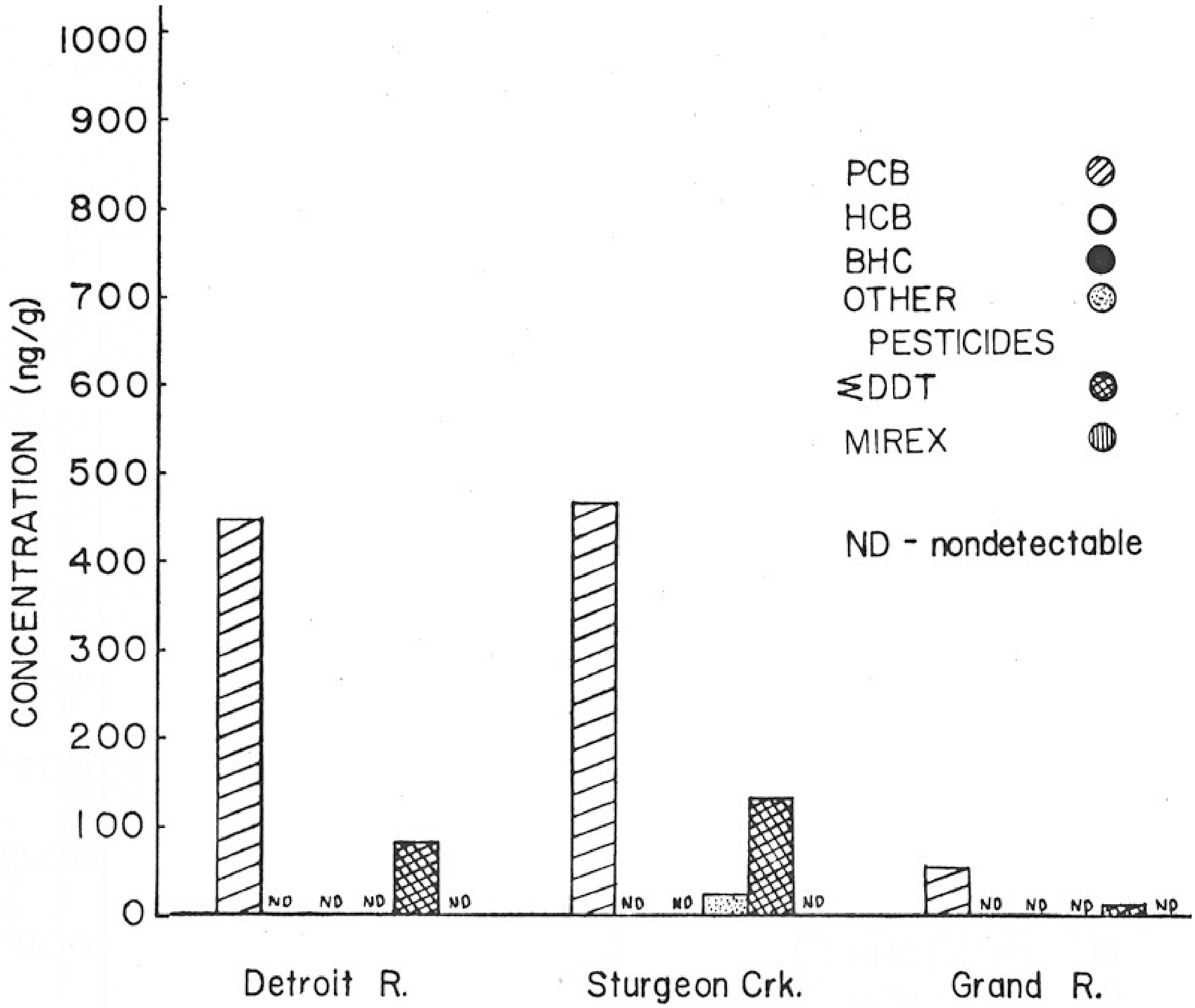
Appendix 9: Concentrations Of Organic Residues Found In Adult Emerald Shiners In Grand River And Oakville Creek, 1976.



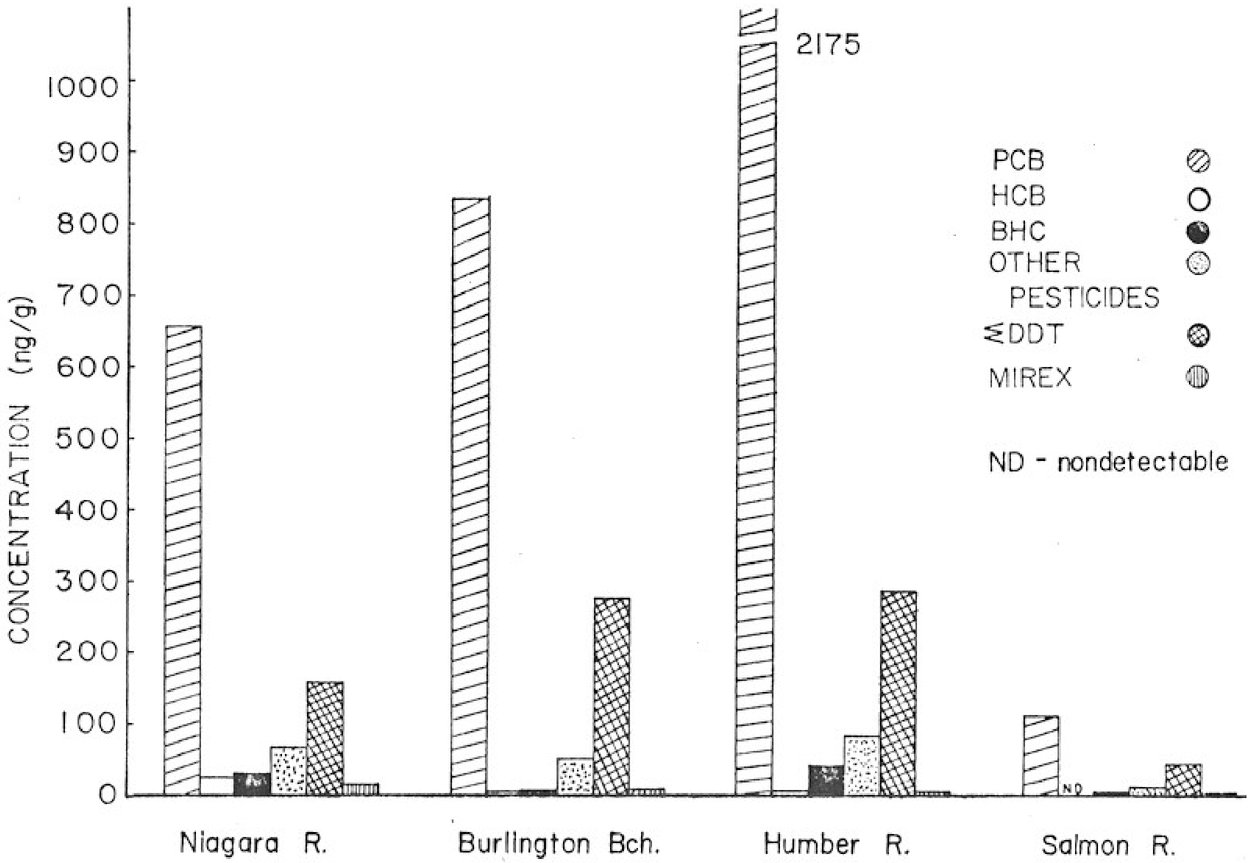
Appendix 10a: Concentrations of organic residues found in spottail shiners, 1977.



Appendix 10b: Concentrations of organic residues found in spottail shiners, 1977.



Appendix 10c:: Concentrations of organic residues found in spottail shiners, I977.



APPENDIX 11. Organochlorine Contaminant Residues Found in Other Minnows Collected, 1977 (ng/g). (Means and 95% Confidence Limits).

SITE LOCATION	Fish Species	Sample No.	Length T.L. (mm)	% Lipid	PCB	ΣDDT	Mirex	HCB	χBHC	Lindane	β BHC	Hepta-chlor	Hepta-chlor Epoxide	Aldrin	Dieldrin	Endrin	Chlordane	
																	χ	γ
GEORGIAN BAY																		
Nottawasaga R.	emerald shiner	10	83±3	10±1	241±72	160±9	ND	ND	7±1	1±1	ND	ND	3±0.4	ND	12±5	4±2	3±1	14±2
LAKE HURON																		
Saugeen R.	emerald shiner	10	81±3	6±1	188±23	100±18	ND	ND	2±1	2±2	ND	ND	1±1	ND	ND	ND	16±5	ND
Saugeen R.	common shiner	10	54±2	5±1	182±39	60±19	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	12±6	ND
LAKE ONTARIO																		
Humber River	emerald shiner	10	58±2	7±0.4	1090±79	289±26	13±1	14±2	50±11	6±2	ND	ND	2±0.3	ND	17±1	3±1	4±1	41±6
Salmon River	golden shiner	10	70±2	4±0.2	144±61	45±9	ND	ND	3±1	ND	ND	ND	ND	ND	ND	ND	2±2	12±3

ND = non detectable

APPENDIX 12: Heavy Metal Residues Found in Other Minnows Collected 1977 (µg/g). (Means and 95% Confidence Limits).

SITE LOCATION	Fish Species	Sample No.	Length T.L. (mm)	Lipid	Hg	Cu	Zn	Pb	As
GEORGIAN BAY									
Nottawasaga River	emerald shiners	10	83±3	10±1	0.048±0.004	-*	-*	-*	-*
LAKE HURON									
Saugeen River	emerald shiners	10	81±3	6±1	0.084±0.03		-*		-*
Saugeen River	common shiners	10	54±2	5±1	0.094±0.008	_*	-*	-*	-*
LAKE ONTARIO									
Humber River	emerald shiners	10	58±2	7±0.4	0.066±0.003	1.35±0.4	39±8		0.18±0.06
Salmon River	golden shiners	10	70±2	4.02	0.023±0.003	_*	-*	-*	-*

* not analyzed for