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Toxic Contaminants in the Niagara River, 1975-1982

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Abstract

Between 1975 and 1982, Water Quality Branch, Ontario Region, collected water quality samples in the Niagara River system. This report summarizes the results obtained for toxic contaminants and trace metals from these monitoring activities. Various types of samples, including unfiltered water samples, suspended and bottom sediments and spottail shiners (*Notropis hudsonius*), have been analyzed for these constituents. In addition, large-volume (200 L) aqueous phase water samples were extracted for toxic organic contaminants. Data have been subdivided into two major categories: (1) data collected at a single fixed station at Niagara-on-the-Lake and (2) data collected at various survey stations throughout the Niagara River system. Violations to the 1978 Great Lakes Water Quality Agreement specific objectives or Ontario Ministry of the Environment guidelines are indicated, and loadings to Lake Ontario have been calculated and presented.

Résumé

Entre 1975 et 1982, la Direction de la qualité des eaux, région de l'Ontario, a prélevé des échantillons d'eau dans la rivière Niagara. Le présent rapport résume le résultat des contrôles des contaminants toxiques et des métaux à l'état de trace. Différents types d'échantillons, dont des échantillons d'eau non filtrée, de sédiments en suspension, de sédiments du lit et de queues à tache noire (*Notropis hudsonius*) ont été analysés au regard de ces constituants. De plus, on a prélevé des échantillons volumineux (200 L) d'eau en vue d'y déceler des contaminants organiques toxiques. Les données ont été subdivisées en deux grandes catégories : 1) celles qui proviennent de la station fixe de Niagara-on-the-Lake et 2) celles de différentes stations le long de la rivière Niagara. Les cas de non-respect de certains objectifs précis de l'Accord de 1978 relatif à la qualité de l'eau dans les Grands lacs ou des lignes directrices du ministère de l'Environnement de l'Ontario ont été notés, et les apports vers le lac Ontario ont été calculés et sont communiqués.

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Executive Summary

This report summarizes the toxic contaminants and trace metal monitoring activities carried out by the Water Quality Branch, Ontario Region, in the Niagara River system between 1975 and 1982. Data have been subdivided into two major categories: (1) data collected at a single fixed station at Niagara-on-the-Lake and (2) data collected at various survey stations throughout the Niagara River system.

Fixed Station

Metals

Unfiltered water samples have been collected weekly from Niagara-on-the-Lake since 1975. The total trace metal results indicate that there has been no apparent change in annual median concentration or loading during the last seven years, except for iron and aluminum, which both increased until 1981. This increase was due to natural factors, primarily higher wind velocities in the eastern basin of Lake Erie, which caused resuspension of bottom sediments.

The results of a number of tests for iron, copper and cadmium exceeded the 1978 Great Lakes Water Quality Agreement specific objectives, but the cause of the excess was always natural, usually increased suspension of bottom sediments in Lake Erie. For example, 1980 data showed that concentrations exceeding the objectives ranged from 2% for measurements of Cd to more than 50% for Fe and 10% for Cu.

Ontario Ministry of the Environment dredge spoil objectives are often exceeded in the suspended sediments collected at Niagara-on-the-Lake. Concentrations of Cd, Pb, Cu, Cr, Ni and Zn in suspended sediments exceeded these objectives more than 70% of the time.

The loading of metals such as Cr, Ni, Pb, Fe and Zn to Lake Ontario is almost completely derived from the suspended sediment rather than from the dissolved phase. The minimum contribution is 70% for Cr, the maximum almost 100% for Pb, Fe and Zn.

Organics

Nineteen organochlorine compounds were measured in raw water and in the suspended sediments at Niagara-on-

the-Lake. Loadings were calculated for both phases, and percentage organochlorine loadings from suspended sediments were less than expected. Suspended sediments contributed more than 40% of the total load for only total DDT (mostly DDE), hexachlorobenzene, total PCBs and mirex. For all the other compounds measured the water fraction contributed more than 60% of the total load. Thus, very low detection limits for water sample analysis are required to obtain accurate total loading estimates.

Of the 19 organochlorine compounds routinely measured in ambient water samples (unfiltered) at Niagara-on-the-Lake, eight were detected in more than 50% of the samples collected (i.e., total PCBs, α - and γ -BHC, dieldrin, HCB, α - and γ -chlordane and p,p'-DDE). Of these, three (total PCBs, and α - and γ -BHC) were detected at median concentrations greater than 1 ng L⁻¹.

Higher PCB loadings to Lake Ontario than previously reported (Frank *et al.*, 1979) have been calculated from these data. Mirex and total DDT loadings remain about the same as previously reported by Frank *et al.* (1979).

Of the 19 organochlorine compounds measured in suspended sediments collected at Niagara-on-the-Lake, 11 (total PCBs, HCB, p,p'-DDE, p,p'-DDT, mirex, α -BHC, dieldrin, γ -chlordane, p,p'-TDE, p,p'-methoxychlor and α -chlordane) were detected in more than 50% of the samples. Of these, total PCBs, HCB and p,p'-DDE occurred at median concentrations above 10 ng g⁻¹. Eleven chlorobenzene compounds have also been measured in suspended sediments at Niagara-on-the-Lake. The compound with the widest usage (i.e. 1,4-dichlorobenzene) (Oliver and Nicol, 1982) was also the most abundant in the suspended sediments.

Survey Data

A series of surveys undertaken in the upper Niagara River in 1979 showed statistically significant ($P \geq 0.05$) cross-stream differences in total iron, total manganese and total zinc in the Tonawanda Channel. Levels of most metals were higher in the Tonawanda Channel than in the Chippawa Channel. Violations of the 1978 Great Lakes Water Quality Agreement specific objectives occurred frequently for total iron, especially during storm events in the eastern basin of Lake Erie. Other parameters such as turbidity, fecal coliform and total phosphorus also showed large increases during these events.

In a survey of trace metals throughout the Niagara River in May 1981, several violations of the 1978 Great Lakes Water Quality Agreement objectives were observed. At one station (34.6B) just downstream from two Buffalo Sewer Authority outfalls, violations of 1978 Agreement objectives were observed for zinc, nickel, cadmium and copper.

Prior to 1979, analytical methodology was unable to detect many of the organochlorines in Niagara River ambient waters. In 1979, with new lower detection limits, lindane and α -BHC were detected in more than 50% of the samples collected. In 1981, total PCBs, and α - and γ -BHC were detected in more than 50% of the samples collected at median values above 1 ng L^{-1} .

A new sampler (McCrea, 1982), capable of extracting organics from a 200-L water sample (operational definition), was used during 1981 surveys on the Niagara River. These data have shown that concentrations of heptachlor epoxide, α -endosulfan, total PCBs, p,p'-DDE, γ -BHC and all of the chlorobenzenes except dichlorobenzene in the aqueous fraction of the Niagara River increase by a factor of more than two from the Fort Erie inlet of the Niagara River to the Niagara-on-the-Lake outlet. This indicates that significant sources of these compounds are present within the basin itself.

Five major areas of contamination were located in the 1981 survey of bottom sediments. These are the lower end of the Black Rock Canal by Scajaquada Creek, the Tonawanda Island-Love Canal-Little River area, the Buffalo River, the Strawberry Island area and the Queenston area. High metal concentrations, often above Ontario Ministry of the Environment dredge spoil criteria, were observed in many of these areas. Levels of metals and numbers of violations were consistently higher on the United States side of the river. Particle size analysis indicated some significant relationships between metals, but not between metals and clay and silt abundances, indicating that metal concentrations are not dependent on sediment adsorptive capability but rather on other factors such as location of input sources or current velocity in the sampling area. High organic contaminant concentrations were also found in these areas. None of the organic contaminants were significantly related to sediment adsorptive capacity characteristics such as percent clay and silt or percent volatile solids. This suggests that contaminant concentrations are not associated with

different sediment types but are more likely related to sources in the areas sampled.

Measurements of suspended sediments at five locations in the Niagara River in 1981 indicated that a higher concentration of suspended sediments occurred at Niagara-on-the-Lake than at Fort Erie. This increase of nearly three times the concentration is probably the result of erosion and scouring of the river bottom as well as inputs. However, organic carbon and nitrogen content of the suspended sediments at Niagara-on-the-Lake were only about 40% of those at Fort Erie. This indicates an addition of inorganic material load to the Niagara River during its course. Mercury concentrations at Niagara-on-the-Lake were about four times higher than at Fort Erie, indicating sources of mercury along the river system.

Some compounds for which Lake Erie suspended sediments appear to be a significant source to the Niagara River are p,p'-DDE, α -BHC, p,p'-TDE, dieldrin, and α -chlordane.

A survey completed in 1979 indicated that suspended sediments carried higher organic contaminant concentrations in the lower Niagara River than in the upper Niagara. Additional data collected in 1981 supported this finding and indicated that suspended sediments in the lower Niagara River were considerably enriched in organics, particularly with respect to total PCBs, p,p'-DDT, α -endosulfan and chlorobenzenes.

In mid-September 1982, collections of spottail shiners (*Notropis hudsonius*) were made at seven stations in the Niagara River. Polychlorinated biphenyls, p,p'-DDE and dieldrin were detected at more than 50% of these locations. Polychlorinated biphenyls at all stations in the Niagara River except the Frenchman's Creek station violated the 1978 Great Lakes Water Quality Agreement specific objective of 100 ng g^{-1} for PCBs in fish. High PCB concentrations were observed in spottail shiners at the stations of the 102nd Street dumpsite (800 ng g^{-1}) and downstream from Hooker Chemical at the search and rescue station, just upstream from the American Falls (2690 ng g^{-1}). Metal concentrations in spottail shiners were also elevated in the lower Niagara River. Cadmium was two to three times higher; nickel and zinc were somewhat higher and lead was three to four times higher in the lower Niagara River than in the upper Niagara River.

Introduction

Contamination of the Niagara River has long been of concern to government agencies and the public. Since the early 1950s, the International Joint Commission has released reports addressing issues of bacterial pollution, phenol and oil problems, excessive levels of iron, phosphorus, chloride and mercury and aesthetic impairment by foams and discolouration (International Joint Commission, 1951, 1967, 1971). With the signing of the 1972 Canada-United States Great Lakes Water Quality Agreement (GLWQA), significant progress has been made in alleviating many of these problems, principally through increased control and treatment of municipal and industrial discharges in response to stricter regulation.

By 1978, however, public concern had arisen over the recurring detection of persistent, bioaccumulating toxic substances, particularly PCBs and mirex, in the biota and bottom sediments of Lake Ontario (Kaiser, 1974; Hallett and Norstrom, 1977).

Coincidentally, the gravity of the Love Canal situation was realized and numerous dumpsites were discovered along the United States side of the Niagara River (Interagency Task Force, 1979). These included Hyde Park, 102nd Street and the S-Area dumpsites. All of these dumpsites were reported to contain toxic chemicals.

In partial fulfillment of Canada's commitments for surveillance and monitoring under the 1972 GLWQA, the Water Quality Branch of Environment Canada's Inland

Waters Directorate, Ontario Region (WQB-OR) began conducting major water quality surveys on the Niagara River in 1975. In addition, a daily sampling program was established at Niagara-on-the-Lake. The strategic location of this station permitted the determination of representative quantities of material transported between Lakes Erie and Ontario (Chan, 1977). Initially, only daily nutrient and weekly major ion and trace metal samples were collected in response to the current environmental concerns. As attention was diverted from the problems of more conventional pollutants to those of toxic organic contaminants, this program was expanded to include weekly monitoring of suspended sediments as a possible source of toxic organics to Lake Ontario.

With the release of the Interagency Task Force report in 1979, the effects of these toxic chemicals on the populace and the ecosystem became a major environmental concern. Therefore, WQB-OR undertook an extensive survey of toxic chemicals in the water, suspended sediments and bottom sediments of the Niagara River in 1981.

This report is a summary of the Water Quality Branch activities in the Niagara River since 1975, as outlined in Table 1. Special emphasis is given to the toxic contaminants and trace metal monitoring completed in the Niagara River system between 1975 and 1982. To avoid confusion there are two major sections: (1) data collected at a single station at Niagara-on-the-Lake and (2) data collected at various stations throughout the Niagara River system.

Table 1. Water Quality Branch, Ontario Region, Activities on the Niagara River

Surveys completed	1975	1976	1977	1978	1979	1980	1981	1982
Daily water quality sampling at Niagara-on-the-Lake	← pH, Specific conductance, Nutrients (daily), Major ions, Metals (weekly) → ← Organics (weekly) →							
Suspended sediment quality at Niagara-on-the-Lake	← Metals, Organics (weekly) or (bi-weekly) →							
Water quality surveys throughout the river								
Water	X				X		X	
Suspended sediment					X		X	
Bottom sediment							X	

Measurements at Niagara-on-the-Lake

AMBIENT WATER

Trace Metals in Ambient Water

Weekly samples of unfiltered water have been collected for trace metal analysis from a station in the Niagara River adjacent to Niagara-on-the-Lake since 1975 (Fig. 1). Analysis included aluminum (extractable), cadmium (total), chromium (total), copper (total), iron (total), lead (total), manganese (total), nickel (total), zinc (total) and mercury (extractable). Annual median concentrations of these metals at Niagara-on-the-Lake are presented in Table 2.

High seasonal variation of iron and aluminum was observed and appeared to be related to natural climatic events such as heavy rainfall or high winds. Yet despite this variation, both metals exhibited a constantly increasing

annual trend until 1981, when a dramatic decrease was observed. In 1982, iron concentrations once again increased to a value slightly higher than in 1980. An analysis of the National Oceanic and Atmospheric Administration data collected at the Buffalo Airport revealed that the frequency of days with average daily winds above 20 mph was lower in 1981 than in 1979 and 1980. During 1979 and 1980, there were 12 and 10 days, respectively, with average wind speeds greater than 20 mph. In 1981, however, there were only six days with average winds of this magnitude, while in 1982, there were 33 days with average winds above 20 mph.

Violations of the 1978 GLWQA objectives, expressed as percentages, are given in Table 3 for the 1975-82 period. The most frequent violations were observed for copper and iron and, to some extent, are related to climatic events such as winds and rainfall.

Trace Metal Loadings to Lake Ontario

Total trace metal loadings to Lake Ontario were calculated from the weekly data collected at Niagara-on-the-Lake since 1975. These figures, given in Table 4, were derived from the product of the median yearly concentrations for each metal and the yearly average flow of the Niagara River as measured at Queenston by Environment Canada ($6448 \text{ m}^3 \text{ s}^{-1}$).

These data indicate substantial increases in total iron and aluminum from 1975 to 1980, a decrease in 1981 and an increase in 1982. These increases are probably the result of greater disturbance caused by wind stress in Lake Erie. The wind stress seems to have been considerably lower in 1981 but then considerably higher in 1982.

Organic Contaminants in Ambient Water

Monitoring of organic contaminants in ambient waters of the Niagara River at Niagara-on-the-Lake has continued since 1980. Several classes of compounds, including PCBs and chlorinated pesticides, have been monitored on a weekly or bi-weekly basis. Results for the 1980-82 period are summarized in Table 5.

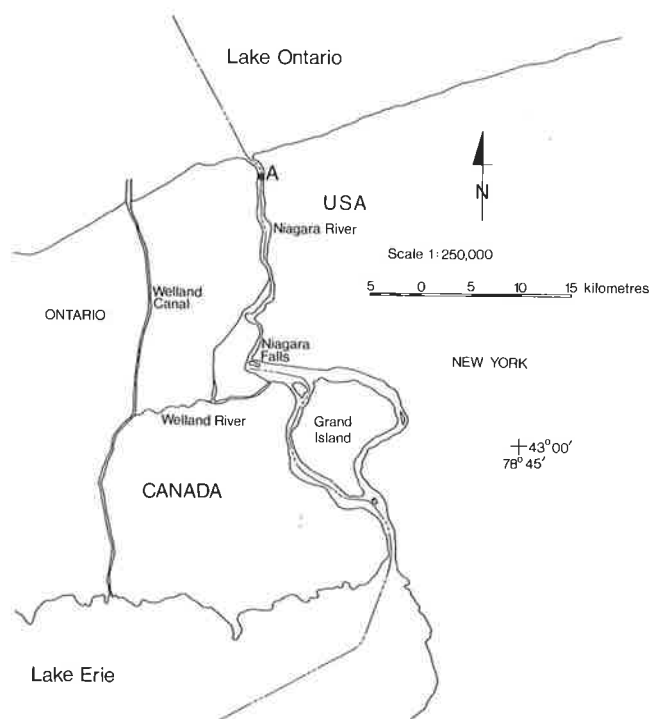


Figure 1. Sampling location on the Niagara River at Niagara-on-the-Lake.

Table 2. Median Concentrations (mg L^{-1}) of Trace Metal Samples Collected in the Niagara River at Niagara-on-the-Lake, 1975-82

Parameter	1975 (19)*	1976 (51)	1977 (48)	1978 (43)	1979 (41)	1980 (62)	1981 (47)	1982 (52)
Iron	0.110	0.110	0.140	0.160	0.200	0.380	0.140	0.390
Aluminum	0.040	0.060	0.050	0.050	0.100	0.150	0.050	0.070
Manganese	0.004	0.010	0.006	0.009	0.008	0.024	<0.010	<0.020
Nickel	0.002	0.003	0.003	0.002	0.003	0.003	0.001	0.001
Zinc	0.003	0.005	0.005	0.004	0.003	0.004	0.002	0.003
Copper	0.003	0.006	0.010	0.004	0.003	0.002	0.003	0.002
Chromium	0.002	0.001	0.002	0.001	0.001	0.003	0.001	0.002
Lead	0.002	0.002	0.001	0.001	0.001	0.002	0.001	<0.001
Cyanide	—	—	—	—	0.002	0.003	0.004	—
Cadmium	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Mercury	—	—	—	—	<0.000 05	<0.000 05	<0.000 05	<0.0005
Arsenic	—	—	—	—	—	0.000 5	0.000 5	0.0006

*Number of observations are given in parentheses.

Table 3. Percentage of Weekly Water Samples Violating 1978 Agreement Objectives in the Niagara River at Niagara-on-the-Lake, 1975-82

Parameter	1978 IJC specific objective (mg L^{-1})	Percentage of violations at Niagara-on-the-Lake							
		1975	1976	1977	1978	1979	1980	1981	1982
Iron	0.300	0	20	15	19	41	52	13	52
Copper	0.005	16	61	79	40	33	11	19	27
Nickel	0.025	0	0	2	0	0	0	0	2
Zinc	0.030	0	0	2	0	0	0	0	0
Cadmium	0.0002	0	6	6	0	5	2	2	0
Chromium	0.100	0	0	0	0	0	0	0	0
Lead	0.025	0	0	0	0	0	0	0	0

Table 4. Yearly Loadings (t yr^{-1}) of Total Trace Metals to Lake Ontario at Niagara-on-the-Lake by the Niagara River, 1975-82

Parameter	1975	1976	1977	1978	1979	1980	1981	1982
Iron	22 400	22 400	28 500	32 560	40 700	77 330	28 490	79 360
Aluminum	8 150	12 200	10 200	10 200	20 300	30 530	10 200	14 240
Manganese	810	2 040	1 220	1 830	1 630	4 880	2 040	<4 070
Nickel	410	610	610	410	610	610	200	200
Zinc	610	1 020	1 020	810	610	810	410	610
Copper	610	1 220	2 040	810	610	410	610	410
Chromium	410	200	410	200	200	610	200	410
Lead	410	410	200	200	200	410	200	200
Cyanide	—	—	—	—	410	610	810	—
Cadmium	200	200	200	200	200	200	200	<200
Mercury	—	—	—	—	10	10	10	<10
Arsenic	—	—	—	—	—	100	100	120

Note: Mean discharge for 1975-82 = $6448 \text{ m}^3 \text{ s}^{-1}$.

Table 5. Organochlorine Concentrations (ng L⁻¹) in Ambient Water at Niagara-on-the-Lake, 1980-82

Parameter (75 samples)	Confirmed detections			
	Percent	Median	Mean	S.D.
Total PCBs	97	11.0	19.9	34.7
α-BHC	100	9.7	10.5	5.2
γ-BHC	99	1.8	2.1	1.5
Dieldrin	93	0.6	0.6	0.3
HCB	95	0.5	0.8	0.9
γ-Chlordane	68	0.3	0.5	0.8
α-Chlordane	64	0.2	0.3	0.3
p,p'-DDE	61	0.1	0.3	0.5
Heptachlor epoxide	47	<0.1	0.5	1.0
p,p'-DDT	40	<0.1	0.2	0.5
β-Endosulfan	15	<0.1	0.1	0.4
α-Endosulfan	13	<0.1	0.1	0.4
Endrin	11	<0.1	<0.1	0.1
p,p'-TDE	9	<0.1	0.1	0.2
p,p'-Methoxychlor	7	<0.1	0.1	0.3
o,p'-DDT	1	<0.1	<0.1	—
Mirex	1	<0.1	<0.1	—
Aldrin	1	<0.1	<0.1	—
Heptachlor	0	<0.1	<0.1	—

Note: Zero was used for detection limit values.

Source: Kuntz and Warry (1983).

Of the 19 organochlorine compounds routinely measured, eight were detected in more than 50% of the samples collected, including total PCBs, α- and γ-chlordane, dieldrin, hexachlorobenzene, α- and γ-BHC and p,p'-DDE. Of these, only total PCBs and α- and γ-BHC were detected at median concentrations greater than 1 ng L⁻¹.

Organic Contaminant Loadings to Lake Ontario

Organochlorine pesticides and PCB loadings to Lake Ontario have been calculated for both suspended sediments and total water fractions (unfiltered) for the Niagara River at Niagara-on-the-Lake (Table 6a). These data, taken from Kuntz and Warry (1983), show higher PCB loadings than previously reported. Mirex and total DDT loadings to Lake Ontario remain about the same as previously observed. One of the most striking observations is that the percentage of the loadings contributed by the suspended sediment fraction is not as important as previously believed. The sediment contribution is important for DDT (mostly DDE), HCB, total PCBs and mirex. For other compounds, however, it accounts for less than 25% of the loading. Therefore accurate total loadings cannot be estimated for many of these compounds without sampling the water fraction.

Yearly total organochlorine loadings to Lake Ontario by the Niagara River for the 1980-82 period for water and suspended sediments are given in Tables 6b and 6c, respectively. These data were calculated from the product

of the yearly median concentrations, the yearly average discharge and the yearly mean sediment concentration.

In Table 7, yearly chlorobenzene loading estimates (from suspended sediment fraction only) are based on median concentrations. These data indicate that substantial quantities of these compounds bound to suspended sediments were entering Lake Ontario via the Niagara River each year.

Chlorobenzenes have been analyzed during 1981 and 1982 in water samples at Niagara-on-the-Lake. Nearly all data, however, are below detection limits.

Table 6a. Organochlorine Loadings to Lake Ontario (kg yr⁻¹) from the Niagara River, 1979-81

Parameter	Suspended sediments	Unfiltered water (total)	Sediment contribution (%)
Total DDT	41	20	>100
p,p'-DDE	31	20	>100
HCB	84	100	84
Total PCBs	850	2200	39
Mirex	8	20	<42
Methoxychlor	3	20	<17
p,p'-TDE	3	20	<17
γ-Chlordane	3	60	6
Dieldrin	7	120	6
α-Chlordane	2	40	5
α-BHC	8	1940	3
o,p'-DDT	10	<20	<50

Source: Kuntz and Warry (1983).

Table 6b. Total Organochlorine Loadings* (kg yr⁻¹ unfiltered water) to Lake Ontario by the Niagara River

Parameter	1980	1981	1982
Total PCBs	2 282	2 373	2 568
α-BHC	2 282	1 344	988
γ-BHC	415	218	197
Dieldrin	124	<79	<79
HCB	207	<79	<79
γ-Chlordane	<83	<79	<79
α-Chlordane	<83	<79	<79
p,p'-DDE	<83	<79	<79
Heptachlor epoxide	<83	<79	<79
p,p'-DDT	<83	<79	<79
β-Endosulfan	<83	<79	<79
α-Endosulfan	<83	<79	<79
Endrin	<83	<79	<79
p,p'-TDE	<83	<79	<79
p,p'-Methoxychlor	<83	<79	<79
o,p'-DDT	<83	<79	<79
Mirex	<83	<79	<79
Aldrin	<83	<79	<79
Heptachlor	<83	<79	<79
Mean discharge (cfs)	232 140	221 210	220 998
Mean discharge (m ³ s ⁻¹)	6 574	6 265	6 259

*Median concentrations used for loading calculations.

Table 6c. Organochlorine Loadings* to Lake Ontario (kg yr^{-1}) by Niagara River Suspended Sediments

Parameter	1979	1980	1981	1982
Total PCBs	727	780	464	655
HCB	91	62	50	23
p,p'-DDE	36	27	10	<2
p,p'-DDT	17	10	<1	<2
Mirex	10	8	3	13
α -BHC	10	4	4	11
Dieldrin	5	8	3	2
γ -Chlordane	<2	2	4	<2
p,p'-TDE	<2	6	5	<2
p,p'-Methoxychlor	<2	4	<1	<2
α -Chlordane	2	2	4	<2
Heptachlor epoxide	<2	2	<1	<2
α -Endosulfan	<2	<2	<1	<2
γ -BHC	<2	<2	<1	<2
o,p'-DDT	<2	<2	<1	<2
Heptachlor	<2	<2	<1	<2
Aldrin	<2	<2	<1	<2
β -Endosulfan	<2	<2	<1	<2
Endrin	<2	<2	<1	<2
Mean discharge (cfs)	222 558	232 140	221 210	220 998
Mean discharge (m^3s^{-1})	6 303	6 574	6 265	6 259
Mean sediment concentration (mg L^{-1})	8.6	9.4	6.9	10.7

*Median concentrations used for loading calculations.

Table 7. Chlorobenzene Loadings* to Lake Ontario (kg yr^{-1}) by Niagara River Suspended Sediments

Parameter	1980	1981	1982
1,3-Di	176	2	2
1,4-Di	138	2	2
1,2-Di	156	2	2
Σ -Di	601	41	2
1,3,5-Tri	27	3	2
1,2,4-Tri	94	3	27
1,2,3-Tri	27	8	2
Σ -Tri	164	53	42
1,2,4,5 + 1,2,3,5-Tetra	39	18	11
1,2,3,4-Tetra	99	34	27
Σ -Tetra	146	44	32
Penta	78	25	29
Hexa	120	46	21
Total chlorobenzenes	1 219	224	186
Mean discharge (cfs)	232 140	221 210	220 998
Mean discharge (m^3s^{-1})	6 574	6 265	6 259
Mean sediment concentration (mg L^{-1})	9.4	6.9	10.7

*Median concentrations used for loading calculations.

SUSPENDED SEDIMENTS

Trace Metals in Suspended Sediments

Results of analysis for cadmium, cobalt, lead, chromium, copper, nickel and zinc (extracted by 0.5 N HCl) are summarized in Table 8a. These data did not show any obvious seasonal distribution. Except for cobalt, each of the metals analyzed exceeded Ontario Ministry of the Environment (MOE) dredge spoil criteria most of the time.

Total metal concentrations in suspended sediments at Niagara-on-the-Lake have also been determined through the generous cooperation of Dr. K. Lum of the National Water Research Institute in 1981 and 1982. These concentrations, shown in Table 8b, were considerably higher than extractable metals, as expected, owing to the use of stronger extracting agents. Yearly variation was not large, and nearly every sample violated the MOE dredge spoil criterion for each metal.

Table 8a. Extractable Metal Concentrations ($\mu\text{g g}^{-1}$) in Suspended Sediments at Niagara-on-the-Lake

Parameter	MOE objective*	1978			1979-80			1981-82		
		No. of observations	Mean	S.D.	No. of observations	Mean	S.D.	No. of observations	Mean	S.D.
Cadmium	1	13	2.4	0.8	35	2.4	1.3	22	1.7	0.8
Lead	50	13	80.0	28.6	35	58.0	18.9	22	51.3	28.0
Cobalt	50	13	6.6	3.3	35	6.5	2.3	22	3.4	0.8
Copper	25	13	46.0	15.1	35	44.0	37.0	22	29.8	12.0
Zinc	100	13	177.0	44.0	35	163.0	50.0	22	170.9	213.5
Nickel	25	13	29.0	16.0	35	24.0	12.0	22	13.6	2.8
Chromium	25	13	39.0	31.0	35	30.0	12.0	22	18.6	8.4

*MOE dredge spoil criterion.

Table 8b. Total Metal Concentrations ($\mu\text{g g}^{-1}$) in Suspended Sediments at Niagara-on-the-Lake*

Parameter	MOE objective†	1981			1982		
		No. of observations	Mean	S.D.	No. of observations	Mean	S.D.
Cadmium	1	14	7.3	4.0	27	4.7	5.2
Lead	50	29	93	61	27	93	57
Cobalt	50	29	46	26	27	27	11
Copper	25	29	70	44	27	57	14
Zinc	100	29	308	191	27	318	246
Nickel	25	29	61	21	27	73	36
Chromium	25	29	134	65	27	130	60
Manganese	—	29	2 414	2 647	27	874	249
Iron	10 000	12	44 000	33 000	26	37 000	9000

*Analysis completed by Dr. K. Lum of the National Water Research Institute.

†MOE dredge spoil criterion.

Table 8c. Total Metal Loadings* (t yr^{-1}) to Lake Ontario by Niagara River Suspended Sediments

Parameter	1981	1982
Cadmium	10	10
Lead	127	197
Cobalt	63	57
Copper	95	120
Zinc	420	673
Nickel	83	154
Chromium	183	275
Manganese	3 290	1 850
Iron	60 000	78 300
Mean discharge (cfs)	221 210	220 998
Mean discharge (m^3s^{-1})	6 265	6 259
Mean sediment concentration (mg L^{-1})	6.9	10.7

*Mean concentrations used for loading calculations.

Total metal loadings, calculated from the product of the mean concentration, the yearly mean discharge and the yearly mean sediment concentration are given in Table 8c. Table 8d presents a comparison between total metal load from the Niagara River from total water analysis and extractable and total metal load from the suspended sediment fraction. From these data, the importance of suspended sediments for determining metal loads is obvious, particularly for zinc, iron, lead, nickel, chromium, manganese and copper.

Table 8d. Suspended Sediment Contribution of Metals to Total Load from the Niagara River to Lake Ontario in 1982

Parameter	Total load to Lake Ontario (t yr ⁻¹)	Extractable metals in suspended sediments (t yr ⁻¹)	Extractable metals in suspended sediments as percent in total load	Total metals in suspended sediments (t yr ⁻¹)	Total metals in suspended sediments as percent in total load
Cadmium	<200	4	>2	10	>5
Copper	410	63	15	120	29
Manganese	<4 070	—	—	1 850	45
Chromium	410	39	10	275	69
Nickel	200	29	14	154	77
Lead	200	108	54	197	98
Iron	79 360	—	—	78 300	99
Zinc	610	361	59	673	>100

Chlorinated Organics in Suspended Sediments

Chlorinated Pesticides and PCBs

A summary of the organochlorine pesticide and PCB data measured in the suspended sediments of the Niagara River is given in Table 9. Of the 19 chlorinated pesticides and PCBs measured, 11 compounds were detected in more than 50% of the samples collected. Ranked in decreasing order of occurrence, they are total PCBs, HCB, p,p'-DDE, p,p'-DDT, dieldrin, γ -chlordane, mirex, α -BHC, α -chlordane, p,p'-TDE and methoxychlor.

Chlorobenzenes

Measurements of chlorobenzene concentrations in suspended sediments during 1980 (Table 10) support the work of Oliver and Nicol (1982), suggesting that Lake Ontario is a sink for the chlorobenzene compounds being discharged to the Niagara River. Each isomer of chlorobenzene occurred in more than 70% of the suspended sediment samples collected. It is particularly noteworthy that the isomer which has the widest usage, i.e., 1,4-dichlorobenzene, is also the most abundant in these samples as well as in the bottom sediments of Lake Ontario (Oliver

Table 9. Organochlorine Concentrations (ng g⁻¹) in Suspended Sediments at Niagara-on-the-Lake, 1979-81

Parameter (70 samples)	Confirmed detections			
	Percent	Median	Mean	S.D.
Total PCBs	100	500	718	597
HCB	100	49	124	320
p,p'-DDE	92	18	23	23
p,p'-DDT	86	6	11	12
Mirex	76	5	12	32
α -BHC	75	4	12	23
Dieldrin	80	4	4	3
γ -Chlordane	79	2	6	9
p,p'-TDE	62	2	4	5
p,p'-Methoxychlor	51	1	7	14
α -Chlordane	67	1	3	4
Heptachlor epoxide	37	<1	1	2
α -Endosulfan	36	<1	4	17
γ -BHC	33	<1	2	4
o,p'-DDT	30	<1	6	14
Heptachlor	8	<1	1	3
Aldrin	7	<1	2	8
β -Endosulfan	4	<1	<1	—
Endrin	1	<1	<1	—

Source: Kuntz and Warry (1983).

Table 10. Chlorobenzene concentrations (ng g⁻¹) Dry Weight in Suspended Sediments at Niagara-on-the-Lake, 1980

Parameter (28 samples)	Percent of time detected	Mean	S.D.	Lake Ontario sediments* (range)
1,2-Di	71	148	139	4-27
1,4-Di	68	180	198	22-210
1,3-Di	71	95	116	15-250
1,3,5-Tri	93	20	13	7-250
1,2,4-Tri	100	61	42	20-220
1,2,3-Tri	86	19	18	1-16
1,2,4,5 + 1,2,3,5-Tetra	86	28	23	7-173
1,2,3,4-Tetra	96	71	52	4-86
Penta	96	58	44	3-84
Hexa	100	94	88	9-320

*Data from Oliver and Nicol (1982).

and Nicol, 1982). Some other isomers occurring at high concentrations were 1,2- and 1,3-dichloro; 1,2,4-trichloro; 1,2,3,4-tetrachloro; pentachloro; and hexachloro. These data indicate that the dichloro isomers occurred at highest concentration in suspended sediments, but hexachlorobenzene occurred in 100% of the samples.

Other Organic Contaminants: PAHs and Phthalates

Some other non-standard organic analyses have been completed on suspended sediment samples from Niagara-on-the-Lake including phthalates and polynuclear aromatic hydrocarbons (PAH). These data are summarized in Table 11. Some of the phthalates, particularly bis-(2-ethylhexyl) and di-*n*-octyl phthalates, occurred at levels of up to $107 \times 10^3 \text{ ng g}^{-1}$. The PAHs occurring at levels up to $20 \times 10^3 \text{ ng g}^{-1}$ were chrysene/benzanthracene and benzo (A) pyrene.

Table 11. Phthalates and PAH Concentrations (ng g^{-1}) in Suspended Sediments of the Niagara River at Niagara-on-the-Lake

Parameter	Concentration range (ng g^{-1})
Phthalates	
Dimethyl	ND
Diethyl	ND
Di- <i>n</i> -butyl	70-1 000
Butyl-benzyl	TR
Bis-(2-ethylhexyl)	1700-107 000
Di- <i>n</i> -octyl	100-19 650
PAHs	
Naphthalene	ND-1 500
Acenaphthylene	TR-16
Acenaphthene	TR-38
2-Chloronaphthalene	ND
Fluorene	TR-42
Anthracene/phenanthrene	TR-4 000
Fluoranthene	120-4 000
Pyrene	TR-4 000
Chrysene/benzanthracene	TR-20 000
Benzo (B) and (K) fluoranthene	190-1 008
Benzo (A) pyrene	190-20 000

ND - Not detected.

TR - Trace quantity.

SUMMARY

Weekly sampling of trace metals in unfiltered water at Niagara-on-the-Lake since 1975 has shown steady increases in both iron and aluminum concentrations and loadings until 1981, when a decrease occurred. These increases are believed to be caused by wind-induced resuspension or erosion of sediments in the eastern basin of Lake Erie or the river itself during this period.

Violations to 1978 Water Quality Agreement objectives were most numerous for iron, copper and cadmium.

Of the 19 organochlorine compounds routinely measured in ambient waters at Niagara-on-the-Lake, eight were detected in more than 50% of the samples collected and three (i.e., total PCBs, and α - and γ -BHC) were detected at median concentrations greater than 1 ng L^{-1} .

Mean concentrations of cadmium, lead, copper, zinc, nickel and chromium in suspended sediments collected at Niagara-on-the-Lake consistently exceeded MOE dredge spoil criteria.

Suspended sediments account for about 70% of the total metals load of the Niagara River to Lake Ontario for chromium and nickel and nearly 100% of the total load for lead, iron and zinc.

Of the 19 organochlorine compounds measured in suspended sediments collected at Niagara-on-the-Lake, 11 occurred in more than 50% of the samples collected, and total PCBs, HCB and p,p'-DDE occurred at median concentrations above 10 ng g^{-1} .

Of the 11 chlorobenzenes measured in suspended sediments at Niagara-on-the-Lake, the compound with the widest usage (i.e., 1,4-dichlorobenzene) (Oliver and Nicol, 1982) was also the most abundant in the suspended sediments.

Higher PCB loadings to Lake Ontario than previously reported have been calculated from Niagara-on-the-Lake input data. Mirex and total DDT loadings remain about the same as previously reported by Frank *et al.* (1979).

Percentage of organochlorine loadings to Lake Ontario by suspended sediments is lower than previously believed. Sediment contributions are above 40% for total DDT (mostly DDE), HCB, total PCBs and mirex. Therefore for accurate total loading estimates, the water fraction must be analyzed and detection limits must be very low.

Distribution throughout the Niagara River System

AMBIENT WATER

Trace Metals in Ambient Water

During four surveys on the upper Niagara River in 1975, extractable filtered and unfiltered total trace metals were analyzed. In 1979, total unfiltered trace metal analyses were completed on six surveys of the upper Niagara River. Station locations are shown in Figure 2 at the end of the chapter and station descriptions are given in Table 12. Data are summarized in Table 13. Values of zero were used in mean calculations for sample results below the detection limit.

Data for both 1975 and 1979 indicated that values of arsenic and selenium in unfiltered water samples, extractable Hg, Cd, Cr, Pb, Cu, Mn, Zn and Ni as well as total Cd, Cu, Cr, Pb, As and Ni were at or near the detection limits of the analytical methods. In 1975, mercury and extractable chromium were never detected. Extractable filtered iron values were much lower than total iron, indicating that a large percentage of the iron present is in particulate form. These data indicated that iron concentrations were significantly higher in 1979 than in 1975. They also indicated that cross-stream differences in total iron (Fig. 3), total manganese and total zinc concentrations were significant at the 95% confidence level (Kuntz and Chan, 1982).

Table 12. Sampling Locations in the Upper Niagara River, 1975 and 1979

Range	Station	Distance from left bank looking downstream (m)	Landmark
19.5 E width 1160 m	A	170	Upstream from North Grand Island Bridge
	B	425	
	C	700	
	D	975	
23.3 E width 760 m	A	180	By Stoney Point Road, Grand Island, N.Y.
	B	325	
	C	490	
	D	640	
20.5 W width 760 m	A	150	600 m upstream from Navy Island
	B	300	
	C	450	
	D	670	
31.0 E width 760 m	A	150	By Blue Water Marina, Grand Island, N.Y.
	B	300	
	C	450	
	D	600	
26.7 W width 670 m	A	135	1830 m downstream from Niagara Parks Commission Marina
	B	270	
	C	400	
	D	540	
36.0 width 790 m	A	150	Under tower transmission line downstream from Peace Bridge, Fort Erie
	B	300	
	C	450	
	D	600	

Table 13. Mean Trace Metal Concentrations (mg L⁻¹) in the Upper Niagara River, 1975 and 1979

Parameter	1975		1979	
	No. of observations	Mean	No. of observations	Mean
As, unfiltered	81	0.000 4 (81)*	94	0.000 4 (94)
Se, unfiltered	81	0.000 1 (73)	95	0.000 1 (65)
Hg, extractable	81	<0.000 05 (0)	144	0.000 01 (21)
Cd, total	81	<0.001 (2)	165	<0.001 (4)
Cr, total	81	0.001 (44)	164	0.001 (63)
Cu, total	80	0.003 (80)	142	0.003 (138)
Fe, total	81	0.216 (81)	165	0.343 (165)
Pb, total	81	0.002 (71)	168	0.001 (129)
Mn, total	81	0.010 (69)	144	0.008 (143)
Ni, total	81	0.002 (81)	167	0.003 (152)
Zn, total	81	0.004 (81)	168	0.006 (149)
Al, extractable, filtered	81	0.007 (77)		
Al, extractable, unfiltered	81	0.087 (81)		
Cd, extractable, filtered	81	<0.001 (3)		
Cr, extractable, filtered	81	<0.001 (0)		
Cu, extractable, filtered	80	0.002 (80)		
Fe, extractable, filtered	81	0.005 (81)		
Pb, extractable, filtered	81	<0.001 (28)		
Mn, extractable, filtered	81	<0.001 (14)		
Ni, extractable, filtered	81	0.001 (60)		
Zn, extractable, filtered	60	0.002 (70)		

*Number of samples above detection limits are given in parentheses.
 Note: Detection limit values entered as zero for mean calculations.

A summary of percentage violations of the 1978 GLWQA specific objectives is given in Table 14. Data indicate that violations occurred infrequently except for iron. Violations for total iron occurred 24% of the time in 1979, half of which were accounted for by the last survey in December. All 24 samples collected during this survey were above the 1978 GLWQA specific objective of 0.300 mg L⁻¹ for total iron. These high values are attributed to high winds measured in this area and in eastern Lake Erie during the three days previous to the survey. This conclusion is substantiated by the large increases in turbidity, total iron, fecal coliform, total phosphorus and several other parameter concentrations relative to previous surveys. Average daily wind speeds for the three days previous to and during the survey, as measured at Buffalo by the National Oceanic and Atmospheric Administration, ranged from 26.4 to 34.0 km h⁻¹. These high winds resulted

in elevated suspended sediment loading to the river because of increased shore erosion and sediment resuspension in the eastern basin of Lake Erie. Figure 4 shows some of the changes that occurred at station 20.5A during this December 1979 survey (Kuntz and Chan, 1982).

During May 1981, a survey of trace metals in ambient water of both the upper and lower Niagara River was completed. Unfiltered water from 25 stations at locations shown in Figure 5 was sampled for total iron, cadmium, copper, lead, manganese, nickel, zinc, cobalt and chromium as well as extractable aluminum.

Data indicate that several areas of concern exist (Figs. 6 to 12) where violations to the 1978 GLWQA have occurred. Metal concentrations are generally higher in the surface waters of the Tonawanda Channel than in the Chippawa Channel, particularly iron, zinc, copper and aluminum. Violations to the 1978 GLWQA have occurred for iron (8), zinc (1), copper (14), aluminum (1)[†] and cadmium (1). A sample collected at station 38.5, located in the Buffalo River, contained elevated iron, lead and manganese concentrations. Station 34.6B is located just downstream from two Buffalo Sewer Authority outfalls. This may explain the high zinc, copper, nickel, cadmium and manganese concentrations observed at this station.

Table 14. Percent of Total Trace Metal Values Exceeding IJC Objectives in 1975 and 1979 in the Upper Niagara River

Parameter	IJC objectives (mg L ⁻¹)	1975 (%)	1979 (%)
Cd	0.0002	2*	2*
Cu	0.005	2	7
Fe	0.300	22	24 (12)†
Pb	0.025	0	0
Zn	0.030	0	1

*Detection limit of analytical method above IJC objective.

†Last survey data eliminated.

[†]MOE objective of 100 µg L⁻¹ for protection of aquatic life.

Table 15. Organic Contaminant Concentrations ($\mu\text{g L}^{-1}$) in the Upper Niagara River, 1979

Parameter	Detection limit ($\mu\text{g/L}$)	Frequency of detection (%)	1978 GLWQA objective ($\mu\text{g/L}$)	Contraventions of GLWQA objectives (%)	Mean value ($\mu\text{g L}^{-1}$)
α -BHC	0.001	100	—	—	0.007
Cyanide	1.0	90	—	—	0.002
γ -BHC (lindane)	0.001	84	0.010	0	0.001
Dieldrin	0.001	32	0.001	0	<0.001
PCBs	0.020	19	—	—	0.005
Phenol	1.0	9	1.0	4	<0.001
p,p'-DDE	0.001	6	—	—	<0.001
Hexachlorobenzene	0.001	3	—	—	<0.001
β -Endosulfan	0.01	3	—	—	<0.001
p,p'-DDT	0.001	1	0.003	0	<0.001

Note: Detection limit values entered as zero for mean calculations.

Station 34.6C was located in the Black Rock Canal, by Scajaquada Creek. Elevated levels of chromium, lead and nickel were observed at this station. A high nickel concentration was also observed at station 19.4 by the north end of Grand Island ($16 \mu\text{g L}^{-1}$). No reason for this anomaly can be given at this time.

Organic Contaminants in Ambient Waters (Total Water)

Analyses for an extensive list of organic contaminants were conducted on samples collected at selected stations on ranges in the upper Niagara River in 1975 (Fig. 2). Detection limits of analytical methods, however, were not low enough to enable detection of many of the compounds sought. Only phenols (9% incidence) and cyanides (100%) were detected in the upper Niagara River. However, detection limits have been reduced significantly since then. As a result, considerably more compounds were detected in 1979 (Table 15). As in 1975, phenols were sometimes detected and cyanides were nearly always detected. Also, γ -BHC in the range from 0.005 to 0.007 mg L^{-1} was always detected. Other organic contaminants detected in order of their decreasing frequency of detection were γ -BHC (lindane), dieldrin, PCBs, p,p'-DDE, hexachlorobenzene, β -endosulfan, and p,p'-DDT. Other compounds analyzed for but never detected were heptachlor, aldrin, heptachlor epoxide, α - and γ -chlordane, α -endosulfan, endrin, o,p'-DDT, p,p'-TDE, mirex and p,p'-methoxychlor. The data for 1979 represent a total of 72 samples collected, 12 per range. Table 15 summarizes the detection limit, frequency of detection, 1978 Agreement specific objective, percentage of time above Agreement specific objectives and mean value for those parameters detected during 1979 surveys. Only phenols were observed to be above the 1978 Agreement specific objective (4% of the time). It should be noted that many of these contaminants do not have Agreement specific objectives.

Two toxic contaminant surveys were completed at five stations in both the upper and lower sections of the Niagara River in 1981 (shown in Fig. 13). Fifteen 4-L total water samples (including suspended materials) were collected for organic contaminants analysis during the July survey and nine during the October–November survey. A total of 19 organochlorine pesticides and PCBs and 11 chlorobenzenes were investigated.

Several of these compounds were never detected, including heptachlor, heptachlor epoxide, aldrin, γ -chlordane, α -endosulfan and o,p'-DDT. Also, p,p'-DDE was not detected in the July survey and γ -BHC, α -chlordane,

Table 16. Organic Contaminants (ng L^{-1}) in Total Water Samples of the Niagara River, 1981

Parameter (15 samples)	Percent of time detected	Range of values	Mean
α -BHC	93	DL–8.2	5.0
Dieldrin	93	DL–4.6	0.6
Total PCBs	73	DL–52.0	13.5
p,p'-DDE	60	DL–0.5	0.2
p,p'-DDT	60	DL–0.6	0.2
γ -BHC	33	DL–8.2	0.2
α -Chlordane	13	DL–0.3	<0.1
Mirex	13	DL–0.1	<0.1
Endrin	7	DL–0.2	<0.1
p,p'-TDE	7	DL–0.1	<0.1
Methoxychlor	7	DL–1.0	<0.1
Chlorobenzenes			
Di	80	DL–40.0	16.7
Tetra	67	DL–4.0	1.4
Tri	60	DL–4.0	1.9
Penta	13	DL–1.0	<0.1

DL – Detection limit.

endrin and p,p'-TDE were not detected in the October-November survey. In addition, HCB, endrin, p,p'-TDE, p,p'-DDT and α -chlordane were detected only once or twice during the July survey. Of the remaining compounds, only α -BHC and total PCBs were detected at mean values above 1 ng L⁻¹ in more than 50% of the samples (Table 16). Also dichloro, trichloro and tetrachlorobenzenes were detected in more than 50% of the water samples collected at levels above 1 ng L⁻¹.

Organic Contaminants in Ambient Waters (Aqueous Fraction — APLE Samples)

As part of the toxic contaminant surveys of 1981 in the upper and lower Niagara River, large-volume (200 L) water samples were collected after the suspended sediment was removed with a Westfalia centrifuge. The remaining aqueous fraction was extracted for 2 h with dichloromethane, which was permitted to settle for 2 h before collection from a bottom drain in the sampler. This method of extracting organics from water samples using an Aqueous Phase Liquid-Liquid Extractor (APLE) is described by McCrea (1982). In this sampler, all material in contact with the water is either Teflon or stainless steel.

The large-volume analysis technique used for these analyses is still mainly a research tool. Extensive quality assurance has been performed by the laboratory to aid the development of this technique. Spike recovery data have been completed for the pesticides and PCBs and are in the order of 80% to 90% recovery. Nevertheless, any data generated must be viewed as resulting from the use of a new analytical scheme not yet proven to provide accurate information, particularly for chlorobenzenes.

It was expected that large seasonal and spatial variation could occur within the Niagara River system, and consequently three surveys were undertaken in May, July and October-November at five stations in the upper and lower Niagara River. These stations were sampled at the midstream locations shown in Figure 13.

Discussion of Parameters Measured

BHC Isomers (Alpha and Gamma)

Levels of the degradation product, α -BHC, were generally three to four times higher than those of the parent isomer (γ -BHC) in the aqueous fraction of Niagara River water (Figs. 14 and 15). Although no obvious seasonal distribution was observed, there was considerable spatial variation. Values in the lower Niagara River, particularly at station 1.5 at Niagara-on-the-Lake, were 2.9 and 1.9

times greater, for γ - and α -BHC, respectively, than those observed at the Fort Erie end of the upper Niagara River, indicating that considerable amounts of these contaminants are being introduced to the river.

Heptachlor and Heptachlor Epoxide

No heptachlor was found in any of the 22 samples analyzed. Since this compound is rapidly hydrolyzed in water (half-life is one to three days) and is also biotransformed to heptachlor epoxide (U.S. EPA, 1979), it is not likely to be present in the aqueous fraction of water samples.

Heptachlor epoxide, with a half-life of several years (U.S. EPA, 1979), is considerably more resistant to chemical and biological transformation than heptachlor in aquatic environments, resulting in its appearance in greater concentrations in the aqueous fraction of the Niagara River. Seasonal and station distributions shown in Figure 16 indicate very low levels during the October-November survey at all five stations, while other surveys showed higher levels in July and May. These data also indicate that considerable heptachlor epoxide is being added to the river system between Fort Erie and Niagara-on-the-Lake. Mean concentrations at Niagara-on-the-Lake were 24 times higher than those observed at Fort Erie.

Chlordane Isomers (Alpha and Gamma)

Alpha-chlordane was detected in three of six samples during the May 1981 survey and seven of eight samples during the July 1981 survey at levels up to 10 ng 200 L⁻¹ in the aqueous fraction of Niagara River water. There is some indication of a possible seasonal cycle for α -chlordane, since it was not detected during the October-November survey.

No γ -chlordane was found in either the May or October-November surveys. Levels up to 3 ng 200 L⁻¹ were found in seven of the eight samples collected during the July survey.

Endosulfan Isomers (Alpha and Beta)

Values of α -endosulfan ranged up to 19 ng 200 L⁻¹ in the aqueous fraction of Niagara River water. This isomer was detected in 10 of the 22 samples analyzed. It also occurred at values ten times as large at Niagara-on-the-Lake as at Fort Erie (Table 17), indicating inputs to the river system. None of the β -isomer was detected in these samples.

Table 17. Distribution of Chlorinated Organics (ng 200 L⁻¹) in the Aqueous Fraction* of the Niagara River, 1981 (as station mean values)

Parameter	Station number					Ratio§
	1.5†	6.8	20.5	19.3	37.7‡	
Heptachlor epoxide	24	ND	16	14	1	24.0
α-Endosulfan	10	ND	1	4	1	10.0
Total PCBs	161	136	37	54	52	3.1
p,p'-DDE	3	4	1	2	ND	3.0
γ-BHC	299	146	135	117	118	2.5
Endrin	4	4	4	1	2	2.0
α-BHC	1107	555	636	878	578	1.9
p,p'-DDT	4	4	8	3	3	1.3
Total DDT	29	16	23	12	22	1.3
p,p'-TDE	22	8	14	7	18	1.2
Dieldrin	53	38	46	36	51	1.0
α-Chlordane	4	ND	2	1	4	1.0

* Sample is taken from Westfalia centrifuge outflow and extracted in APLE sampler with dichloromethane.

† Niagara-on-the-Lake.

‡ Fort Erie.

§ Ratio Niagara-on-the-Lake to Fort Erie.

ND - Not detected.

Aldrin, Dieldrin and Endrin

Aldrin was not detected in the aqueous fraction of the Niagara River during these 1981 surveys. This is not surprising, since aldrin is volatilized in a few days and is also biotransformed to dieldrin in about one day (U.S. EPA, 1979).

Endrin occurred at levels of about 1-10 ng 200 L⁻¹ in these samples. It was observed in 16 of the 22 samples collected, and values at Niagara-on-the-Lake were about twice as high as at Fort Erie. Seasonal distributions shown in Figure 17, indicate low spring values and much higher summer values.

Dieldrin, the most commonly occurring of these three compounds, occurred in all 22 samples collected. This compound is non-biodegradable and is reported to be more persistent than DDT, endrin or aldrin (U.S. EPA, 1979). Therefore, it is not surprising that it occurs more frequently and at higher concentrations (3-81 ng 200 L⁻¹) in the aqueous fraction of Niagara River water. This compound also appears to show relatively even distribution throughout the river system (Fig. 18), indicating that most of the dieldrin in the Niagara River is input from Lake Erie.

DDT and its Metabolites

Technical grade DDT consists of 70% to 73% p,p'-DDT and 12% to 21% o,p-DDT (U.S. EPA, 1979). Perhaps

the lower levels of o,p-DDT in the original product can account for its disappearance in the aqueous phase of the Niagara River. It was not observed in any of the 22 samples collected in the Niagara River during these 1981 surveys.

Parent DDT (p,p'-DDT) was found in 12 of the 22 samples analyzed. Seasonal distributions, as shown in Figure 19, indicate that higher values were observed in May and particularly in July, but no p,p'-DDT was observed during the October-November survey. Warry and Chan (1981) observed similar high spring concentrations in the suspended sediments collected at Niagara-on-the-Lake. The persistence of this compound (half-life of 4-150 years) (U.S. EPA, 1979) may explain its common occurrence at levels of between 2 and 24 ng 200 L⁻¹ in the aqueous phase. It was also observed to be present at Niagara-on-the-Lake in concentrations about 1.3 times that of Fort Erie (Table 17).

The p,p'-DDE was detected at levels between 0.5 and 7.2 ng 200 L⁻¹ in 16 of 22 samples analyzed. Since it is a degradation product of DDT and is more stable than either DDT or TDE (DDD) (U.S. EPA, 1979), it is found frequently in the aqueous fraction in the Niagara River. Seasonal and spatial variabilities shown in Figure 20 indicate levels three times higher at Niagara-on-the-Lake than at Fort Erie during the May survey (Table 17).

The p,p'-TDE (DDD) was detected in 12 of 22 samples at levels between 5 and 62 ng 200 L⁻¹. Although no p,p'-TDE was detected during the May survey, high levels were detected during the July survey followed by low levels during the October-November survey at all stations except 1.5 at Niagara-on-the-Lake (Fig. 21). Concentrations of p,p'-TDE at Niagara-on-the-Lake are about 1.2 times greater than at Fort Erie (Table 17).

Seasonal and spatial distributions of total DDT shown in Figure 22 indicate that concentrations were high throughout the entire Niagara River in July. Observed concentrations on the October-November survey dropped at every station except 1.5 at Niagara-on-the-Lake. Again, concentrations of total DDT at Niagara-on-the-Lake are about 1.2 times greater than at Fort Erie.

Mirex

Mirex was observed in the aqueous fraction of only 6 of 22 samples collected in the Niagara River at levels of between 0.1 and 1.5 ng 200 L⁻¹ during July and October-November surveys. During the May survey, mirex was not observed at any of the five stations sampled.

Methoxychlor

Methoxychlor was detected in only one of the 22 samples collected.

Total PCBs

Total PCBs were detected in 20 of 22 samples collected. Concentrations ranged from 19 to 274 ng 200 L⁻¹. While no seasonal distribution was present, concentrations in the lower Niagara River were 3.1 times higher at Niagara-on-the-Lake than at Fort Erie (Table 17, Fig. 23).

BOTTOM SEDIMENTS

Trace Metals in Bottom Sediments

In May 1981, bottom sediment samples were collected at 16 stations in the upper and lower Niagara River. Attempts to collect samples at 17 more stations failed owing to the gravel or firm glacial-lacustrine bottom types present at these stations (Fig. 30).

Sampling Methods

Bottom sediment samples were collected at the station locations identified in Figure 24 using a USBM-54 sampler shown in Figure 25. This sampler is equipped with tail fins to maintain its position in the current. When supported by a cable or rope, the sampler is set in the open position for taking a bed sample. When tension on the cable is released by resting the sampler on the stream bed, about the top inch (2.54 cm) of sediment is collected. The bucket surrounds and encloses the sample so that it is not washed out when the sampler is raised to the water surface.

Descriptions of the bottom sediments collected are given in Tables 18 and 19. Metals were analyzed according to methods contained in the *Analytical Methods Manual* (Environment Canada, 1979), and concentration distributions are given for each of the following:

- (1) Total (arsenic, selenium, mercury)
- (2) Extractable using 0.5 N HCl (cadmium, lead, cobalt, copper, zinc, nickel, chromium)
- (3) Particulate organic carbon and particulate nitrogen.

In addition, particle size distribution, i.e., percent gravel (>8000 μm), percent sand (63-8000 μm) and percent silt and clay (<63 μm), was completed and volatile solids were determined on each of these samples. A summary of

these data is given in Table 20 and distributions are shown in Figures 26, 27 and 28.

Table 18. Lower Niagara River Bottom Sediment Description

Station	Date	Distance from shore (m)	Sediment description
6.8A	May 6	Mid-channel	No sediments (gravel)
6.8B	May 6	30	Sand and gravel
6.3	May 6	15	Sand and gravel
5.6	May 7	15	No sediments (rocks)
4.8	May 6	30	Sandy
3.7	May 6	15	No sediments
2.8	May 7	30	Sand and gravel
1.5	May 8	Mid-channel	No sediments

Table 19. Upper Niagara River Bottom Sediment Description

Station	Date	Distance from shore (m)	Sediment description
38.5 Buffalo River	May 6	Mid-channel	Black silty clay
37.7	May 9	Mid-channel	No sediments (rocks)
36.2A	May 9	30	No sediments
36.2B	May 9	15	No sediments
34.6A	May 9	7	No sediments
34.6B	May 9	7	No sediments
34.6C	May 9	7	Black silty clay, oily
32.9C	May 8	15	Sand and silty clay
32.9B	May 8	15	Sand and silty clay
31.3	May 8	Mid-channel	No sediments
27.2	May 8	15	Clay, silt and sand
24.5	May 8	15	Clay
20.5	May 8	Mid-channel	No sediments (rocks)
19.4	May 8	30	No sediments (rocks)
18.0	May 8	15	No sediments (rocks)
31.4	May 8	Mid-channel	No sediments
29.8	May 8	15	Sand and silty clay
27.3	May 8	15	Sand and silty clay
25.4	May 8	Mid-channel	Sand and silty clay
23.3	May 8	15	Sand and pebbles
21.4	May 8	Mid-channel	Sand and silty clay
20.1	May 8	Mid-channel	Black silty clay
19.3	May 8	Mid-channel	No sediments (gravel)
18.9	May 8	15	No sediments (rocks)
17.6	May 8	15	No sediments (rocks)

Cadmium

In general, higher cadmium concentrations were found along the United States portion of the river from the Buffalo River to the Love Canal area. Exceptionally high values were found in the Black Rock Canal by Scajaquada Creek, in the Buffalo River, by Two Mile Creek, near the Love Canal and at one station in the lower Niagara (Fig. 29). All of these sites except that on the lower Niagara indicate that possible sources of cadmium may be present

Table 20. Bottom Sediment Characteristics in the Niagara River, May 1981

Station	Percent gravel ($> 8000 \mu\text{m}$)	Percent sand ($63 - 8000 \mu\text{m}$)	Percent silt and clay ($< 63 \mu\text{m}$)	Percent volatile solids
2.8	2.3	84.3	13.4	1.23
4.8	0.0	97.1	2.8	0.58
6.3	0.0	67.6	32.4	1.99
6.8B	0.0	96.4	3.6	1.03
20.1	0.0	52.3	47.7	6.37
21.4	9.8	88.3	1.9	1.11
23.3	7.8	46.8	45.3	2.47
24.5	0.0	11.7	88.3	3.83
25.4	0.0	95.2	4.8	1.86
27.2	0.0	76.5	23.5	2.76
27.3	2.4	95.9	1.7	2.49
29.8	6.4	87.2	6.3	4.57
32.9A	0.0	85.3	14.7	1.94
32.9B	0.0	53.4	46.6	5.43
34.6C	0.0	38.6	61.4	12.40
38.5 Buffalo River	7.3	24.7	68.0	5.60

in these areas. Many of these high values were above the MOE objective of $1000 \mu\text{g kg}^{-1}$.

Chromium

Chromium values in the bottom sediments of the Niagara River were generally below the MOE objective of 25 mg kg^{-1} except in the Black Rock Canal and downstream thereof, near the Love Canal and by Two Mile Creek (Fig. 30).

Cobalt

All cobalt values ranged from 1 to 5 mg kg^{-1} in the bottom sediments of the Niagara River and were never above the MOE objective of 50 mg kg^{-1} (Fig. 31).

Copper

Violations of the MOE objective of 25 mg kg^{-1} occurred at several locations, nearly all of which were on the United States side of the river. Most elevated values were observed in the Black Rock Canal and downstream thereof, in the Buffalo River, by Two Mile Creek, near the Love Canal and in the lower Niagara River (Fig. 32).

Lead

Violations of the MOE objective of 50 mg kg^{-1} occurred at most stations along the United States side of the river from the Buffalo River to the Love Canal area. Highest values were observed in the Black Rock Canal off Scajaquada Creek and downstream from the canal (Fig. 33).

Nickel

Violations of the MOE objective of 25 mg kg^{-1} occurred at only one station in the Black Rock Canal near Scajaquada Creek (Fig. 34).

Zinc

Violations of the MOE objective of 100 mg kg^{-1} occurred at several stations along the United States side of the river from the Buffalo River to the Love Canal area. The highest values were found in the Black Rock Canal, in the Love Canal area and at one station in the lower Niagara (Fig. 35).

Total Mercury

Very high mercury concentrations (over ten times higher than on the Canadian side) were observed at nearly every station along the United States shore from the Buffalo River to the Love Canal area (Fig. 36). Values over $1000 \mu\text{g kg}^{-1}$ were observed in the Black Rock Canal by Scajaquada Creek, downstream from the Black Rock Canal, and near the Love Canal. Elevated values were also observed in the lower Niagara River relative to the Chippawa Channel of the upper Niagara River. Violations of the MOE objective of $300 \mu\text{g kg}^{-1}$ were observed at several stations including the Buffalo River, the Black Rock Canal and downstream thereof, and near the Love Canal.

Total Arsenic

Levels of total arsenic were generally below the MOE objective of 8 mg kg^{-1} except the Buffalo River, in the Black Rock Canal and downstream from the Black Rock Canal (Fig. 37).

Total Selenium

Total selenium values were evenly distributed with values below $500 \mu\text{g kg}^{-1}$ throughout the Niagara River system. Somewhat elevated values were found near the Love Canal and at one station in the lower Niagara (Fig. 38).

Organic Carbon

Values of organic carbon ranged from 1% to 4% in the bottom sediments with a high of 6% observed in the Black Rock Canal by Scajaquada Creek. This corresponds to a percent loss on ignition of 10%. This value exceeds the MOE limit of 6% for percent loss on ignition (Fig. 39).

Organic Nitrogen

Organic nitrogen values were usually below 100 mg kg^{-1} except for stations in the Buffalo River, the Black Rock Canal, by Frenchman's Creek and near the Love Canal (Fig. 40).

Interrelationships between Metals and Sediment Characteristics in Niagara River Bottom Sediments

In addition to metals analysis, these bottom sediment samples were also analyzed for particle size and percentage of volatile solids. Using a Pearson correlation calculation, data shown in Table 21a indicate that percentage of clay and silt was significantly related to percentage of volatile solids at the 90% confidence level. Copper and nickel concentrations were also related to percent volatile solids at the 90% confidence level. Copper was also correlated with chromium, lead, nickel and zinc at the 90% confidence level. However, the copper-nickel relationship was found to be a spurious correlation when the partial correlations were calculated. Therefore, the volatile solids account for this relationship and copper and nickel are not in themselves significantly correlated. In addition, lead and zinc were also correlated at the 90% confidence level. These data imply that several of the metals are derived from similar sources. The fact that the percentage of clay and silt does not correlate well with any of the metals indicates that the metal concentrations are not dependent on sedi-

Table 21a. Correlation Matrix Showing Degree of Relationship between Variables Including Trace Metals in Bottom Sediments of the Niagara River, May 1981

Parameter	Percent sand	Percent clay and silt	Percent volatile solids	Cadmium	Chromium	Copper	Lead	Nickel	Zinc	Mercury	Selenium
Sand (%)	1.000										
Clay and silt (%)	<u>-0.679*</u>	1.000									
Volatile solids (%)	-0.343	<u>0.646</u>	1.000								
Cadmium	0.610	-0.511	-0.487	1.000							
Chromium	0.198	0.024	0.404	-0.456	1.000						
Copper	0.051	0.161	<u>0.626</u>	-0.522	<u>0.658</u>	1.000					
Lead	0.227	-0.010	0.400	-0.206	0.408	<u>0.622</u>	1.000				
Nickel	-0.009	0.342	<u>0.886</u>	-0.419	0.541	<u>0.755†</u>	0.607	1.000			
Zinc	0.327	-0.081	0.211	0.019	0.341	<u>0.651</u>	<u>0.706</u>	0.386	1.000		
Mercury	0.443	-0.142	0.156	0.045	0.601	0.271	0.409	0.242	0.257	1.000	
Selenium	0.065	0.237	0.371	-0.212	0.187	0.324	0.121	0.490	0.044	0.194	1.000

*Underlined values are significant at the 90% confidence level.

†Spurious correlation which was not correlated when partial correlation was calculated.

Table 21b. Correlation Matrix Showing Degree of Relationship between Variables Including Organic Contaminants in Bottom Sediments of the Niagara River, May 1981

Parameter	Percent sand	Percent clay and silt	Percent volatile solids	α -BHC	p,p'-DDE	p,p'-TDE	Methoxychlor	Total PCBs	Dichlorobenzenes
Sand (%)	1.000								
Clay and silt (%)	<u>-0.679*</u>	1.000							
Volatile solids (%)	-0.343	<u>0.646</u>	1.000						
α -BHC	-0.088	0.187	0.266	1.000					
p,p'-DDE	0.178	-0.081	0.170	-0.083	1.000				
p,p'-TDE	0.274	-0.205	0.046	-0.110	0.054	1.000			
Methoxychlor	0.024	0.112	0.134	-0.123	0.035	-0.001	1.000		
Total PCBs	-0.019	0.194	-0.031	0.070	-0.340	0.021	-0.005	1.000	
Dichlorobenzenes	0.097	0.215	0.167	-0.090	-0.051	0.115	-0.168	0.307	1.000

*Underlined values are significant at the 90% confidence level.

ment adsorptive capacity or size but are probably more dependent on location of sources and also on river velocity in the area of their deposition. If the river velocity is higher, the fine particles will be washed away and the metals will be carried away as well. The percentage of volatile solids correlated slightly better with a few metals, namely copper and nickel, and probably indicates that volatile solids are associated with other contaminant inputs as well as metals.

Organic Contaminants in Bottom Sediments

BHC Isomers (Alpha and Gamma)

Levels of α -BHC (a breakdown product of lindane) were generally at or near the detection limit except for stations in the Black Rock Canal ($32 \mu\text{g kg}^{-1}$), near the Love Canal ($2260 \mu\text{g kg}^{-1}$) and in the lower Niagara River ($151 \mu\text{g kg}^{-1}$). Lindane (γ -BHC) was found in highest concentrations near the Love Canal ($21 \mu\text{g kg}^{-1}$) and the lower Niagara River ($87 \mu\text{g kg}^{-1}$) (Figs. 41 and 42).

Heptachlor and Heptachlor Epoxide

Heptachlor epoxide was identified in only 4 of the 16 samples collected. Of these, highest values were observed in the Buffalo River ($8 \mu\text{g kg}^{-1}$), near the Love Canal ($10 \mu\text{g kg}^{-1}$) and by Two Mile Creek ($19 \mu\text{g kg}^{-1}$). No heptachlor was detected at any of the 16 stations sampled (Fig. 43).

Chlordane Isomers (Alpha and Gamma)

Alpha-chlordane was detected at only 4 of the 16 stations sampled. All but one of these stations, i.e., 34.6C in the Black Rock Canal, where a value of $49 \mu\text{g kg}^{-1}$ was measured, were below $7 \mu\text{g kg}^{-1}$ (Fig. 44).

Gamma-chlordane was detected at only two locations. Once again the Black Rock Canal station (34.6C) was high, with $94 \mu\text{g kg}^{-1}$. The other station (25.4), located between Tonawanda Island and the United States mainland, had a value of $20 \mu\text{g kg}^{-1}$, indicating a source from Ellicott Creek or the Erie Canal (Fig. 45).

Endosulfan Isomers (Alpha and Beta)

Values of α -endosulfan were generally low except for the Buffalo River, the Black Rock Canal and downstream from the Black Rock Canal (Fig. 46).

Values of β -endosulfan were low throughout the entire river system except near the Love Canal where a value of $28 \mu\text{g kg}^{-1}$ was observed (Fig. 47).

DDT and its Metabolites

Parent DDT, or p,p' -DDT, was found in 5 of the 16 stations sampled (Fig. 48). Since use of this compound was banned in Canada in 1972, it is puzzling to see its persistence in sediments near Frenchman's and Miller creeks on the Canadian side. Either this compound is still being used illegally or it is undegraded in the sediments nearly nine years after its use. Even higher values were observed on the United States side downstream from the Black Rock Canal and some p,p' -DDT was observed in the Buffalo River.

Low levels of p,p' -DDE were observed at many stations throughout the Niagara River (Fig. 49). High values were observed in the Black Rock Canal and downstream from it and between Tonawanda Island and the United States mainland, indicating a source from Ellicott Creek or the Erie Canal.

Generally, values of p,p' -TDE were low throughout the river system (Fig. 50). However, somewhat elevated levels were observed along the United States mainland side of the river and the Tonawanda Channel, particularly near Two Mile Creek.

The o,p -DDT metabolite was not found at any of the 16 stations sampled.

Aldrin, Dieldrin and Endrin

No aldrin was detected at any of the 16 stations sampled.

Dieldrin was detected in only two of the samples collected near the Love Canal and between Tonawanda Island and the United States shore (Fig. 51).

Endrin was detected at five stations, all along the United States mainland from the Buffalo River to Tonawanda Island (Fig. 52). Highest values were observed in the Black Rock Canal ($181 \mu\text{g kg}^{-1}$) and near Two Mile Creek ($50 \mu\text{g kg}^{-1}$). These areas are probable sources of this compound.

Mirex

Mirex values throughout the entire river system were very low except at one station near the Love Canal (Fig. 53). At this station a very high value of $890 \mu\text{g kg}^{-1}$ was observed. This peak was confirmed with GC/MS analysis. This was not unexpected, since Hooker Chemical was the sole producer of this compound and large quantities of it are known to have been disposed of in the nearby Love Canal dumpsite.

Methoxychlor

Elevated concentrations of this compound were observed downstream from the Black Rock Canal, near Two Mile Creek and Miller Creek, and at one station in the lower Niagara River (Fig. 54).

Total PCBs

Elevated values of total PCBs were observed at every station along the United States mainland side of the river and also in the lower Niagara River, indicating sources to the river (Fig. 55). Values along the Chippawa Channel, however, were relatively low. Very high values were observed in the Black Rock Canal ($10\,200\ \mu\text{g kg}^{-1}$) and downstream from it ($2820\ \mu\text{g kg}^{-1}$), and between Tonawanda Island and the United States mainland ($17\,900\ \mu\text{g kg}^{-1}$), indicating a large source, probably Ellicott Creek or the Erie Canal. Less elevated values were also observed near the Love Canal ($630\ \mu\text{g kg}^{-1}$) and in the Buffalo River ($480\ \mu\text{g kg}^{-1}$). Values in the lower Niagara River ranged from 100 to $300\ \mu\text{g kg}^{-1}$, indicating an increase in concentration from those observed in the Chippawa Channel of the upper Niagara.

Chlorobenzenes

Of the three dichlorobenzenes, the one with the widest usage (i.e., the 1,4-dichloro isomer [Oliver and Nicol, 1982]) also occurs in the highest concentrations and with the widest distribution in the bottom sediments of the Niagara River (Figs. 56 to 60). All of the chlorobenzene groups measured, i.e., di, tri, tetra, penta and hexachlorobenzenes were found at elevated concentrations at a station near the Love Canal area, indicating a possible source of these compounds in this area. Dichlorobenzene and trichlorobenzene isomers were also found at increased levels at a station in the Black Rock Canal by Scajaquada Creek. Trichlorobenzene isomers and pentachlorobenzene were also found to be higher in the bottom sediments

sampled in the Buffalo River. One station in the lower Niagara River was found to contain higher concentrations of hexachlorobenzene and dichlorobenzene. Elevated concentrations of hexachlorobenzene were also observed at a station between Tonawanda Island and the United States mainland.

Interrelationships between Organics and Sediment Characteristics in the Bottom Sediments of the Niagara River

The data shown in Table 21b (page 16) indicate that the percentage of silt and clay was correlated to the percentage of volatile solids, but none of the organic contaminants was significantly correlated to sediment characteristics at the 90% confidence level. This indicates that the variations in contaminant concentrations are not associated with different types of sediments but are more likely associated with sources in the areas sampled.

SUSPENDED SEDIMENTS

As part of the 1981 toxic sources survey completed on the upper and lower Niagara River, suspended sediments were collected for approximately 20-h periods using three Westfalia centrifuges. Sampling was conducted on consecutive days at five different stations (Fig. 13). Suspended sediment concentration as well as organic carbon and nitrogen, total arsenic and total mercury were determined on the samples. Results are presented in Table 22.

Concentrations of Suspended Sediments

In general, suspended sediment concentrations (Fig. 61) increased from station 37.7 at the Fort Erie end of the river to Niagara-on-the-Lake by about three times. High suspended sediment concentrations measured at mid-river stations during the May survey at stations 20.5 and 19.3 were both the result of high winds and the resultant erosion and resuspension of sediments in Lake

Table 22. Suspended Sediment Characteristics of the Niagara River, 1981 (as station mean values)

Parameter	Station number					Ratio‡
	1.5*	6.8	20.5	19.3	37.7†	
Sediment concentration (mg L^{-1})	4.1	3.5	4.9	8.4	1.4	2.9
Mercury, total (ng g^{-1})	333	357	80	170	83	4.0
Arsenic, total (mg kg^{-1})	12.1	11.4	13.7	13.0	9.9	1.2
Particulate organic carbon (%)	9.5	16.8	12.7	8.0	21.2	0.45
Particulate nitrogen (%)	1.2	1.2	1.5	1.0	3.1	0.38

* Niagara-on-the-Lake.

† Fort Erie.

‡ Ratio Niagara-on-the-Lake to Fort Erie.

Table 23a. Summary of Number of Detections and Mean Concentrations of Pesticide and Total PCB Residues in Suspended Sediments at Two Locations in the Niagara River, April 1979 to April 1980

Residue	Niagara-on-the-Lake confirmed detections				Grand Island confirmed detections			
	Total No. of samples	No.	Mean (ng g ⁻¹)	S.D.	Total No. of samples	No.	Mean (ng g ⁻¹)	S.D.
Mirex	41	27	19.4	49.5	3	0	ND	NC
Methoxychlor	41	18	17.3	23.3	3	0	ND	NC
α -Chlordane	41	17	5.9	5.9	3	1	8.0	NC
γ -Chlordane	41	26	10.9	7.8	3	1	7.0	NC
Σ -Chlordane	41	27	15.8	12.8	3	2	7.5	0.5
p,p'-DDT	41	33	10	10	3	2	8.0	2.1
p,p'-DDE	41	38	24	12	3	2	15.5	1.5
p,p'-TDE (DDD)	41	16	5	4	3	0	ND	NC
o,p-DDT	41	1	15.0	NC	3	1	11.0	NC
DDT	41	41	30.4	16.3	3	3	21.7	11.6
α -Endosulfan	41	10	9.5	5.3	3	0	ND	NC
β -Endosulfan	41	0	ND	NC	3	0	ND	NC
Dieldrin	41	26	5	3	3	1	23.0	NC
Endrin	41	0	ND	NC	3	1	ND	NC
Aldrin	41	0	ND	NC	3	0	ND	NC
Heptachlor	41	0	ND	NC	3	0	ND	NC
Heptachlor epoxide	41	7	3	3	3	0	ND	NC
Lindane	41	7	3.7	3.3	0	0	ND	NC
PCBs	41	41	961	2196	3	3	260	35.0

ND — Not detected.

NC — Not calculated.

Source: Warry and Chan (1981).

Erie. Similarly, high suspended sediment concentrations were measured at station 19.3 during the November survey.

Metals in Suspended Sediments

Total Mercury

Total mercury concentrations in suspended sediments of the Niagara River were consistently three to four times higher in the lower Niagara River than in the upper Niagara River (Fig. 62). This indicates that there are considerable sources of mercury to the Niagara River, probably between stations 19.3 and 6.8.

Total Arsenic

Total arsenic appears to be evenly distributed in the suspended sediments of the Niagara River (Fig. 63), although slight increases were observed from Fort Erie to Niagara-on-the-Lake.

Organic Carbon and Nitrogen

Both organic carbon and nitrogen analysis indicate that suspended sediments at Fort Erie are higher in these elements than at Niagara-on-the-Lake (Figs. 64 and 65). This may be due to the influence of Lake Erie on the Niagara River. It may be that the heavier, more inorganic sediments have already settled to the lake bottom, and

Table 23b. Revised Means If High Values Are Removed

Residue	No. of observations	Mean (ng g ⁻¹)	S.D.
Mirex	26	10.2	14.0
	25	7.8	5.4
PCBs	38	534	489

therefore the suspended material is carbon-rich. Then, after entering the river and flowing to Niagara-on-the-Lake, some inorganic material is picked up, either from inputs or scouring of the banks and bottom of the river, so that the carbon content is actually less at Niagara-on-the-Lake or about 40% of what it is at Fort Erie.

Organic Contaminants in Suspended Sediments

Water Quality Branch, Ontario Region, began collecting suspended sediments in the Niagara River for organic contaminants analysis in 1979. These data, previously reported by Warry and Chan (1981), indicated that higher quantities of organic contaminants such as PCBs, mirex and p,p'-DDT were present in the lower Niagara River below Grand Island than in the upper Niagara River (Tables 23a and 23b).

Therefore, in 1981, WQB-OR undertook a more extensive toxic contaminants survey in both the upper and lower Niagara River. Results of these surveys are presented as follows.

BHC Isomers (Alpha and Gamma)

Since α -BHC is a breakdown product of lindane (γ -BHC) (U.S. EPA, 1979), it is not surprising that the γ -BHC isomer was never detected in these suspended sediment samples. The α -BHC isomer was detected in about 50% of the samples collected. No obvious seasonal distribution was apparent (Fig. 66), although levels were very low at every station during the July survey. The October–November survey showed increasing concentrations in the sediments from Fort Erie to Niagara-on-the-Lake. Levels at Niagara-on-the-Lake were about 1.3 times those at Fort Erie (Table 24).

Heptachlor Epoxide and Heptachlor

No heptachlor was found in any of the 15 suspended sediment samples analyzed. Seasonal and spatial distributions shown in Figure 67 show low values at all stations except 37.7 during the July survey. These data do not indicate any consistent pattern.

Chlordane Isomers (Alpha and Gamma)

The α -chlordane isomer was detected in 10 of the 15 suspended sediment samples collected with values up to $21 \mu\text{g kg}^{-1}$ (Fig. 68). Concentrations at station 37.7 were generally as high as or higher than anywhere else in the river. The ratio of values at Niagara-on-the-Lake to those at Fort Erie indicates that Lake Erie is a probable source for this compound.

Endosulfan Isomers (Alpha and Beta)

The β -endosulfan isomer was detected in only 2 of the 15 samples collected in the range from 20 to $30 \mu\text{g kg}^{-1}$. The α -endosulfan isomer was detected in 12 of the 15 samples collected (Fig. 69) at concentrations up to $98 \mu\text{g kg}^{-1}$. No seasonal cycle was detected in these data. This isomer also was found in higher concentrations at Niagara-on-the-Lake with values 1.4 times higher than those observed at Fort Erie.

Aldrin, Dieldrin and Endrin

No aldrin was detected in any of the 15 samples collected. Endrin was detected in 2 of the 15 samples collected with values in the range from 7 to $12 \mu\text{g kg}^{-1}$. Dieldrin was the most commonly occurring of these three compounds at levels up to $19 \mu\text{g kg}^{-1}$ (Fig. 70). While this compound appears to be evenly distributed throughout the Niagara River system, values at Niagara-on-the-Lake were lower than at Fort Erie, indicating that Lake Erie is a probable source.

DDT and its Metabolites

Parent DDT (p,p' -DDT) was found in 6 of the 15 suspended sediments collected. Seasonal and spatial distributions shown in Figure 71 indicate that concentrations are usually higher (up to 25 times) in the lower Niagara River than in the upper Niagara River (Table 24), indicating that sources of this compound in the Niagara River remain. This is rather surprising, since its use was banned in Canada in 1972. The persistence of this compound is well known, and perhaps its occurrence in the Niagara River in 1981 can be explained by surface erosion of soil particles and their subsequent entrance to the Niagara River system. Frank *et al.* (1981) sampled suspended solids from 105 streams on the Canadian side of the Great Lakes. Their data showed that the highest concentrations of DDT occurred in 1974 in streams draining the Niagara peninsula, where many of these compounds have been used on orchards in the past.

The o,p -DDT metabolite of DDT was detected in only one of the 15 samples collected at the level of $3 \mu\text{g kg}^{-1}$.

The p,p' -DDE was detected in 14 of the 15 suspended sediment samples collected (Fig. 72). Distribution appears to be widespread throughout the river system. Levels at Niagara-on-the-Lake were lower than those observed at Fort Erie (Table 24). Since this compound is formed under biological conditions from DDT and is less susceptible

Table 24. Distribution of Chlorinated Organics ($\mu\text{g kg}^{-1}$ dry weight) in the Suspended Sediments of the Niagara River, 1981 (as station mean values)

Parameter	Station number					Ratio†
	1.5*	6.8	20.5	19.3	37.7†	
Total PCBs	367	613	ND	13	ND	>367
p,p' -DDT	25	7	8	2	1	25
α -Endosulfan	27	31	42	6	5	5.4
Total DDT	35	40	20	28	25	1.4
α -BHC	12	14	3	ND	9	1.3
Mirex	1	3	1	ND	ND	>1.0
Dieldrin	6	11	14	3	9	0.7
p,p' -DDE	9	16	4	25	21	0.4
α -Chlordane	3	4	1	8	12	0.3
Chlorobenzenes						
Hexa	73	75	2	1	1	73
Tetra	60	70	ND	ND	ND	>60
Penta	37	47	2	ND	ND	>37
Tri	53	26	40	3	17	3.1
Di	190	110	155	39	81	2.3
Total	413	326	198	42	99	4.2

* Niagara-on-the-Lake.

† Fort Erie.

‡ Ratio Niagara-on-the-Lake to Fort Erie.

to biotransformation than either DDT or TDE (DDD) (U.S. EPA, 1979), it is not surprising that it occurs the most frequently of the isomers of DDT in the suspended sediments of the Niagara River.

The p,p'-TDE was detected in only 3 of the 15 suspended sediment samples collected at a range of 2-36 $\mu\text{g kg}^{-1}$.

Seasonal and spatial distributions for total DDT given in Figure 73 indicate that no clear seasonal pattern was evident. Data presented in Table 24 indicate that concentrations at Niagara-on-the-Lake are about 1.4 times those at Fort Erie.

Mirex

Mirex was detected at the level of 2 $\mu\text{g kg}^{-1}$ in only one of the nine samples collected in the upper Niagara River (station 20.5) (Fig. 74). However, it was detected in all six samples collected in the lower Niagara River in 1981, indicating that sources still exist.

Methoxychlor

Methoxychlor was detected in only 4 of the 15 samples collected at a range of between 15 and 74 $\mu\text{g kg}^{-1}$.

Total PCBs

Total PCBs were detected in all six samples collected in the lower Niagara River, but only in one of the nine samples collected in the upper Niagara River (Fig. 75). Samples collected at Niagara-on-the-Lake were much higher (367 $\mu\text{g kg}^{-1}$) than those collected at Fort Erie (less than 1 $\mu\text{g kg}^{-1}$) (Table 24). This indicates that sources of PCBs exist between the upper and lower sections of the Niagara River.

Chlorobenzenes

Data presented in Table 24 indicate that mean concentrations of chlorobenzene isomers in suspended sediments at Niagara-on-the-Lake were always higher than at Fort Erie. Ratios of these concentrations varied from 73 for hexachlorobenzene to 2.3 for dichlorobenzenes. A major increase in concentrations appears to have occurred between the upper and lower sections of the Niagara River (Figs. 76 to 81). This indicates that significant inputs of these materials are occurring in the Niagara River. The most likely source is the sewage treatment plant in Niagara Falls, New York.

BIOTA - SPOTTAIL SHINERS (*Notropis hudsonius*)

During recent years, there has been growing concern over the increasing concentrations of toxic contaminants in fish and biota in the Great Lakes Basin, particularly Lake Ontario. Many of these fish contain contaminant concentrations which pose a risk for human consumption because of their content of such materials as mercury, PCBs and mirex. Other investigators (Suns and Rees, 1978) have found that the spottail shiner (*Notropis hudsonius*) is a useful biological integrator of organochlorine contaminants in nearshore habitats because of its limited mobility. With this in mind, samples were collected at seven different stations in the upper and lower sections of the Niagara River in mid-September 1982 (Fig. 82).

Sample Collection and Analysis

Samples were collected by using a 20-m long, 0.6-cm mesh bag-seine net in the nearshore area of the river. Most of these samples were collected through the generous cooperation of Mr. Karl Suns of the Ontario Ministry of the Environment. Details of the seven sampling locations are given in Table 25.

Table 25. Spottail Shiner Station Descriptions in the Niagara River, 1982

Station	Description
A	Just upstream from Niagara-on-the-Lake water intake
B	In Peggy's Eddy near SCA outfall
C	By Queenston, downstream from sand dock
D	At search and rescue station, on United States shore just upstream from American Falls
E	Just offshore from 102nd Street dumpsite
F	By the mouth of Frenchman's Creek
G	Just downstream from the Peace Bridge on Canadian side

After this collection, the fish were immediately frozen in dry ice and kept frozen until analysis.

Identification and quantification of contaminants were completed at the WQB-OR laboratory in Burlington, according to methods described in the *Analytical Methods Manual* (Environment Canada, 1979).

Organic Contaminants in Spottails

Eighteen organochlorine contaminants, including total PCBs and eleven chlorobenzenes, were measured at

each of the seven sampling locations. Of the 18 organochlorines measured, lindane (γ -BHC), heptachlor, aldrin, heptachlor epoxide, γ -chlordane, α - and β -endosulfan, endrin, p,p'-TDE, p,p'-DDT and methoxychlor were not detected at levels above the 4 ng g⁻¹ detection limit. Other compounds listed in decreasing order of their numbers of detection are PCBs (6), p,p'-DDE (4), dieldrin (4), mirex (3), α -BHC (2), α -chlordane (1) and o,p-DDT (1). Of the 11 chlorobenzenes measured, only 1,4-dichlorobenzene was detected in more than two of the samples collected (four times). Several other isomers, namely 1,2,4-trichloro and 1,2,3,4-tetrachloro and pentachloro, were not detected in any of the samples collected.

Spatial distributions of the most commonly occurring contaminants are given in Figures 83 to 87. These data indicate relatively high values for PCBs, particularly at stations D and E. All samples collected within the river, except at Frenchman's Creek, violated the 1978 GLWQA specific objective of 100 ng g⁻¹ for PCBs in fish. Mirex concentrations were below the analytical detection limit of 4 ng g⁻¹ except at the three stations A, B and C in the lower Niagara River. Total DDT concentrations mainly consisting of p,p'-DDE, varied from 5 ng g⁻¹ at station D to 51 ng g⁻¹ at station B. No obvious pattern was evident in these data. Two stations, A and E, had concentrations of total DDT below the detection limit of 4 ng g⁻¹. Dieldrin in these spottail shiners occurred at concentrations near or below the detection limit of 4 ng g⁻¹ at all seven stations. Of the 11 chlorobenzenes measured, only 1,4-dichlorobenzene occurred at levels above the detection limit of 50 ng g⁻¹ at four stations (A, C, D, and G).

Trace Metals in Spottails

Some metals analyses (Cd, Cr, Cu, Ni, Pb and Zn) have been completed for three of the seven sampling locations given in Figure 82. Metals were analyzed only on these three stations because there were insufficient fish available for analysis from the other four stations.

Table 26. Metals (mg kg⁻¹) in Spottail Shiners in the Niagara River, September 1982

Parameter	Niagara-on-the-Lake (A)	Queenston (C)	Frenchman's Creek (F)
Cadmium	0.070	0.080	0.030
Chromium	0.20	0.20	0.20
Copper	0.51	0.71	0.84
Nickel	0.030	0.040	0.025
Lead	0.080	0.080	0.025
Zinc	31.6	40.9	38.2

Those stations analyzed for metals were Frenchman's Creek (F) in the upper Niagara, and Queenston (C) and Niagara-on-the-Lake (A) in the lower Niagara River. Complete data are given in Table 26.

Chromium was not detected in these three locations at levels above the detection limit of 0.20 mg kg⁻¹. Cadmium was two to three times higher in spottail shiners collected in the lower Niagara River. Nickel and zinc were somewhat higher in the lower Niagara than the upper Niagara River sample. Lead was three to four times higher in the lower Niagara River samples. Zinc did not appear to show an increasing trend from upper to lower Niagara River.

SUMMARY

Cross-stream differences in total iron, total manganese and total zinc were significant at the 95% confidence level in the Tonawanda Channel during 1979 surveys. Levels of most metals were significantly higher in the Tonawanda Channel than in the Chippawa Channel.

Violations to the 1978 Great Lakes Water Quality Agreement occurred frequently for total iron especially during storm events in the eastern basin of Lake Erie. Other parameters such as turbidity, fecal coliform and total phosphorus also showed large increases during the storms.

In a survey of trace metals throughout the Niagara River in May 1981, several violations to 1978 Agreement objectives were observed. At one station (34.6B) just downstream from two Buffalo Sewer Authority outfalls, violations to 1978 Agreement objectives were observed for zinc, nickel, cadmium and copper.

Prior to 1979, analytical methodology was unable to detect many of the organochlorines in Niagara River ambient waters. In 1979, with new lower detection limits, lindane and α -BHC were detected in more than 50% of the samples collected. In 1981, total PCBs, α -BHC and di, tri and tetrachlorobenzenes were detected in more than 50% of the samples collected at mean values above 1 ng L⁻¹.

A new sampler (McCrea, 1982), capable of extracting organics from a 200-L water sample, was used during 1981 surveys on the Niagara River. These data have shown that concentrations of heptachlor epoxide, α -endosulfan, total PCBs, p,p'-DDE and γ -BHC in the aqueous fraction (operational definition) increase by a factor of more than two from the Fort Erie end of the Niagara River to Niagara-on-the-Lake. This indicates that significant sources of these compounds are present within the basin itself.

Five major areas of contamination were located in the 1981 survey of bottom sediments. These are the lower end of the Black Rock Canal, the Scajaquada Creek area, the Tonawanda Island-Love Canal-Little River area, the Buffalo River, the Strawberry Island area and the Queenston area. High metal concentrations often above MOE dredge spoil criteria were observed in many of these areas. These analyses are for 0.5 N HCl extractable metals. The objectives are for total metals. Therefore the number of violations is conservative because this analysis gives lower values than the total metals extraction method. Levels of metals and numbers of violations were consistently higher on the United States side of the river. Particle size analysis indicated some significant relationships between metals but not between metals and clay and silt abundance, indicating that metal concentrations are not dependent on sediment adsorptive capability but rather on other factors such as location of input sources or current velocity in the sampling area. High organic contaminant concentrations were also found in these areas. None of the organic contaminants was significantly related to sediment adsorptive capacity characteristics such as percent clay and silt or percent volatile solids. This indicates that contaminant concentrations are not associated with different sediment types but are more likely related to sources in the areas sampled.

Measurements of suspended sediments at five locations in the Niagara River in 1981 indicate that higher suspended sediment concentrations occur at Niagara-on-the-Lake than at Fort Erie. This increase of nearly three times the concentration is probably the result of erosion and scouring of the river bottom and inputs. However, organic carbon and nitrogen content of the suspended sediments at Niagara-on-the-Lake were only about 40% of those at Fort Erie. This indicates an addition of inorganic

material load to the Niagara River during its course. Mercury concentrations at Niagara-on-the-Lake were about four times higher than at Fort Erie, indicating sources of mercury along the river system. Some compounds for which Lake Erie appears to be a significant source to the Niagara River are p,p'-DDE, α -BHC, p,p'-TDE, dieldrin, and α -chlordane.

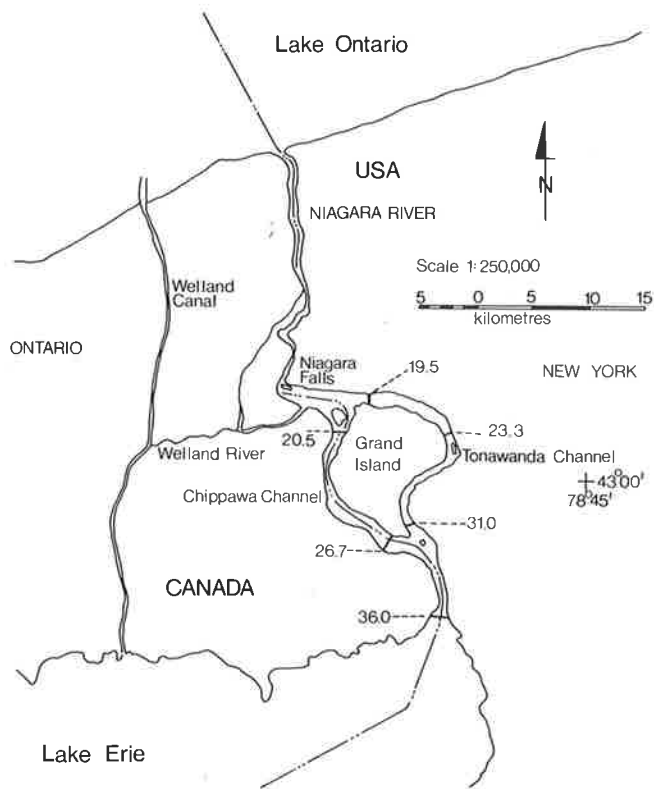
A survey in 1979 indicated that suspended sediments carried higher organic contaminant concentrations in the lower Niagara River than in the upper Niagara. Additional data collected in 1981 showed that suspended sediments were considerably enriched in organics, particularly PCBs, p,p'-DDT, α -endosulfan and chlorobenzenes in the lower Niagara River.

Polychlorinated biphenyls, p,p'-DDE and dieldrin were detected at more than 50% of the spottail shiner sampling locations.

High PCBs were observed in spottail shiners at the two stations on the United States side of the upper Niagara River near the 102nd Street dumpsite and directly downstream from Hooker Chemical at the search and rescue station upstream from the American Falls.

Polychlorinated biphenyls at all six stations in the Niagara River except the Frenchman's Creek station violated the 1978 GLWQA specific objective of 100 ng g⁻¹ for PCBs in fish.

Cadmium was two to three times higher; nickel and zinc were slightly higher and lead three to four times higher in spottail shiners in the lower Niagara River than in the upper Niagara River.



← Figure 2. Sampling locations on the upper Niagara River.

Figure 4. December 1979 storm effects at station 20.5A in the upper Niagara River.

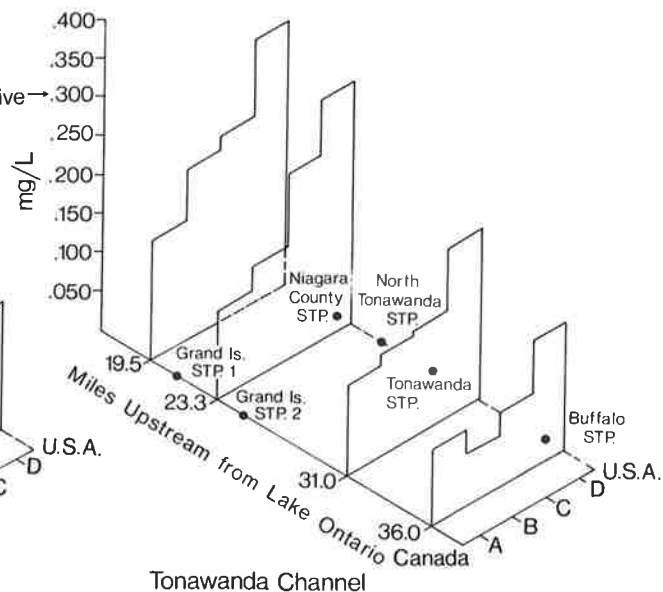
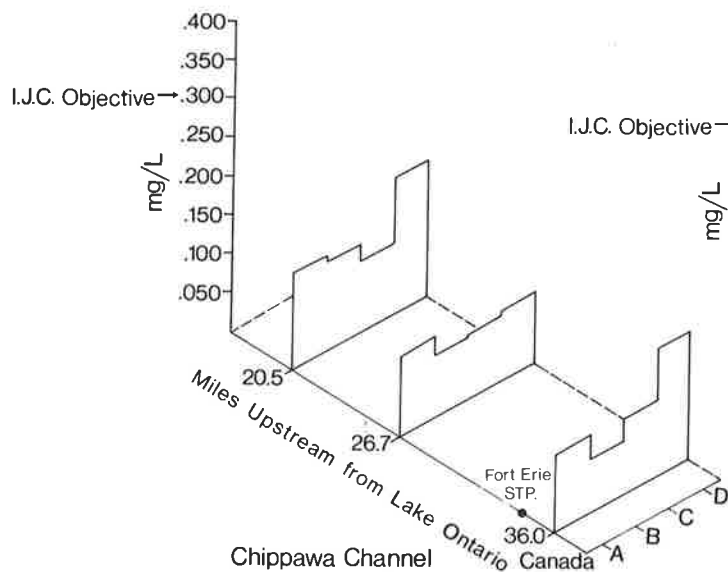
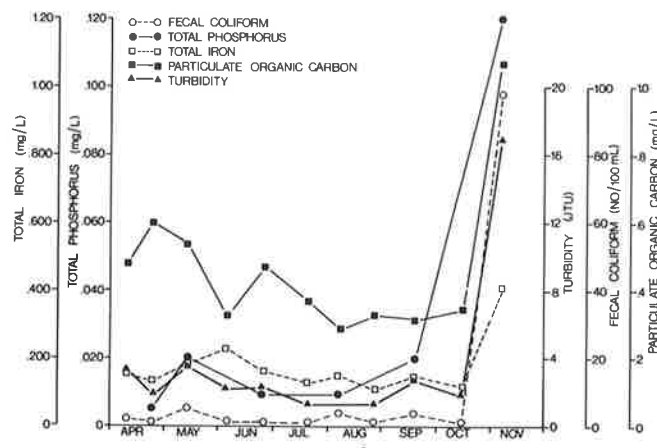


Figure 3. Mean total iron concentrations (mg L^{-1}) in the upper Niagara River, 1979.

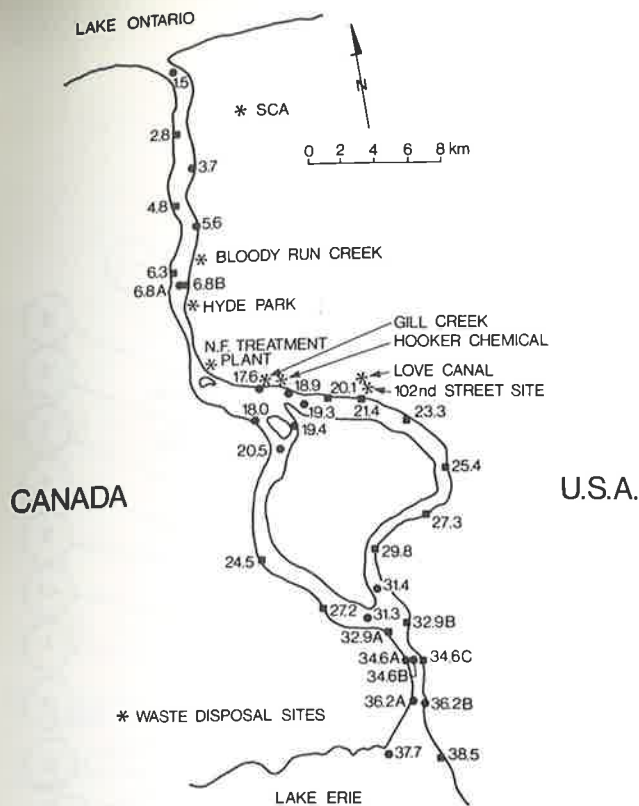


Figure 5. Sampling locations on the Niagara River, May 1981 Trace Metal Survey.

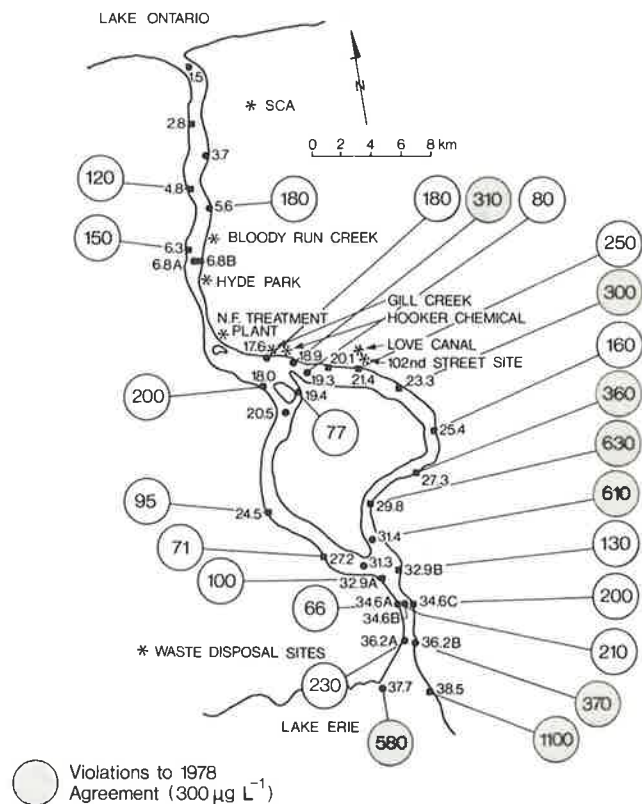


Figure 6. Total iron concentrations ($\mu\text{g L}^{-1}$) in water of the Niagara River, May 1981.

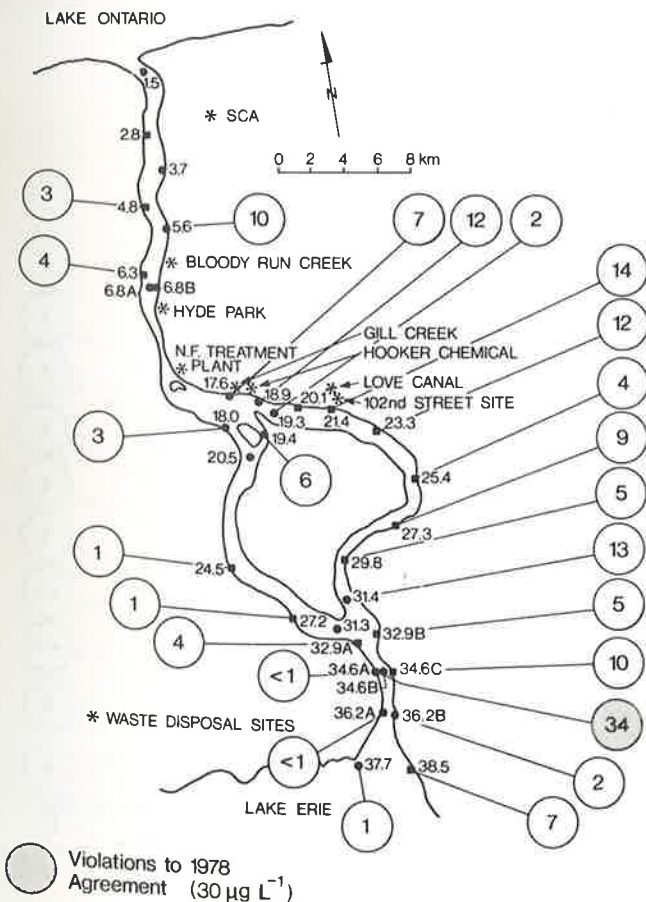


Figure 7. Total zinc concentrations ($\mu\text{g L}^{-1}$) in water of the Niagara River, May 1981.

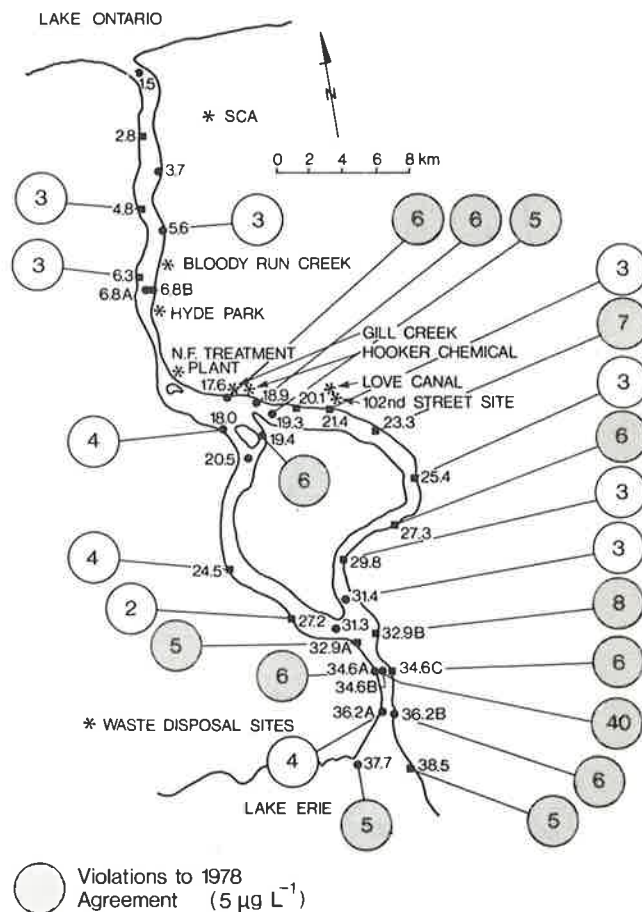


Figure 8. Total copper concentrations ($\mu\text{g L}^{-1}$) in water of the Niagara River, May 1981.

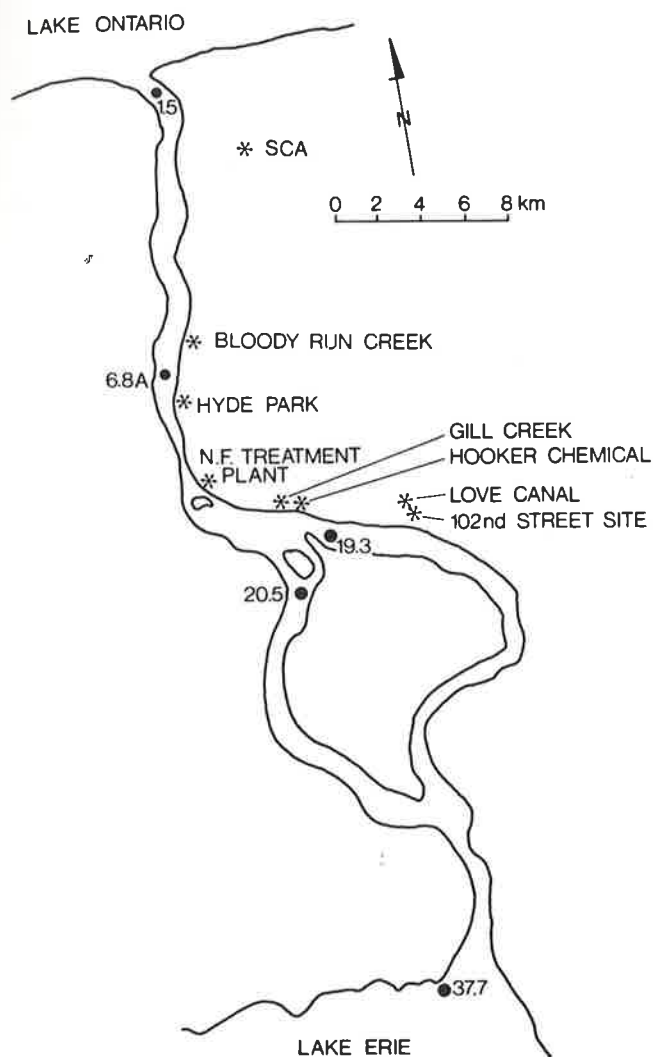


Figure 13. Station locations in the Niagara River for total water and large-volume aqueous samples, 1981.

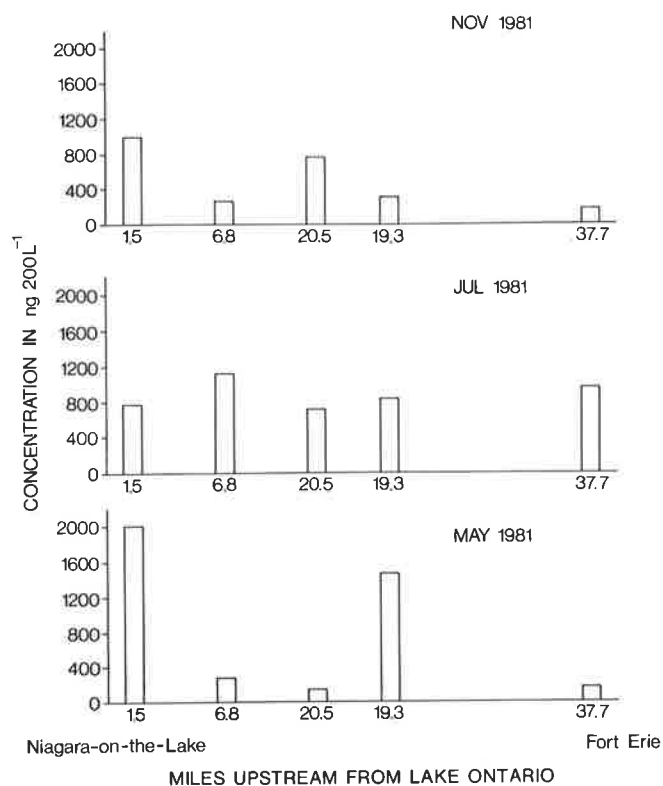


Figure 14. Distribution of α -BHC (ng 200 L⁻¹) in the aqueous phase of the Niagara River, 1981.

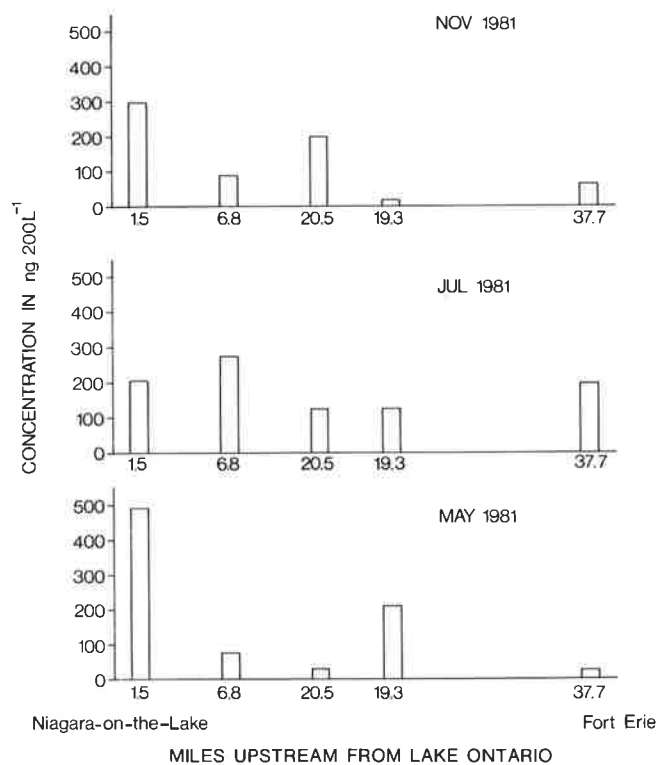


Figure 15. Distribution of γ -BHC (ng 200 L⁻¹) in the aqueous phase of the Niagara River, 1981.

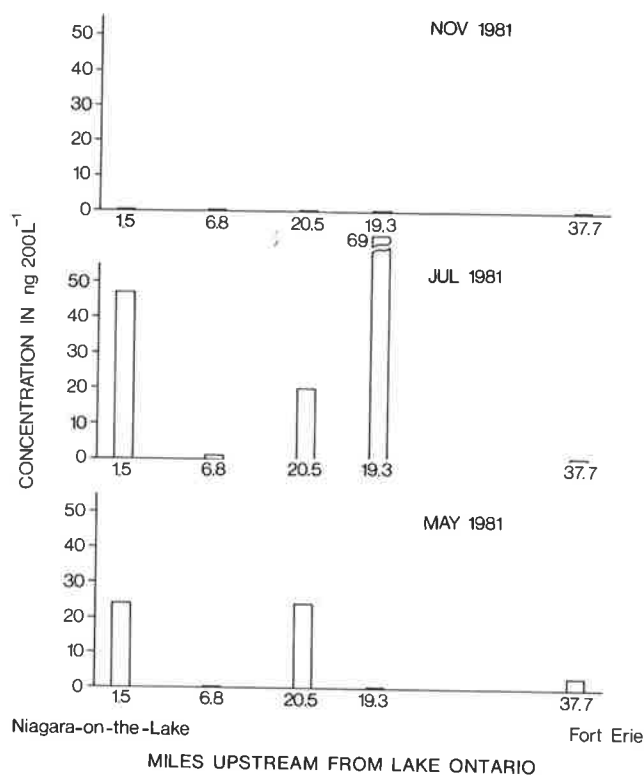


Figure 16. Distribution of heptachlor epoxide ($\text{ng } 200 \text{ L}^{-1}$) in the aqueous phase of the Niagara River, 1981.

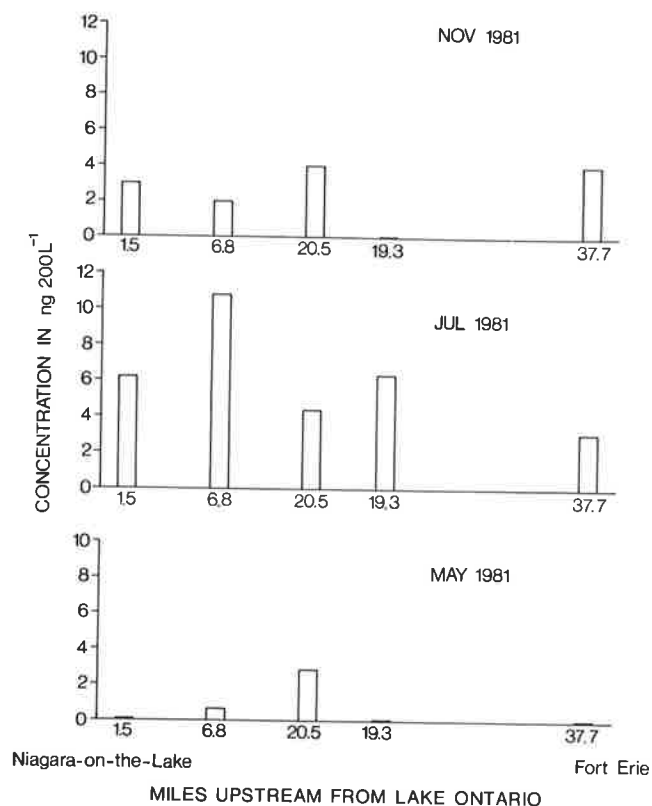


Figure 17. Distribution of endrin ($\text{ng } 200 \text{ L}^{-1}$) in the aqueous phase of the Niagara River, 1981.

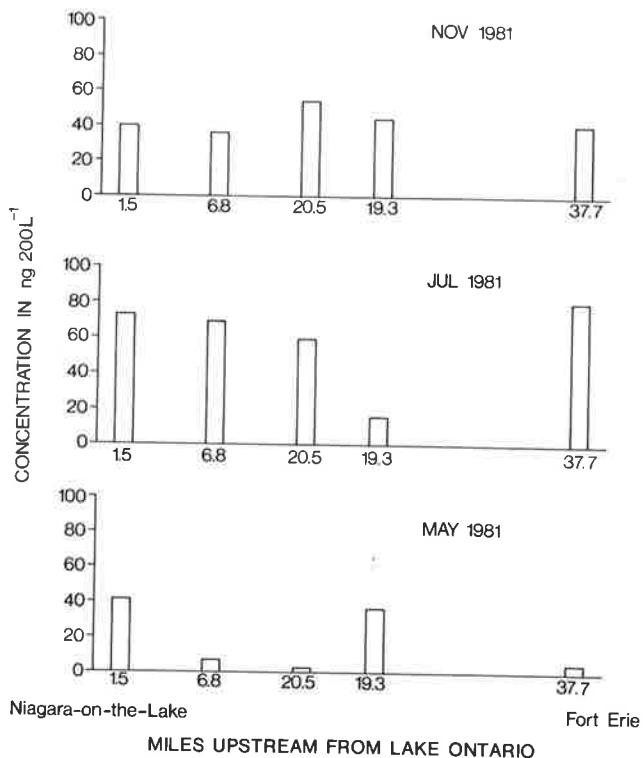


Figure 18. Distribution of dieldrin ($\text{ng } 200 \text{ L}^{-1}$) in the aqueous phase of the Niagara River, 1981.

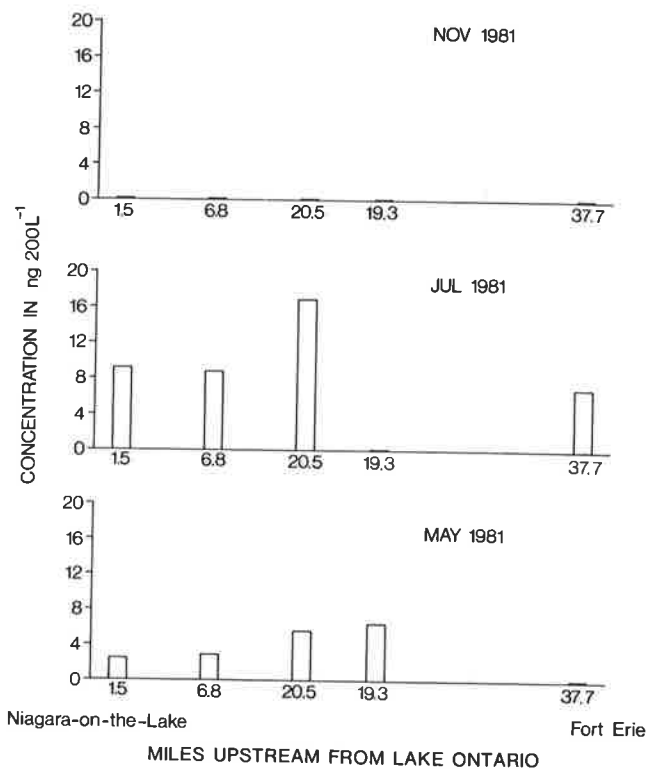


Figure 19. Distribution of p,p'-DDT ($\text{ng } 200 \text{ L}^{-1}$) in the aqueous phase of the Niagara River, 1981.

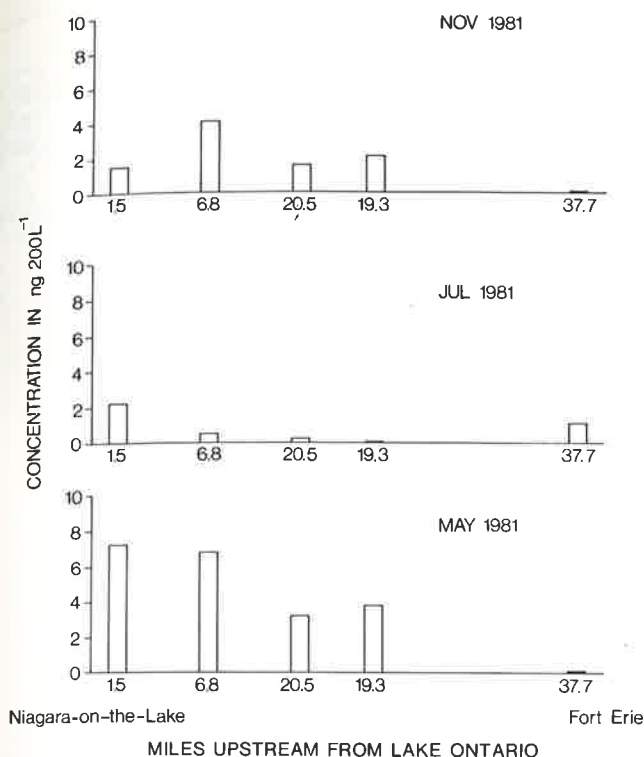


Figure 20. Distribution of p,p'-DDE (ng 200 L⁻¹) in the aqueous phase of the Niagara River, 1981.

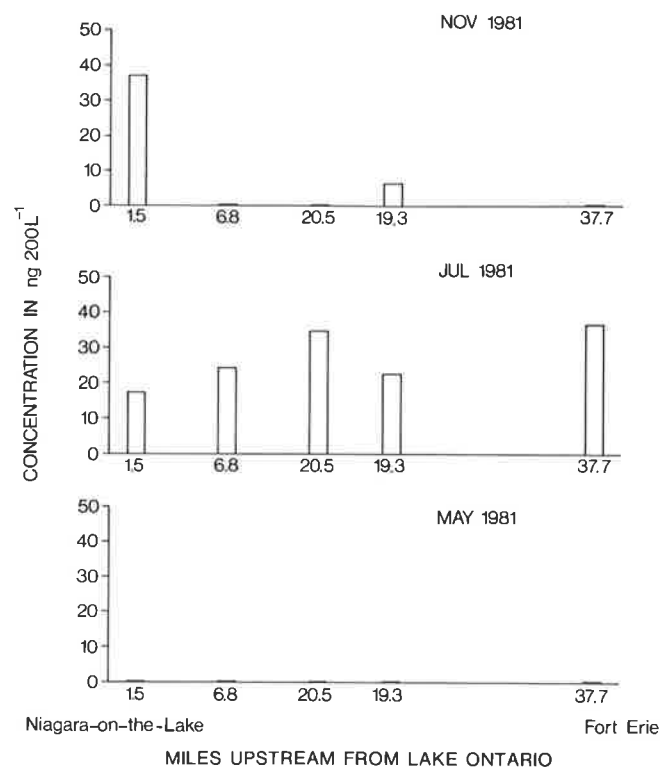


Figure 21. Distribution of p,p'-TDE (ng 200 L⁻¹) in the aqueous phase of the Niagara River, 1981.

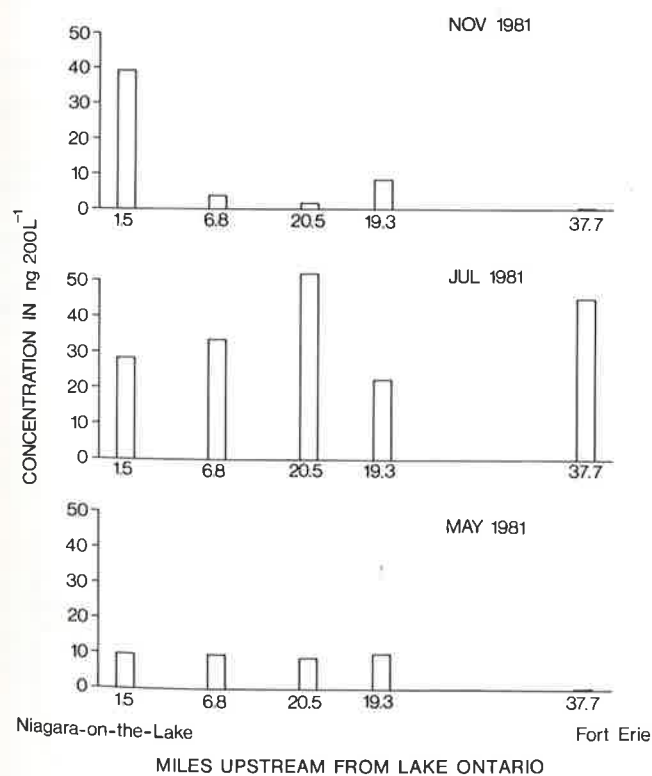


Figure 22. Distribution of total DDT (ng 200 L⁻¹) in the aqueous phase of the Niagara River, 1981.

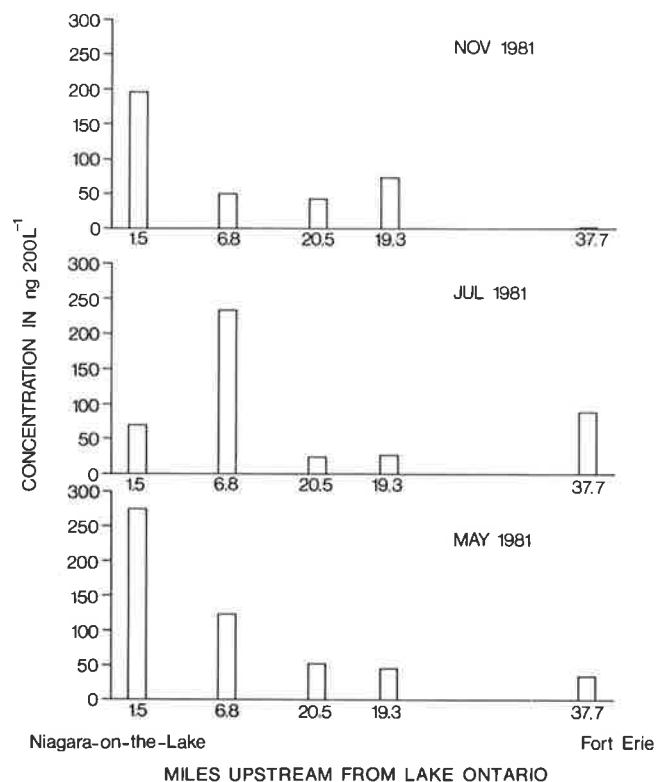


Figure 23. Distribution of total PCBs (ng 200 L⁻¹) in the aqueous phase of the Niagara River, 1981.

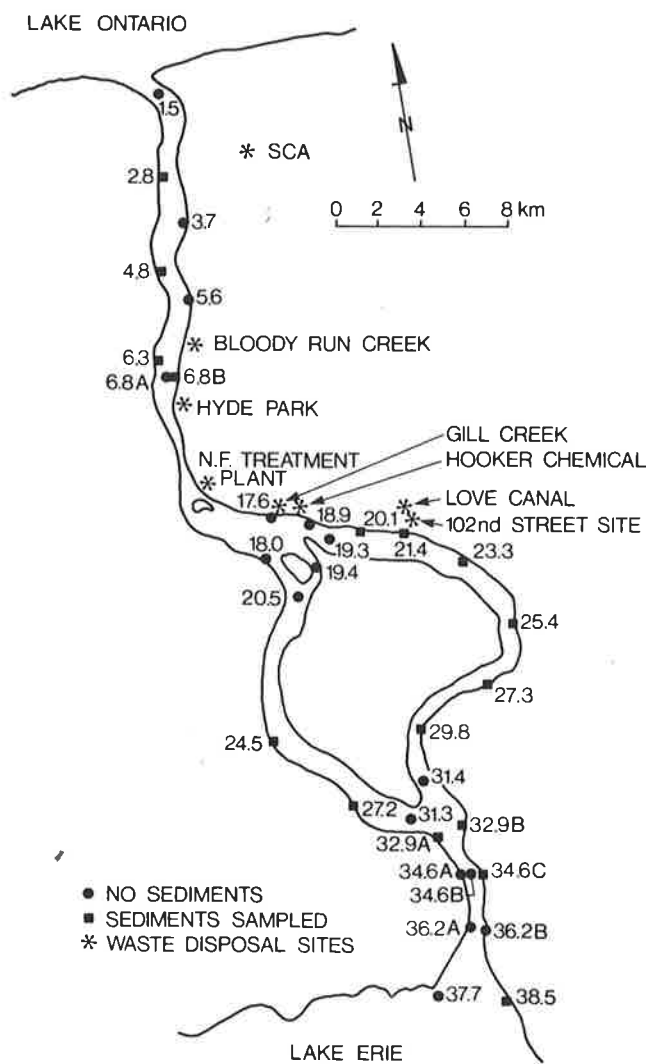


Figure 24. Bottom sediment sampling locations in the Niagara River, May 1981.

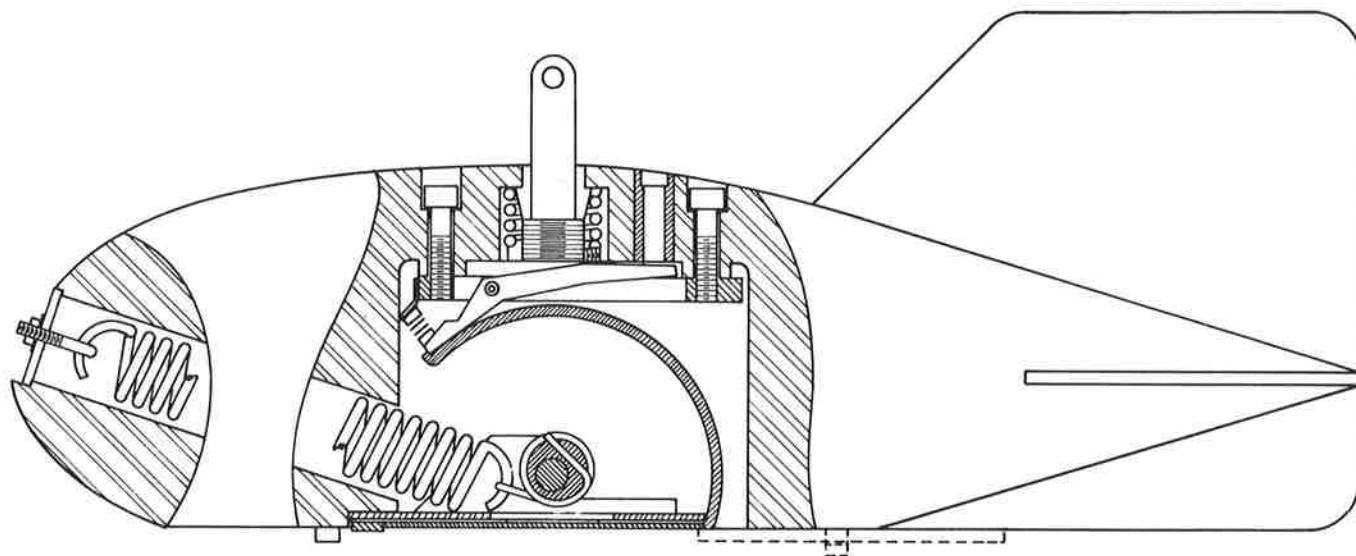


Figure 25. Bottom sediment sampler (USBM-54) used in the Niagara River, 1981.

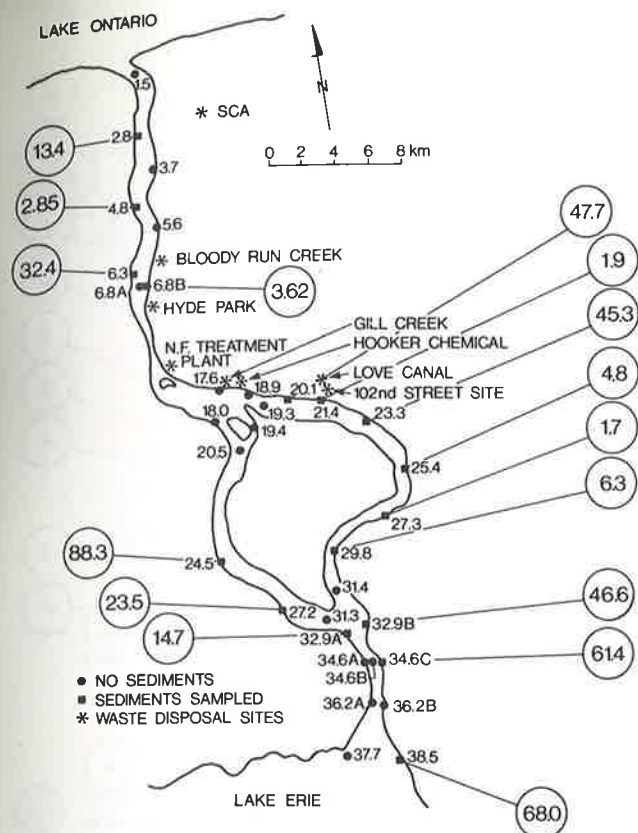


Figure 26. Distribution of clay and silt (percent) in bottom sediments of the Niagara River, May 1981.

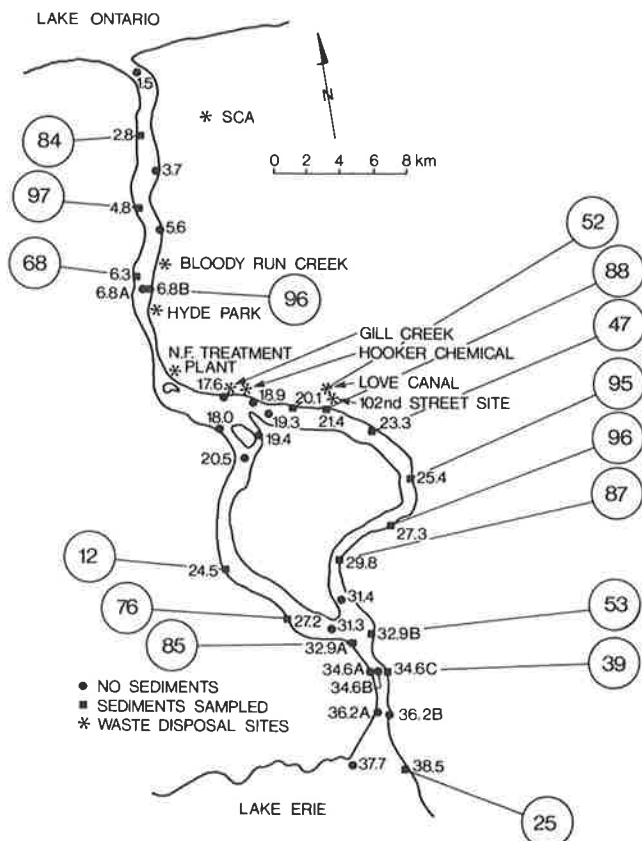


Figure 27. Distribution of sand (percent) in bottom sediments of the Niagara River, May 1981.

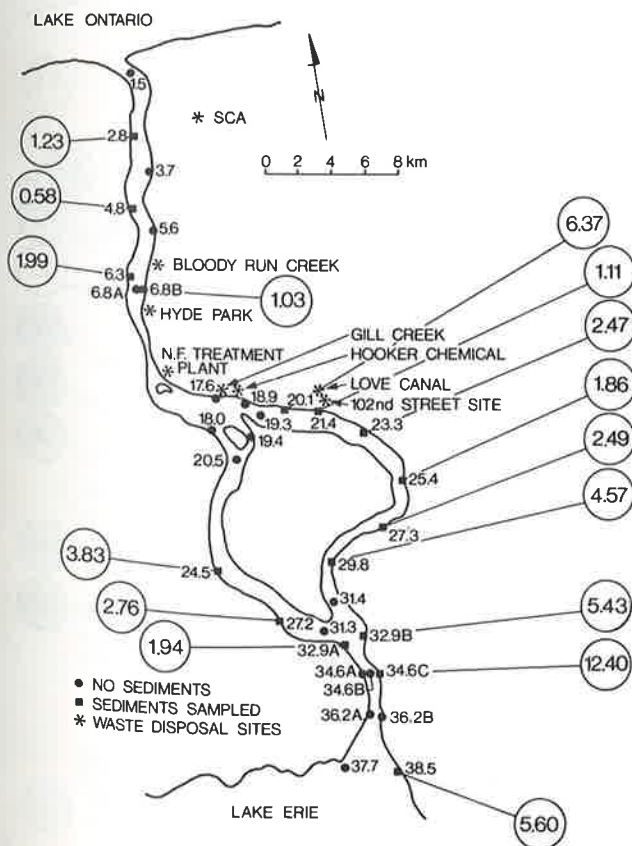


Figure 28. Distribution of volatile solids (percent) in bottom sediments of the Niagara River, May 1981.

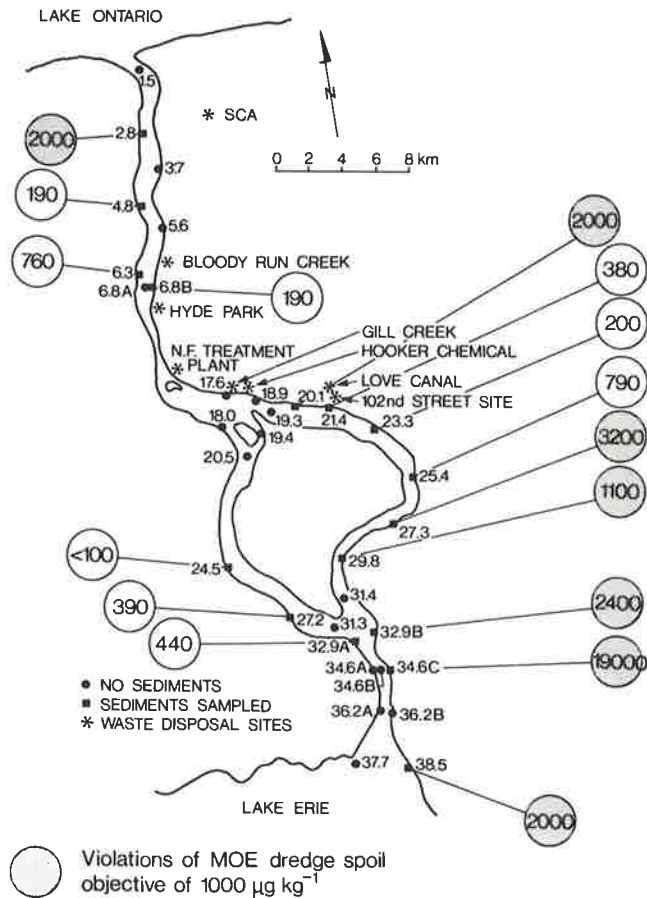


Figure 29. Distribution of extractable (0.5 N HCl) cadmium ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

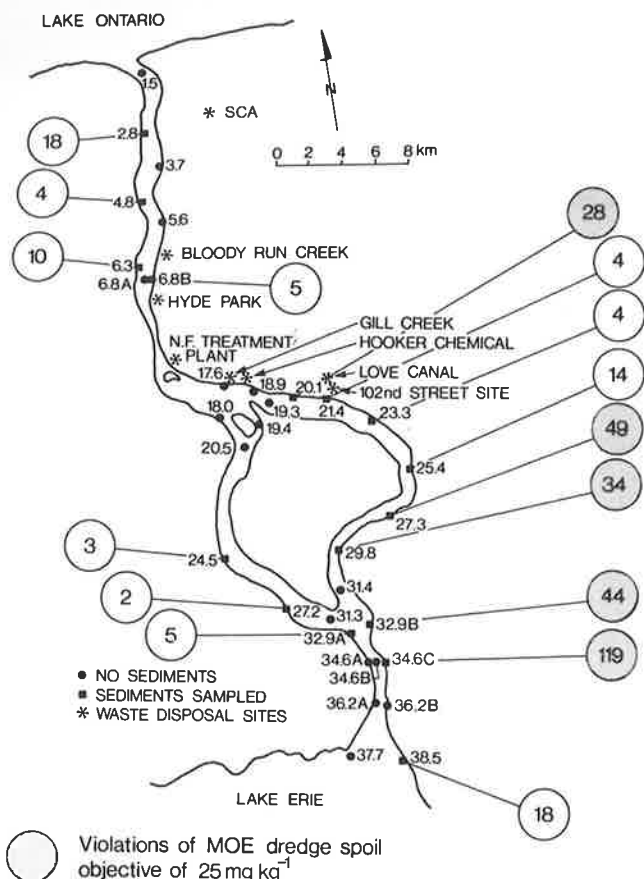


Figure 30. Distribution of extractable (0.5 N HCl) chromium (mg kg^{-1}) in bottom sediments of the Niagara River, May 1981.

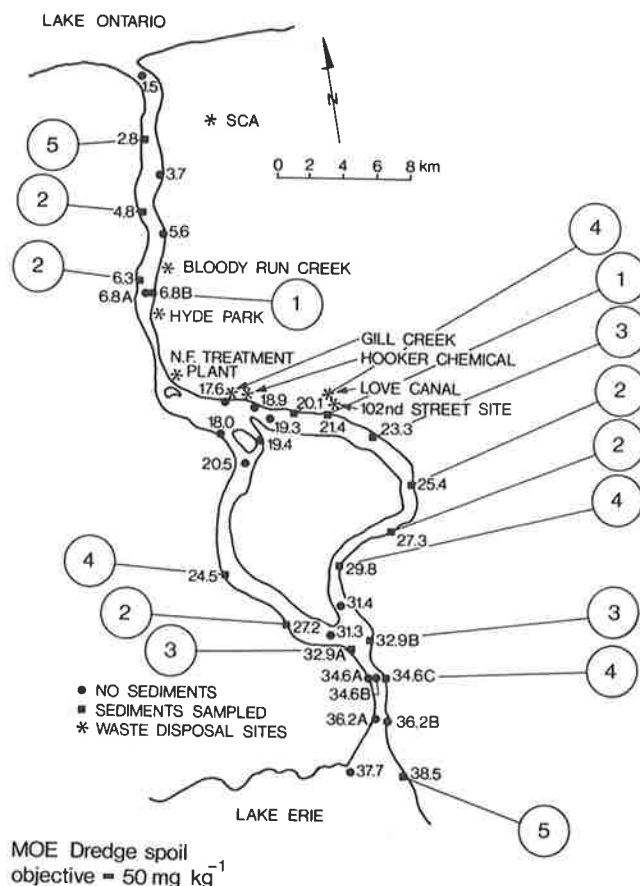


Figure 31. Distribution of extractable (0.5 N HCl) cobalt (mg kg^{-1}) in bottom sediments of the Niagara River, May 1981.

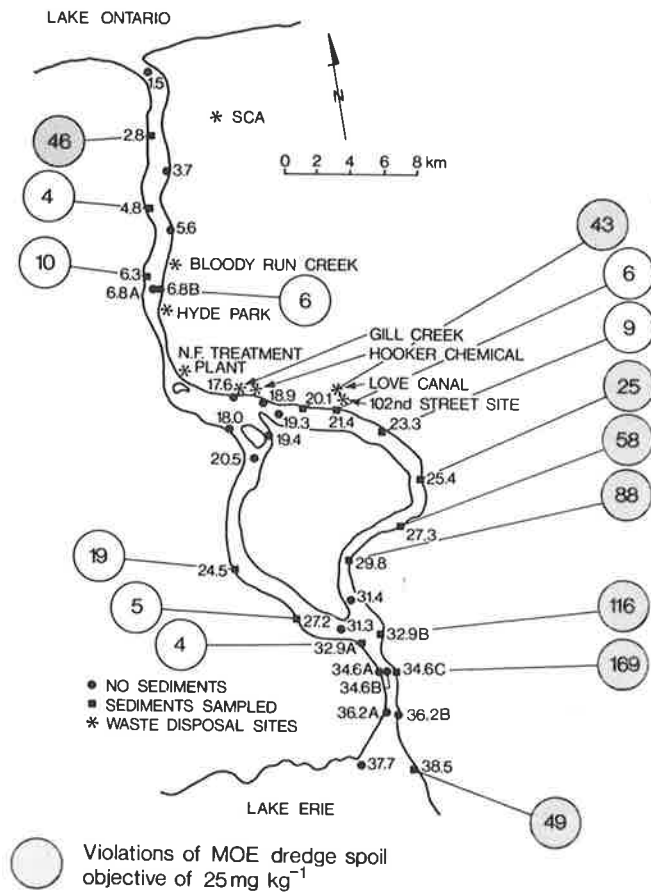


Figure 32. Distribution of extractable (0.5 N HCl) copper (mg kg^{-1}) in bottom sediments of the Niagara River, May 1981.

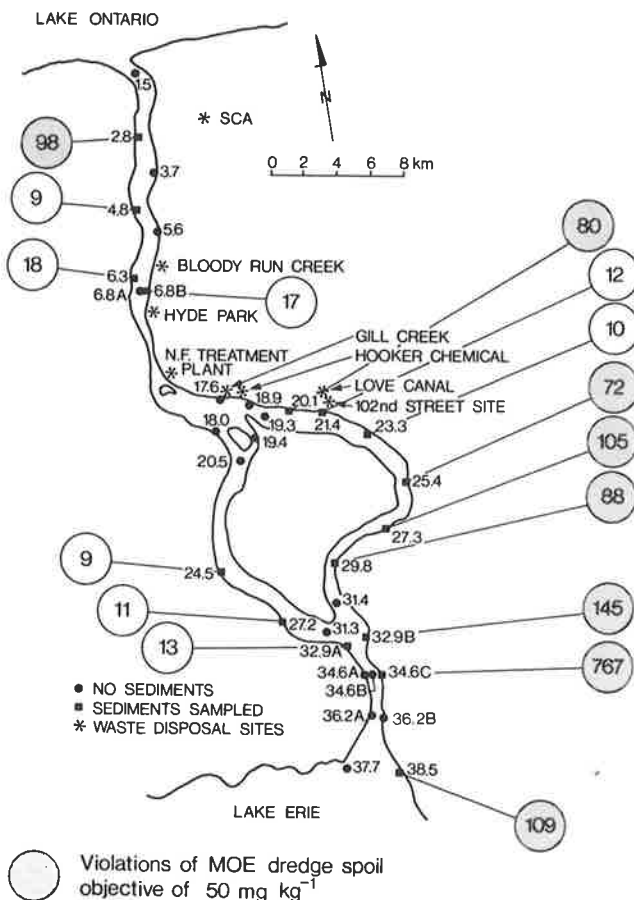


Figure 33. Distribution of extractable (0.5 N HCl) lead (mg kg^{-1}) in bottom sediments of the Niagara River, May 1981.

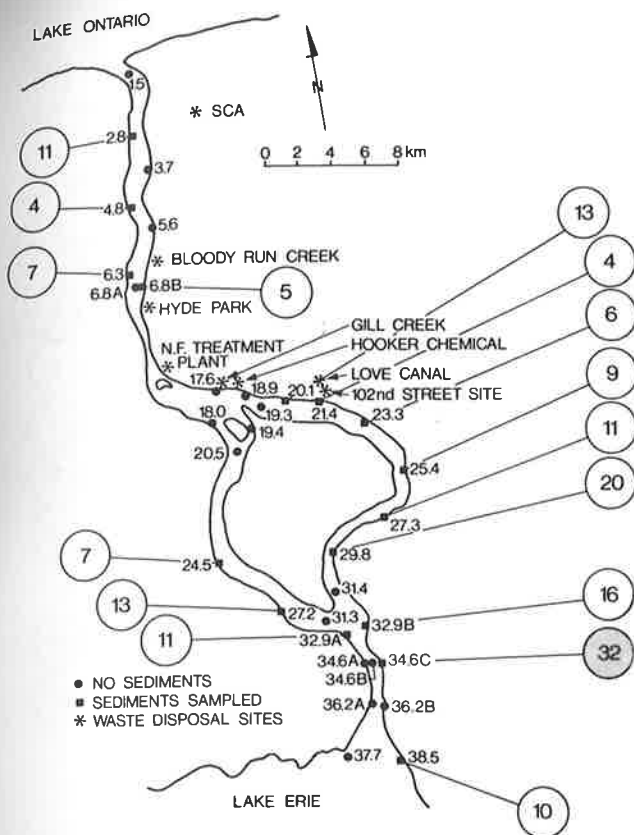


Figure 34. Distribution of extractable (0.5 N HCl) nickel (mg kg^{-1}) in bottom sediments of the Niagara River, May 1981.

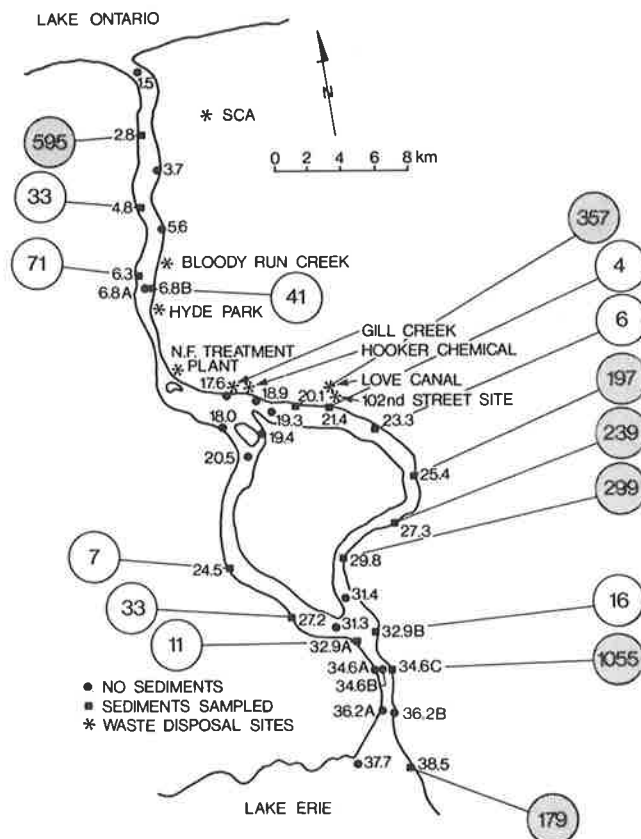


Figure 35. Distribution of extractable (0.5 N HCl) zinc (mg kg^{-1}) in bottom sediments of the Niagara River, May 1981.

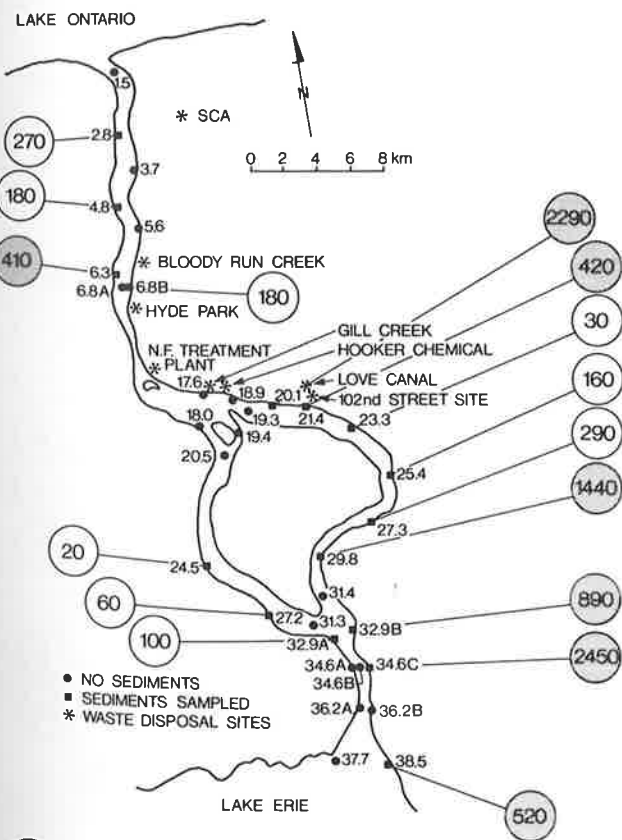


Figure 36. Distribution of total mercury ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

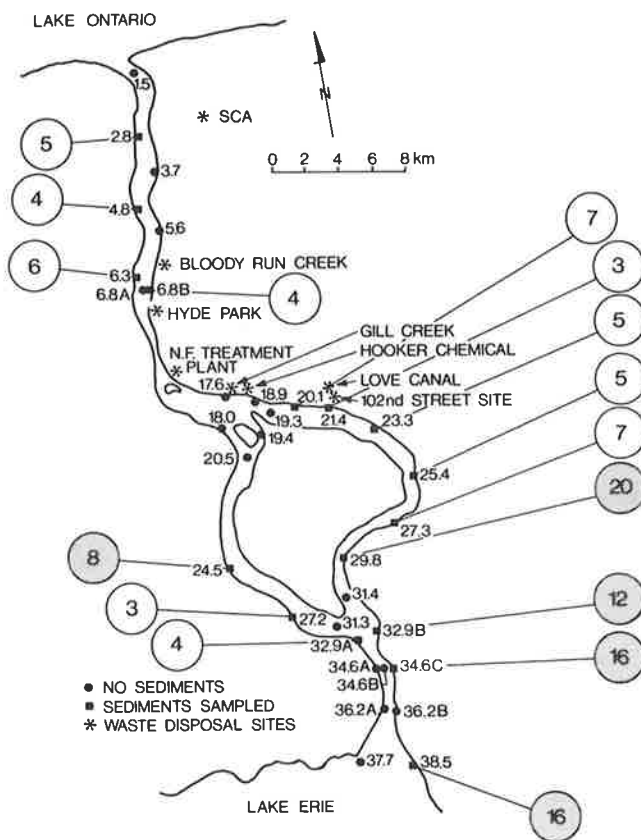


Figure 37. Distribution of total arsenic (mg kg^{-1}) in bottom sediments of the Niagara River, May 1981.

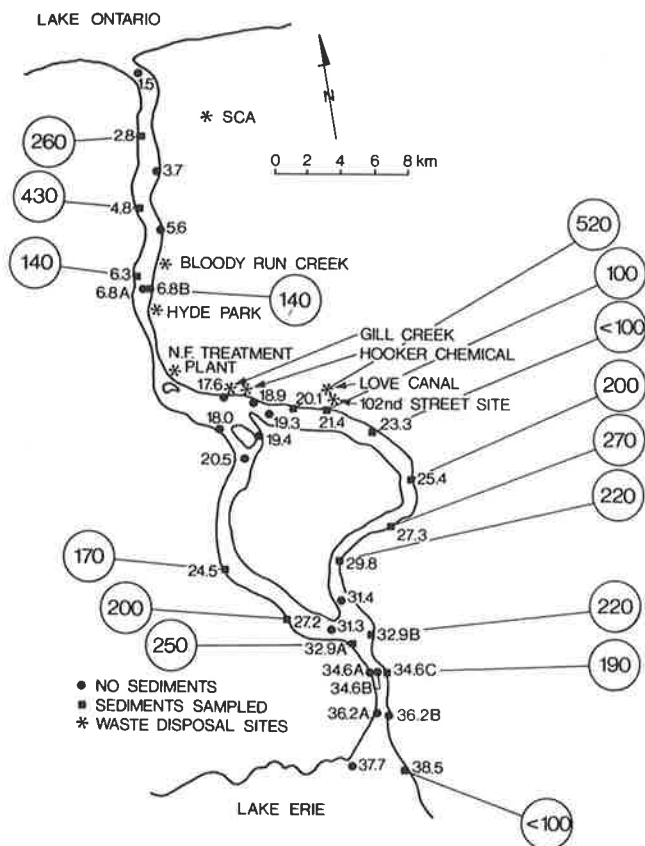


Figure 38. Distribution of total selenium ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

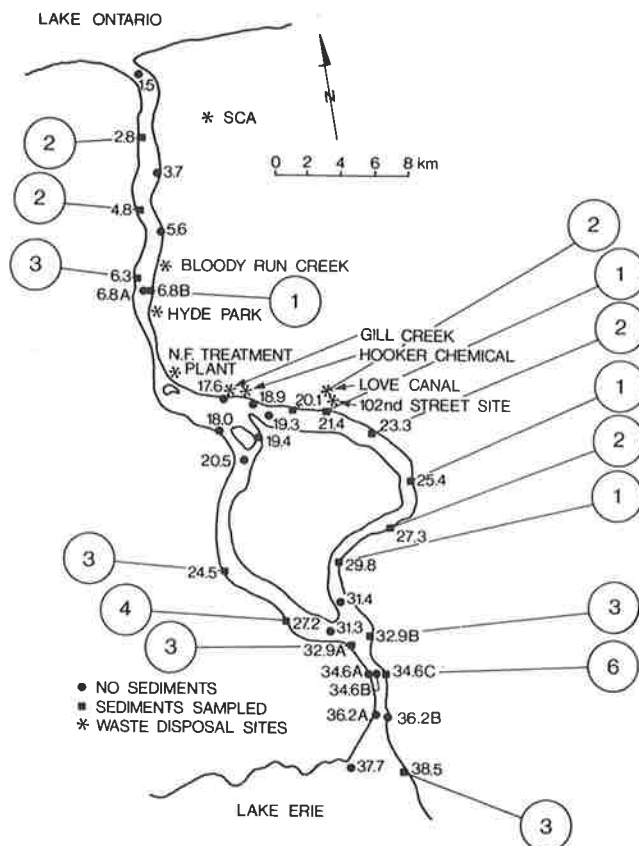


Figure 39. Distribution of organic carbon (percent) in bottom sediments of the Niagara River, May 1981.

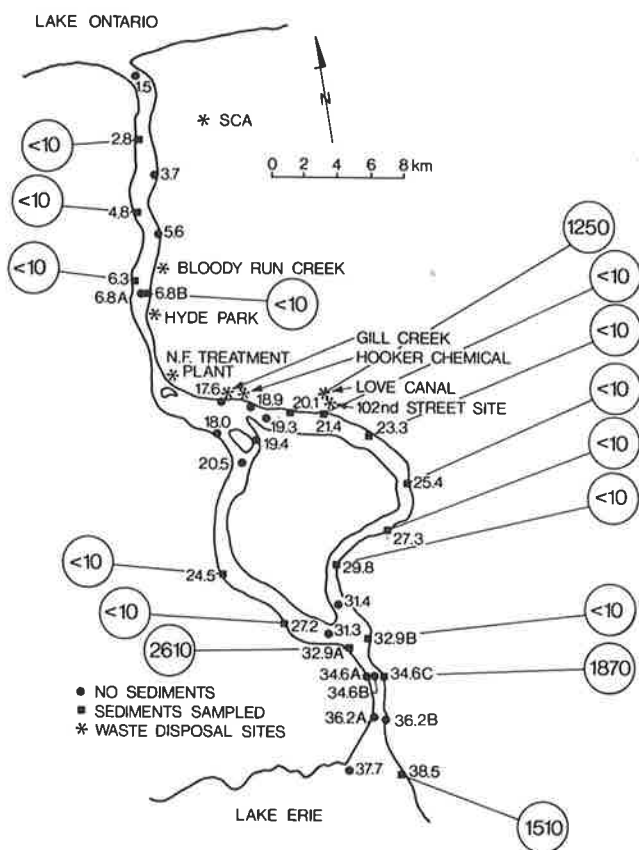


Figure 40. Distribution of organic nitrogen (mg kg^{-1}) in bottom sediments of the Niagara River, May 1981.

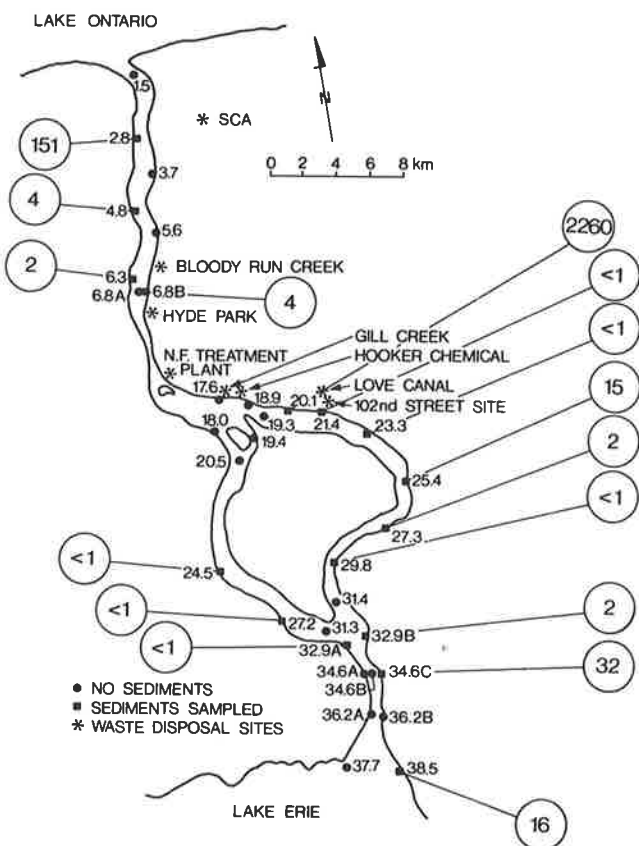


Figure 41. Distribution of α -BHC (lindane) ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

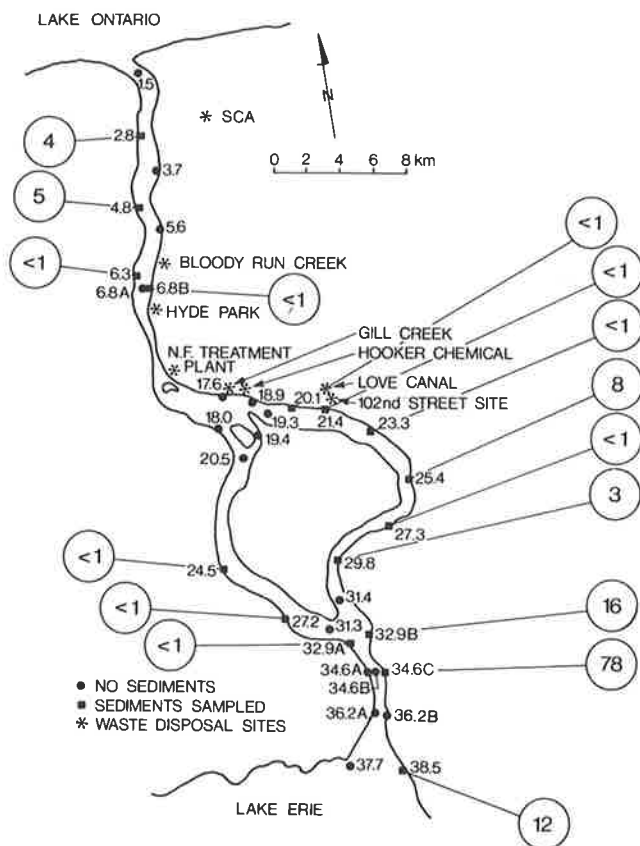


Figure 46. Distribution of α -endosulfan ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

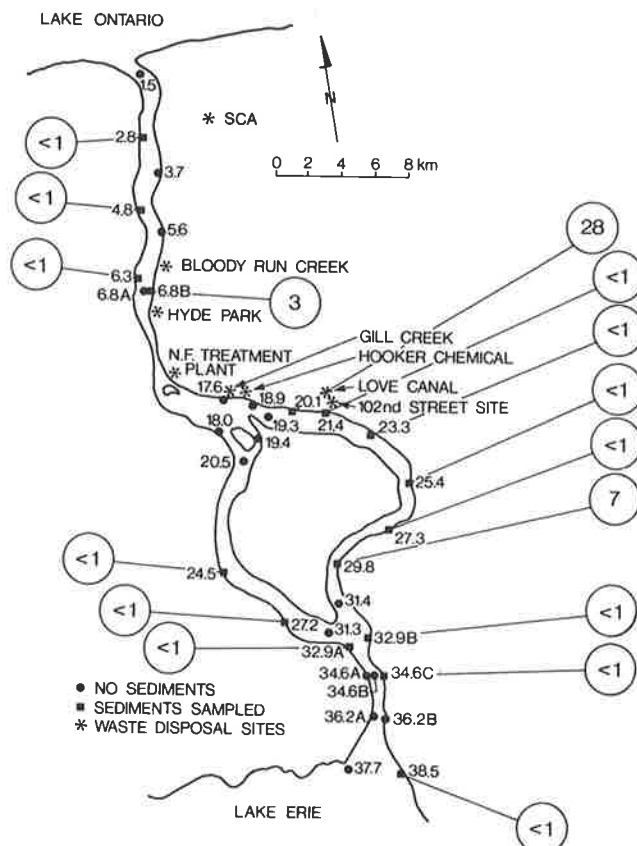


Figure 47. Distribution of β -endosulfan ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

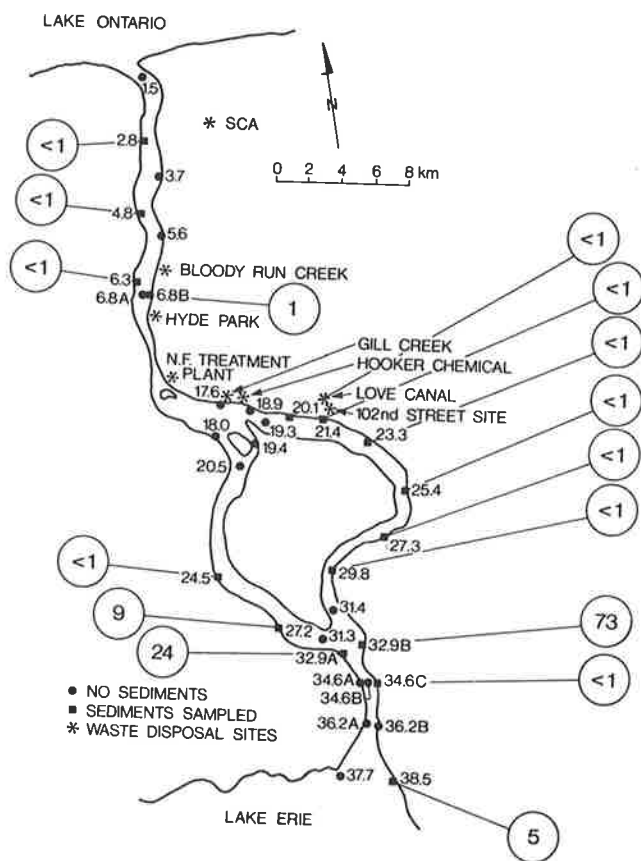


Figure 48. Distribution of p,p'-DDT ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

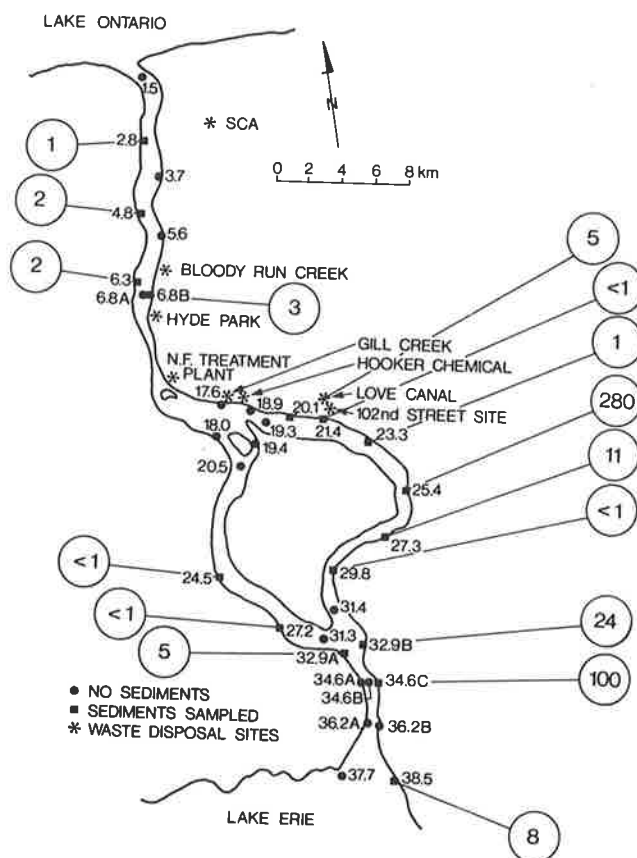


Figure 49. Distribution of p,p'-DDE ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

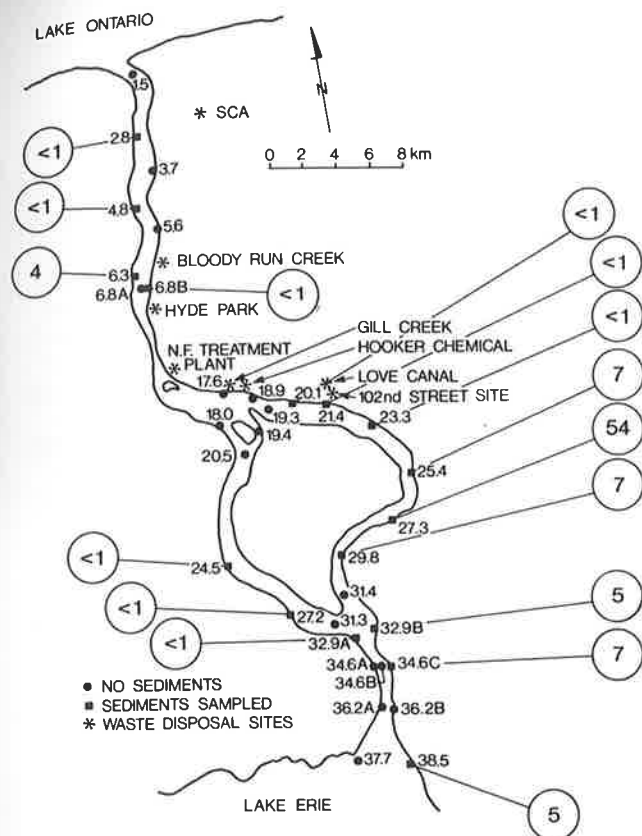


Figure 50. Distribution of p,p'-TDE ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

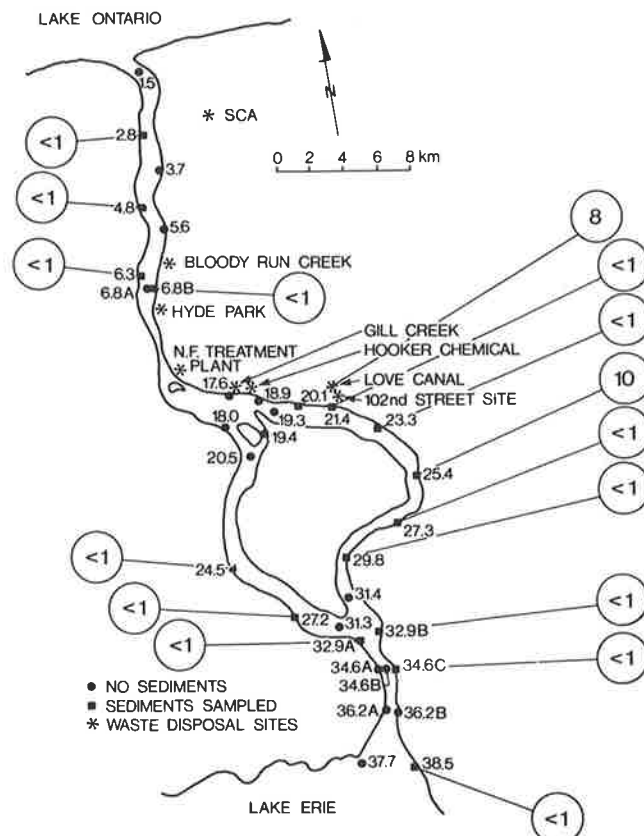


Figure 51. Distribution of dieldrin ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

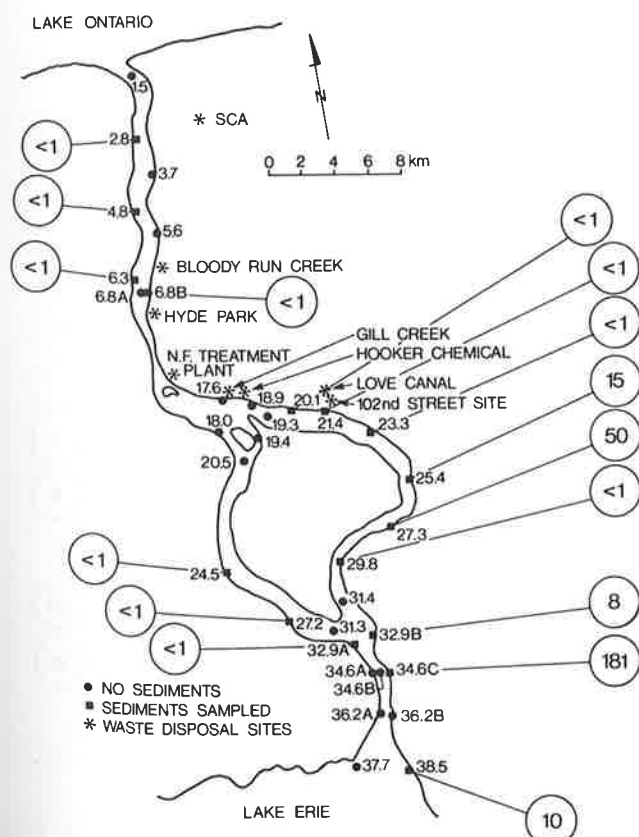


Figure 52. Distribution of endrin ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

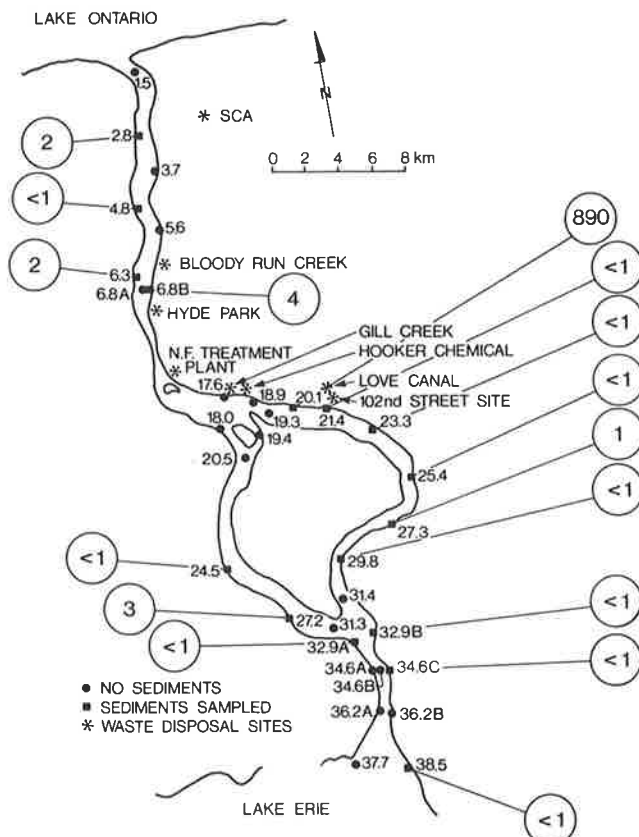


Figure 53. Distribution of mirex ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

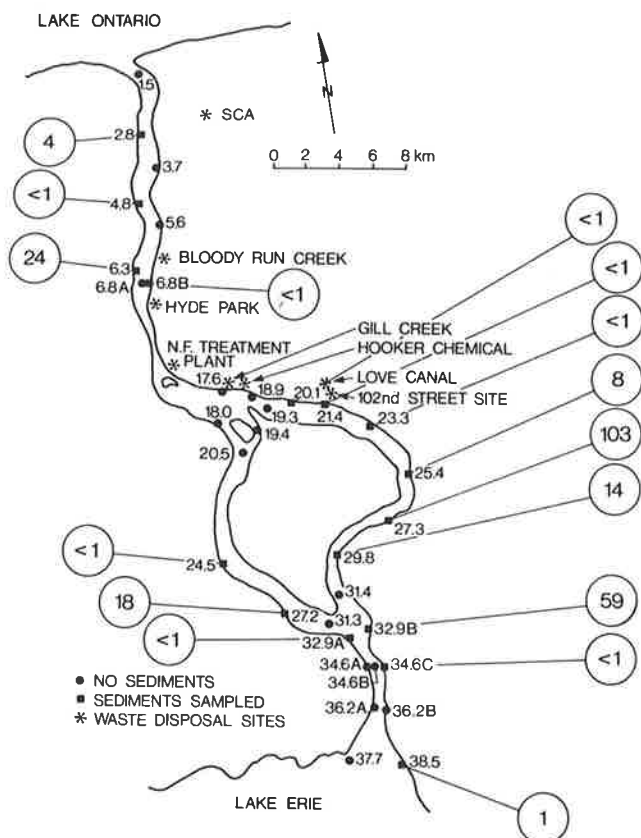


Figure 54. Distribution of methoxychlor ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

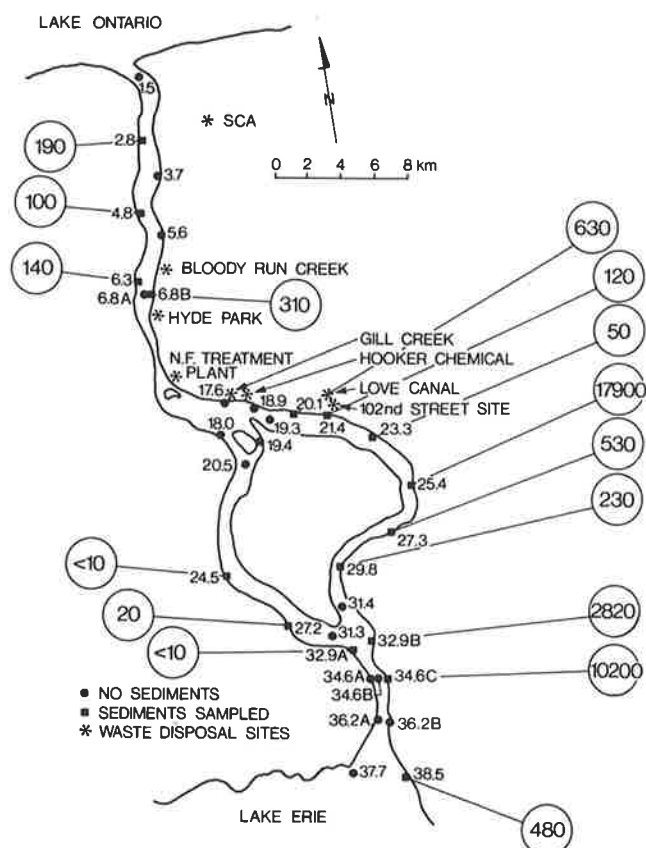


Figure 55. Distribution of total PCBs ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

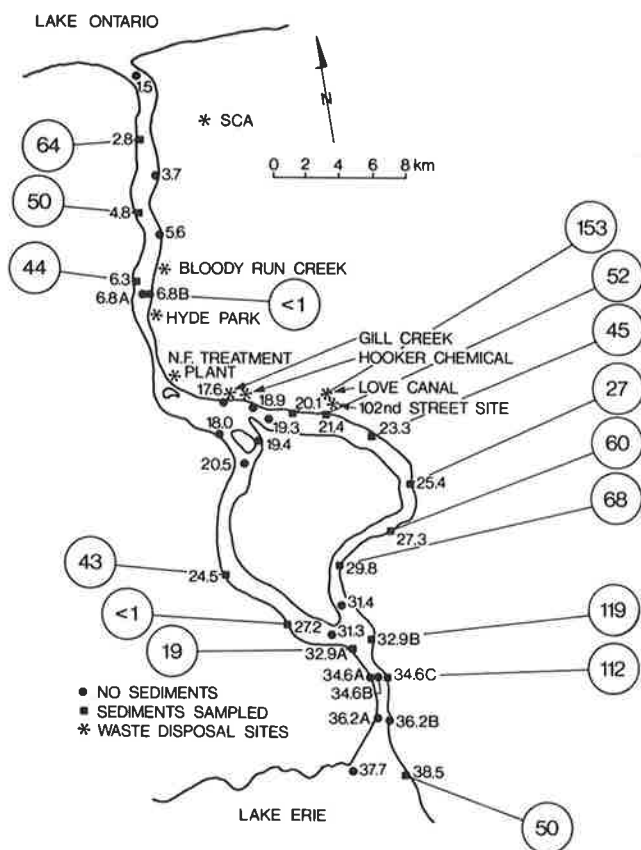


Figure 56. Distribution of dichlorobenzenes ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

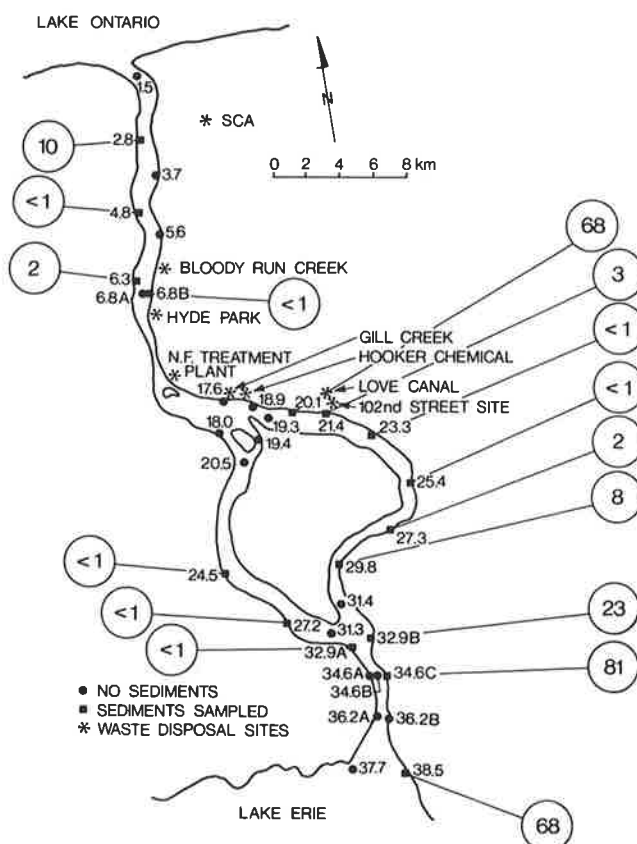


Figure 57. Distribution of trichlorobenzenes ($\mu\text{g kg}^{-1}$) in bottom sediments of the Niagara River, May 1981.

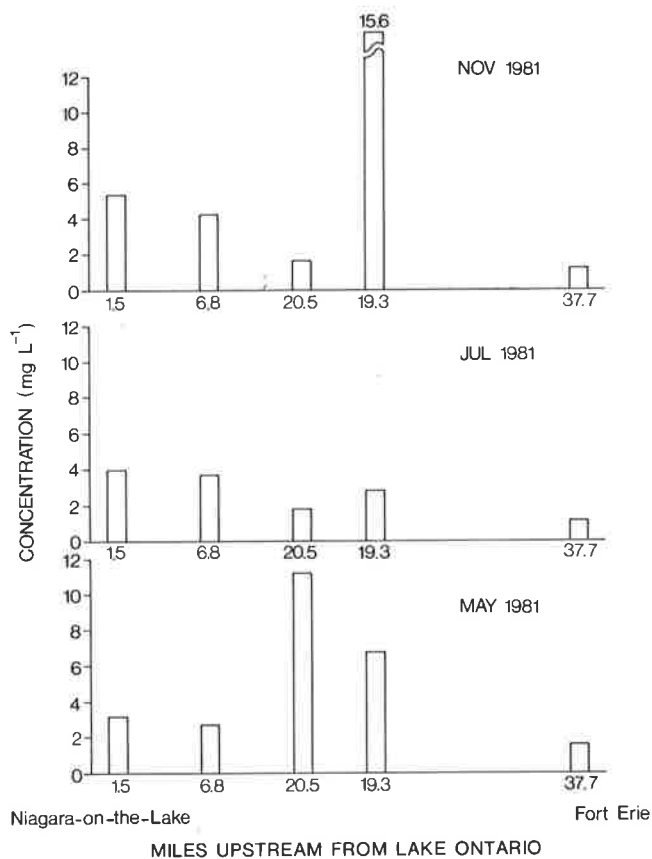


Figure 61. Distribution of suspended sediments (mg L⁻¹) in the Niagara River, 1981.

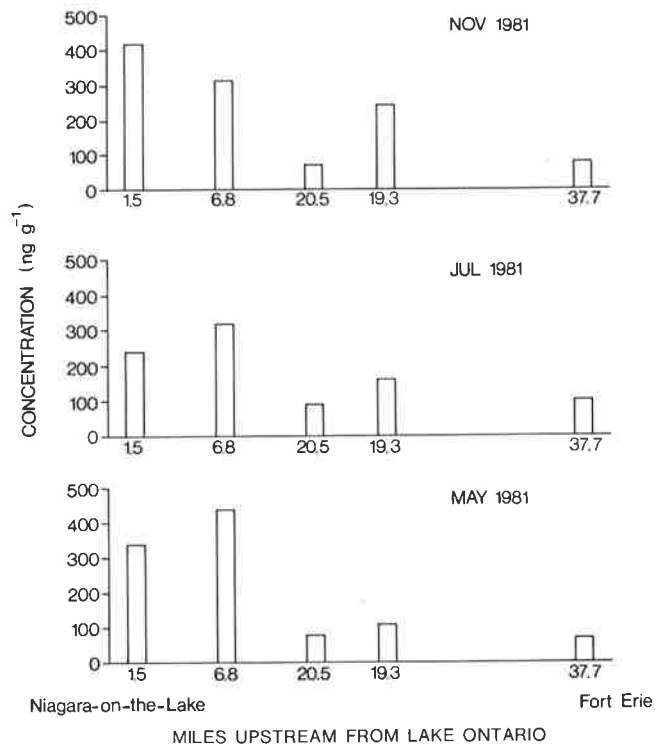


Figure 62. Distribution of total mercury (ng g⁻¹) in suspended sediments of the Niagara River, 1981.

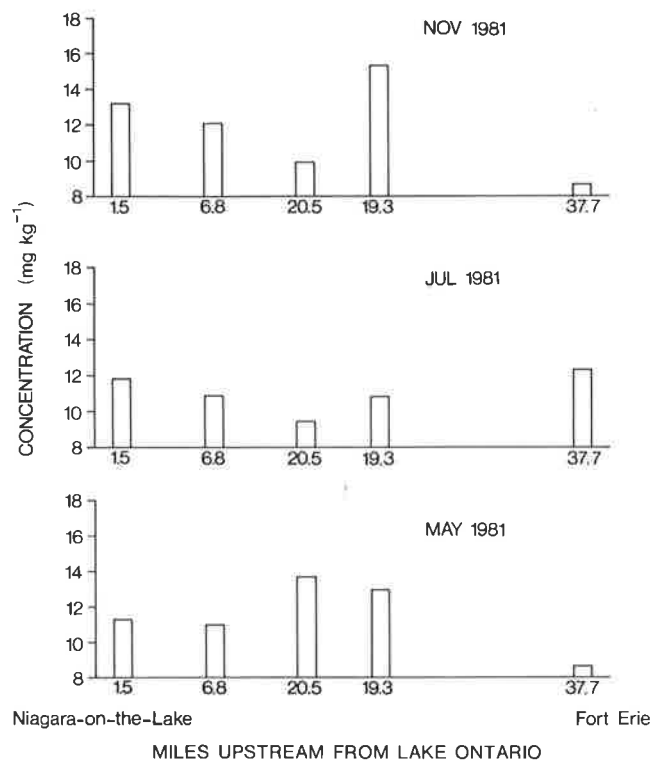


Figure 63. Distribution of total arsenic (mg kg⁻¹) in suspended sediments of the Niagara River, 1981.

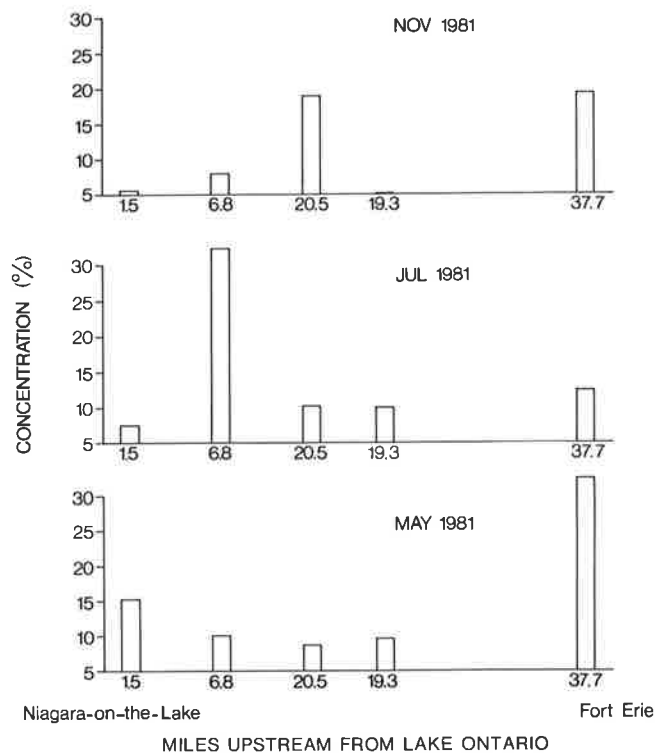


Figure 64. Distribution of organic carbon (percent) in suspended sediments of the Niagara River, 1981.

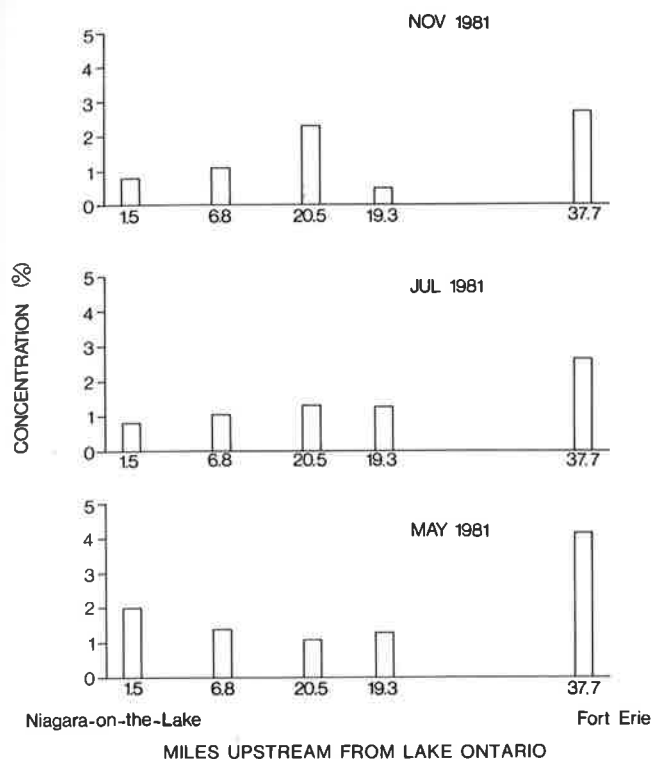


Figure 65. Distribution of organic nitrogen (percent) in suspended sediments of the Niagara River, 1981.

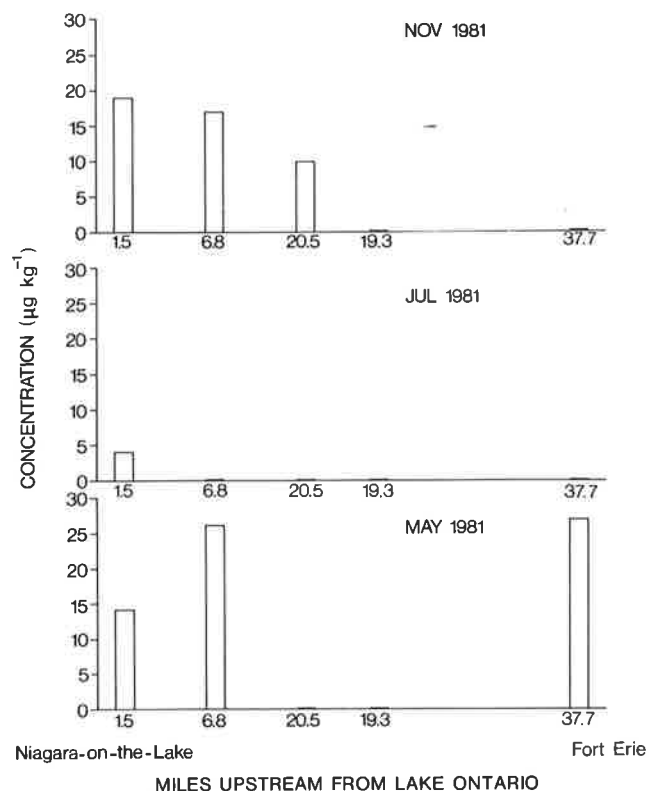


Figure 66. Distribution of α -BHC ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

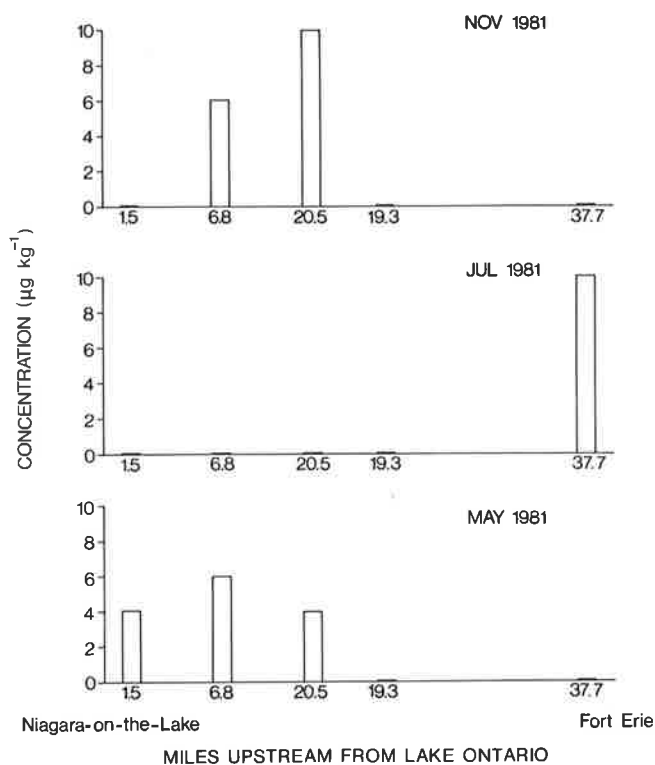


Figure 67. Distribution of heptachlor epoxide ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

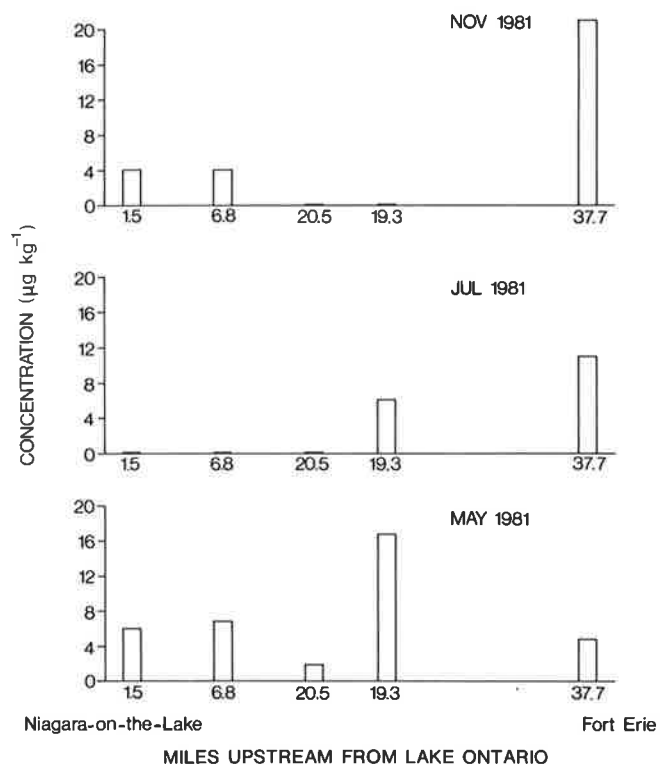


Figure 68. Distribution of α -chlordane ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

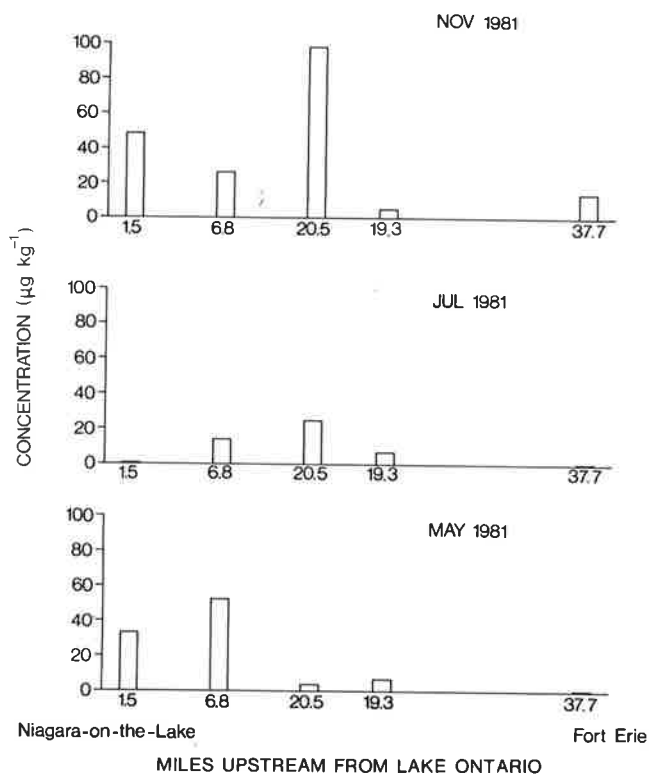


Figure 69. Distribution of α -endosulfan ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

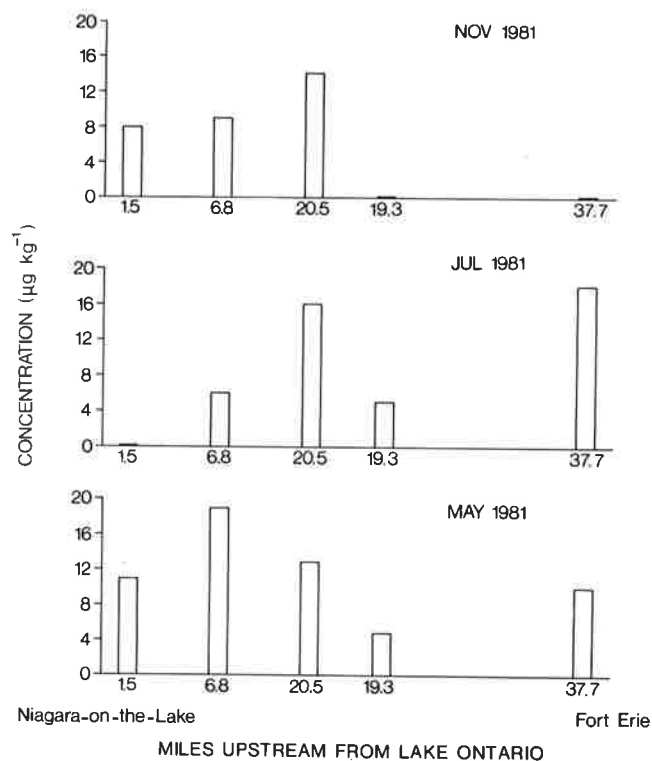


Figure 70. Distribution of dieldrin ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

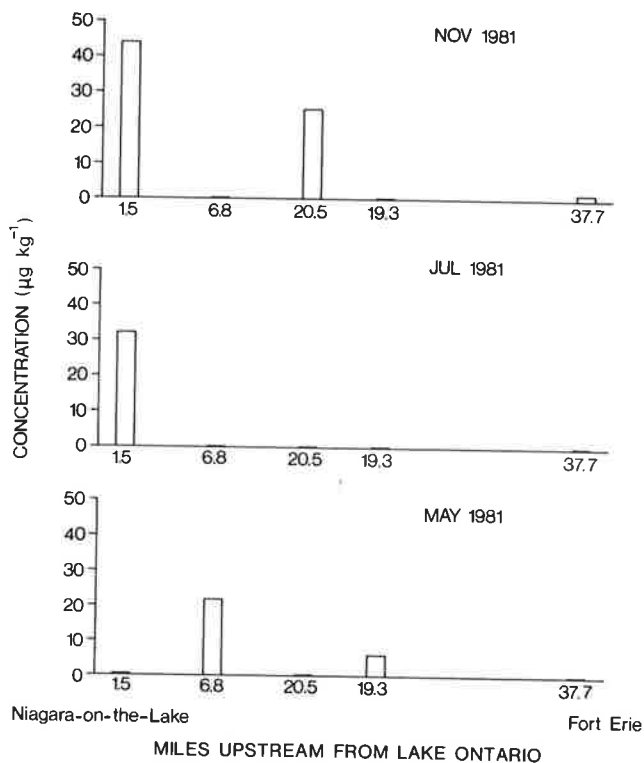


Figure 71. Distribution of p,p'-DDT ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

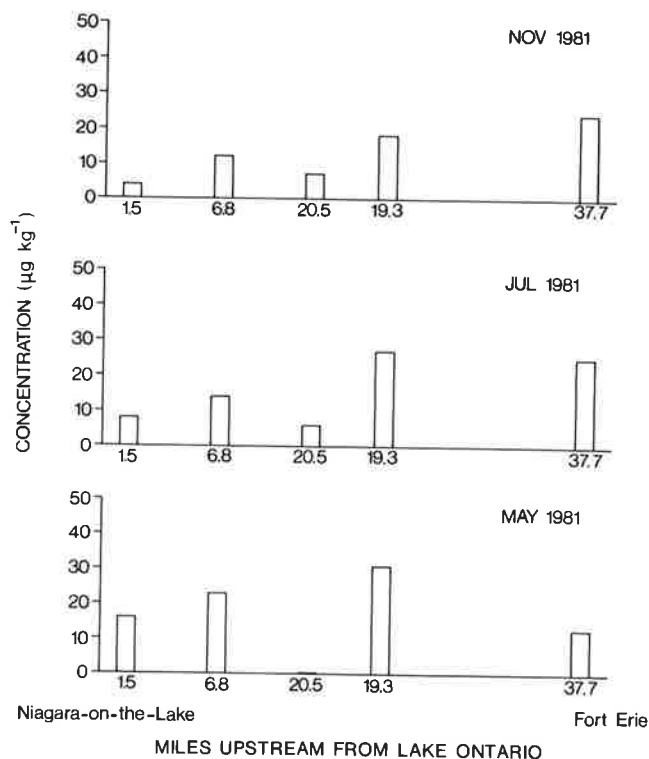


Figure 72. Distribution of p,p'-DDE ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

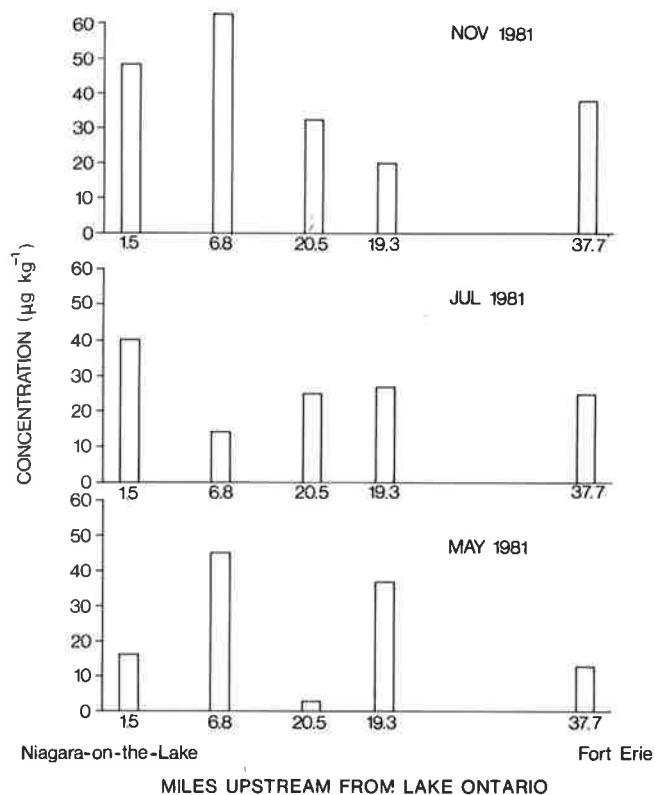


Figure 73. Distribution of total DDT ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

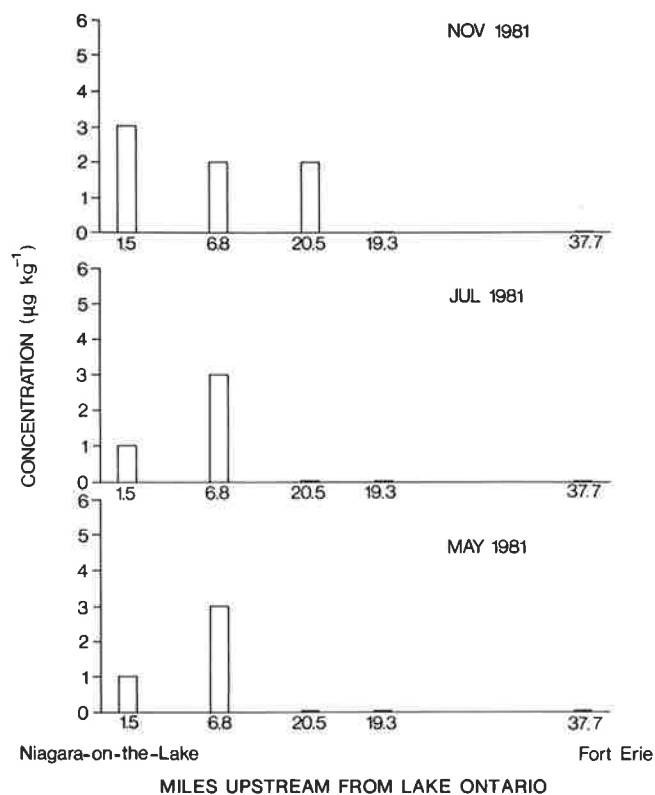


Figure 74. Distribution of mirex ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, May 1981.

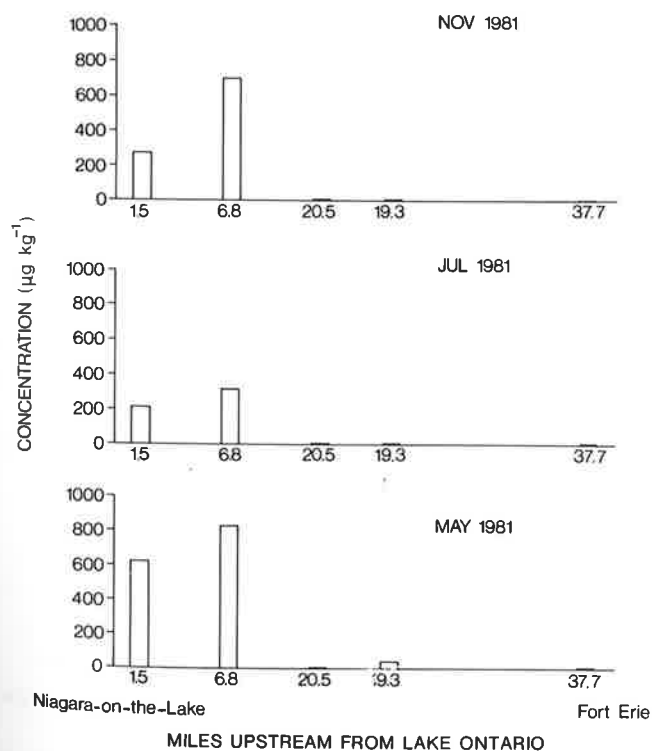


Figure 75. Distribution of total PCBs ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

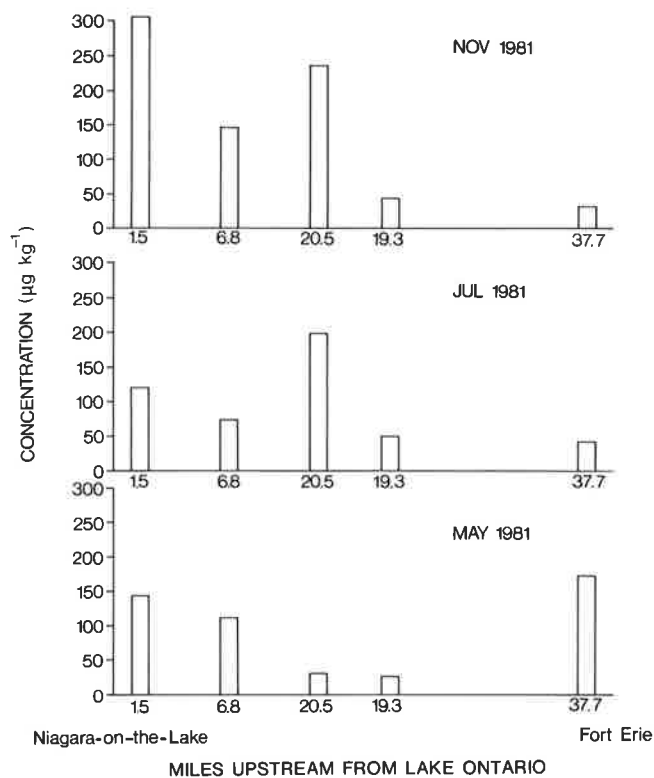


Figure 76. Distribution of dichlorobenzenes ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

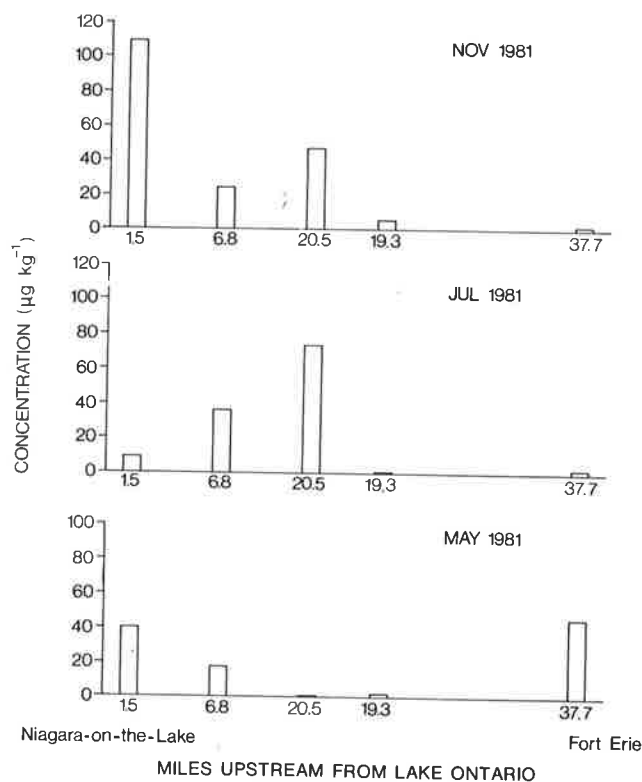


Figure 77. Distribution of trichlorobenzenes ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

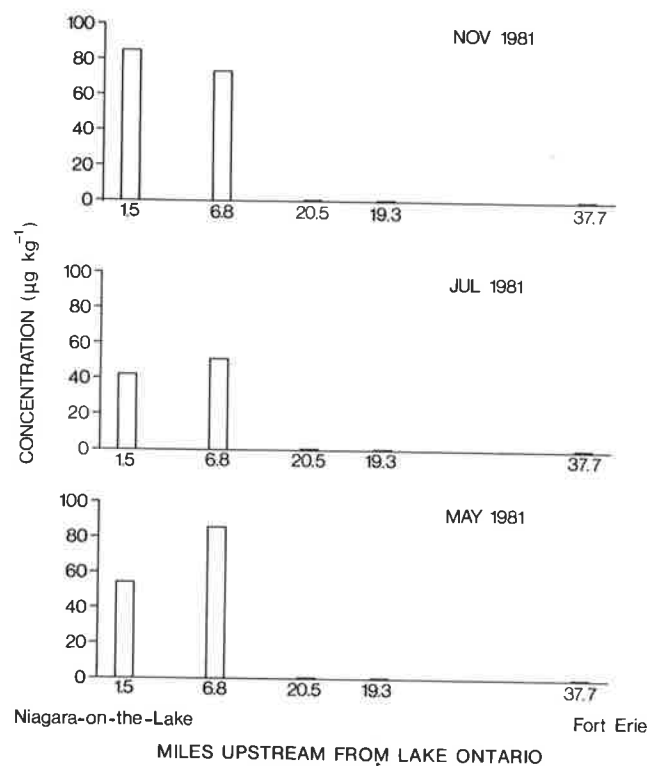


Figure 78. Distribution of tetrachlorobenzenes ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

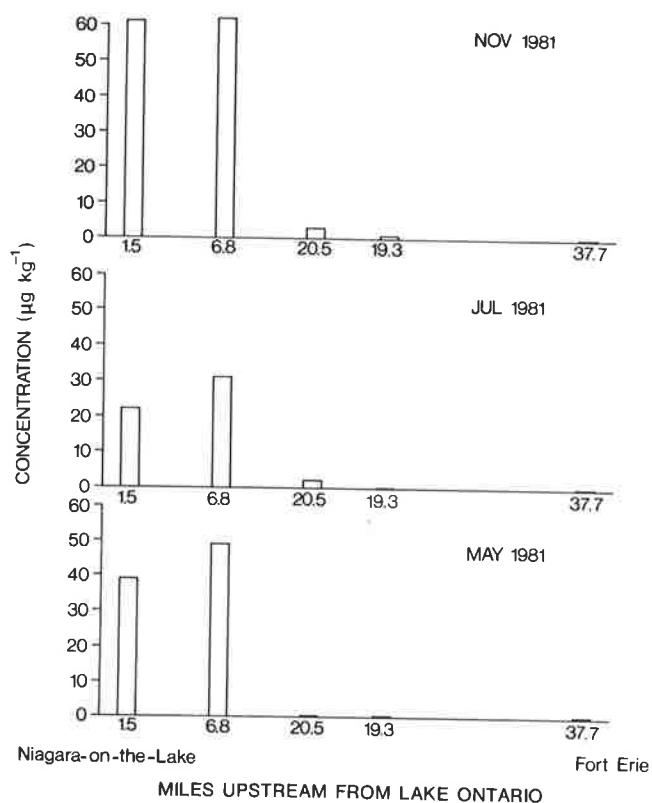


Figure 79. Distribution of pentachlorobenzenes ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

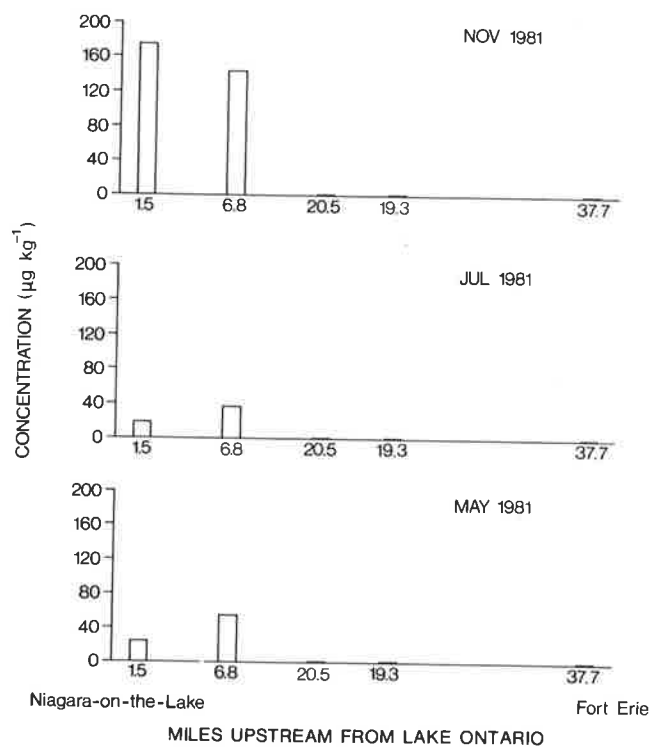


Figure 80. Distribution of hexachlorobenzenes ($\mu\text{g kg}^{-1}$) in suspended sediments of the Niagara River, 1981.

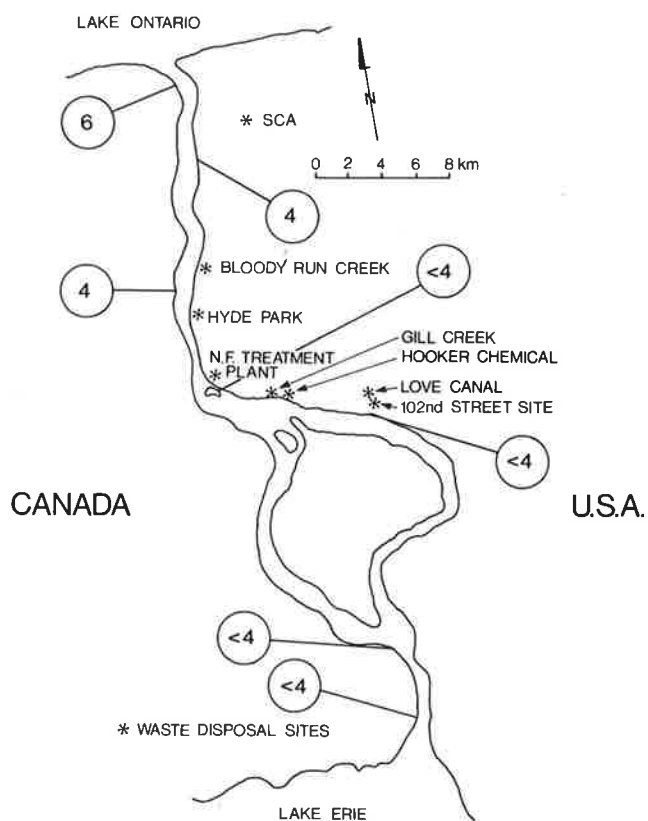


Figure 84. Mirex (ng g^{-1}) in spottail shiners in the Niagara River, September 1982.

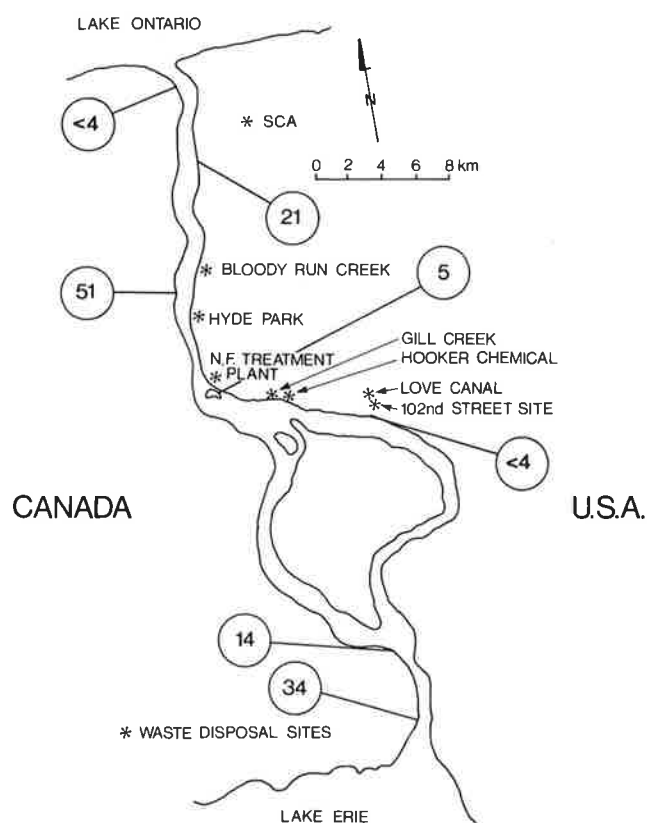


Figure 85. Total DDT (ng g^{-1}) in spottail shiners in the Niagara River, September 1982.

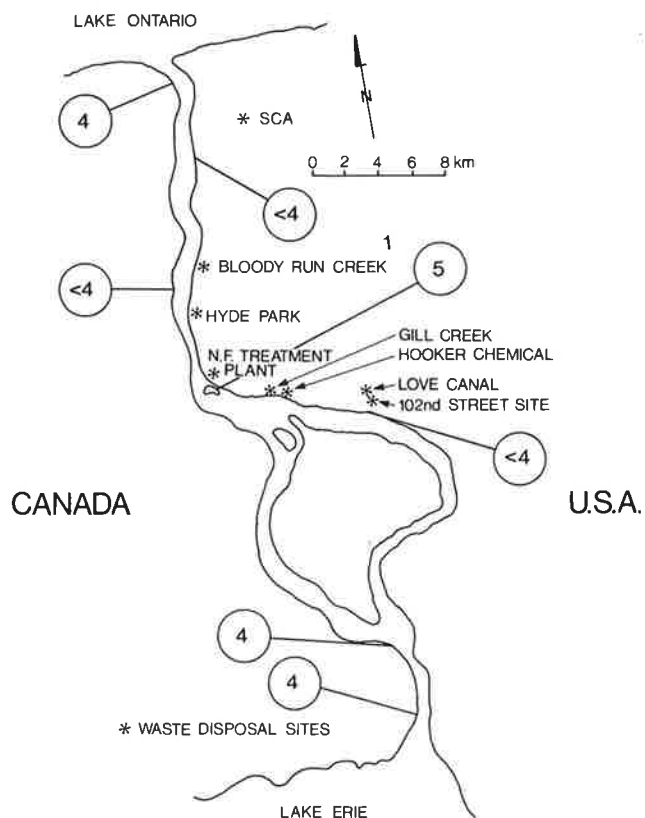


Figure 86. Dieldrin (ng g^{-1}) in spottail shiners in the Niagara River, September 1982.

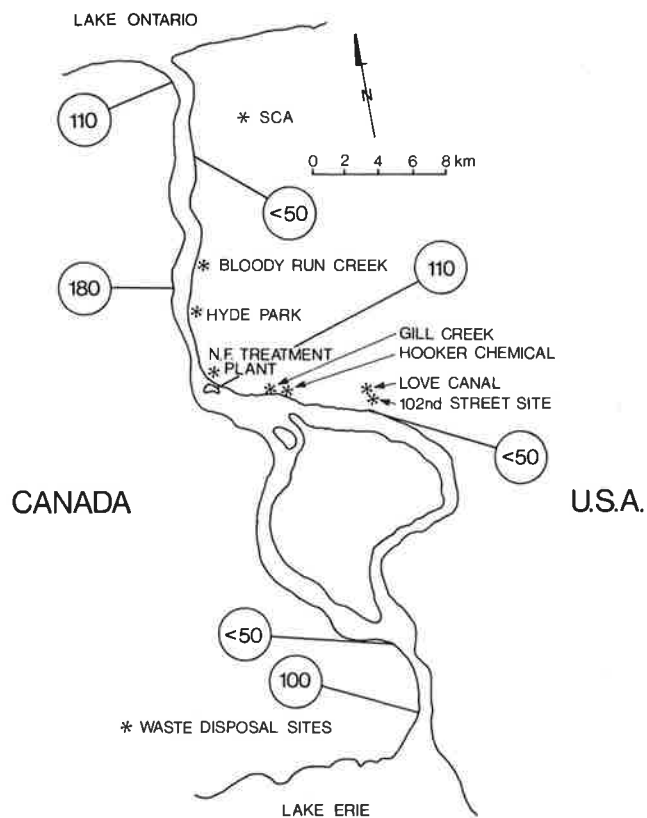


Figure 87. 1,4-Dichlorobenzene (ng g^{-1}) in spottail shiners in the Niagara River, September 1982.

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