

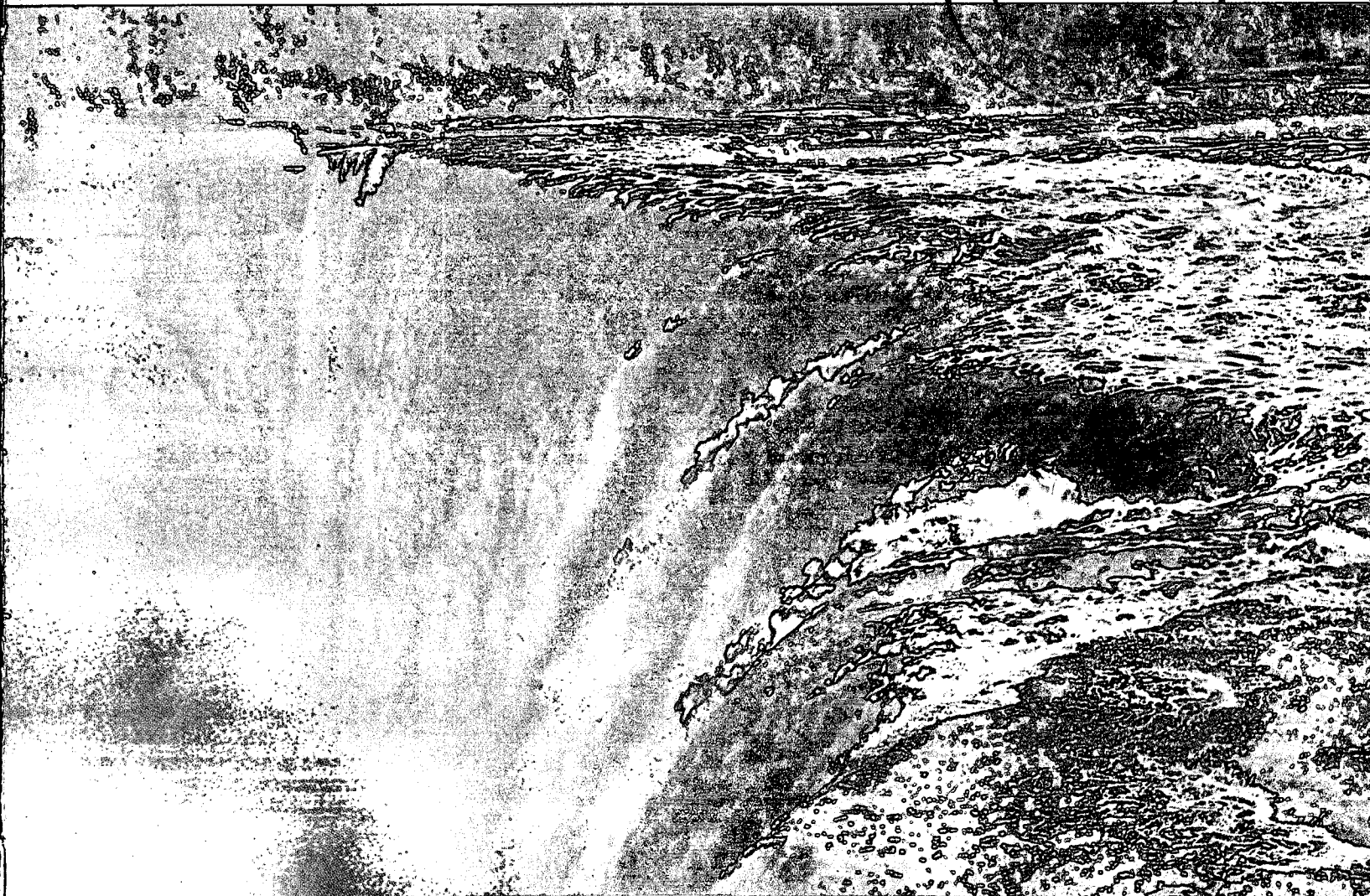
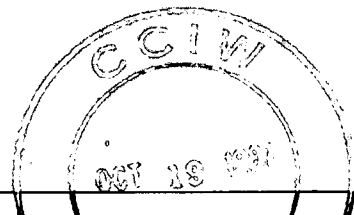


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Organochlorines and Polyaromatic Hydrocarbons in the St. Lawrence River at Wolfe Island, 1982/84

A. Sylvestre



TECHNICAL BULLETIN NO. 144

INLAND WATERS/LANDS DIRECTORATE
ONTARIO REGION
WATER QUALITY BRANCH
BURLINGTON, ONTARIO, 1987

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Abstract

Whole water and suspended sediment samples were collected monthly at Wolfe Island on the St. Lawrence River from April 1982 to December 1984. Samples were analyzed for organochlorines and polyaromatic hydrocarbons.

α - and γ -BHC and dieldrin were found in more than 40% of the whole water samples. α -BHC, dieldrin, PCBs, and tDDT occurred in more than 50% of the suspended sediment samples, and mirex, α -chlordane, and β -endosulfan were measured 20% to 35% of the time. Higher chlorinated chlorobenzenes such as hexa, penta, 1,2,3,4-tetra, and 1,2,4-tri were also detected in more than 50% of the suspended sediment samples. Rough estimates of the loading budget for PCBs, tDDT, and tBHC for Lake Ontario suggest that these compounds remain in the lake or are volatilized. Recommendations for future monitoring programs are discussed.

Résumé

D'avril 1982 à décembre 1984, on a prélevé mensuellement dans le Saint-Laurent, au niveau de l'île Wolfe, des échantillons d'eau non filtrée et de sédiments en suspension pour l'analyse des organochlorés et des hydrocarbures aromatiques polycycliques.

Dans plus de 40 % des échantillons d'eau non filtrée, on a décelé de l' α -BHC et du γ -BHC ainsi que de la dieldrine. L' α -BHC, la dieldrine, les BPC et le DDT total ont été trouvés dans plus de la moitié des échantillons de sédiments en suspension, tandis que le mirex, l' α -chlordane et le β -endosulfan ont été mesurés de 20 % à 35 % du temps. Les chlorobenzènes fortement chlorés tels que l'hexachlorobenzène, le pentachlorobenzène, le 1, 2, 3, 4-tétrachlorobenzène et le 1, 2, 4-trichlorobenzène ont été détectés dans plus de la moitié des échantillons de sédiments en suspension. Une estimation grossière du bilan des BPC, du DDT total et du BHC total dans le lac Ontario, porte à croire que ces composés demeurent en grande partie dans le lac ou se volatilisent.

Organochlorines and Polyaromatic Hydrocarbons in the St. Lawrence River at Wolfe Island, 1982/84

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INTRODUCTION

In the last decade, pollution problems in the Great Lakes basin have shifted in focus from excess nutrients to toxic contaminants. The intensive agricultural use of persistent pesticides between 1950 and 1970 and improper disposal methods for many other toxic substances are among the practices responsible for the current problem in the Great Lakes basin.

Scientific and public attention have been concentrated on the Niagara River and the western part of Lake Ontario. Until recently, however, toxic contaminant problems in the eastern end of the lake were rarely reported.

On three separate occasions in 1975, 1977, and 1981, the Water Quality Branch, Ontario Region (WQB/OR), reported the existence of organic contaminants in the international section of the St. Lawrence River. To better evaluate the extent of this contamination, the Water Quality Branch added organic sampling to its regular water quality monitoring program for the Wolfe Island permanent station located on the south channel of the St. Lawrence River.

The purpose of this report is to present and evaluate the results from the first three years of data collection at this site. A description of the station and sampling procedures is provided in the first part. The second part presents the occurrence and concentration of organochlorine pesticides, PCBs, chlorobenzenes, and polyaromatic hydrocarbons, and also estimates the loadings to the St. Lawrence River for the main contaminants. Finally, recommendations for further studies and the future direction of this program are presented.

METHODOLOGY

Sampling Station

The sampling station is located on Wolfe Island between Banford Point and the U.S. shore at latitude $44^{\circ}12'24''$ N by longitude $76^{\circ}14'18''$ W (Fig. 1).

Wolfe Island divides the St. Lawrence River into two channels. The south channel receives about 60% of the flow from Lake Ontario, and the north channel the remaining 40% (Casey and Salbach, 1974).

Banford Point, on the south channel, was chosen as the most suitable location for a permanent water quality monitoring station because there was little direct human influence in the channel there. Initial operation of the station began in October 1976, and only the main water quality parameters (pH, specific conductance, turbidity, nutrients, major ions, and trace metals) were monitored. In April 1982 sampling for organic compounds (organochlorine pesticides, PCBs, polyaromatic hydrocarbons, and chlorobenzenes) was added to the initial program.

Sampling Procedure

Suspended sediments were collected using an intake line, pump, and Westfalia separator. The intake line was a 3/4-inch polyethylene tube. It was located about 122 m from the shore at a depth of 14 m and was held 6 m off the bottom of the river. Over the sampling period, two different types of pumps were used. From April 1982 to June 1984, the sampling was done with a Moyno Model FA-11. After June 1984, a March 5C-MD submersible magnetic-drive pump was used. Water was pumped through the Westfalia centrifuge at an approximate rate of 6 L/min. In order to collect enough sediments for analysis, the centrifugation process was extended over a period of 24 hours.

Suspended sediments were removed from the centrifuge bowls in the laboratory by scraping them from the walls of the bowl chambers with a Teflon scraper. The resulting sediment-water slurry was pressure filtered through a 5- μ m Teflon filter. The filter was then air dried in a desiccator. After drying completely, the sediments were removed from the filter, homogenized with a mortar and pestle, and submitted to the National Water Quality Laboratory (NWQL) for analysis. Analytical methodology for the sediments is described in the *Analytical Methods Manual Update 1982* (Environment Canada, 1983).

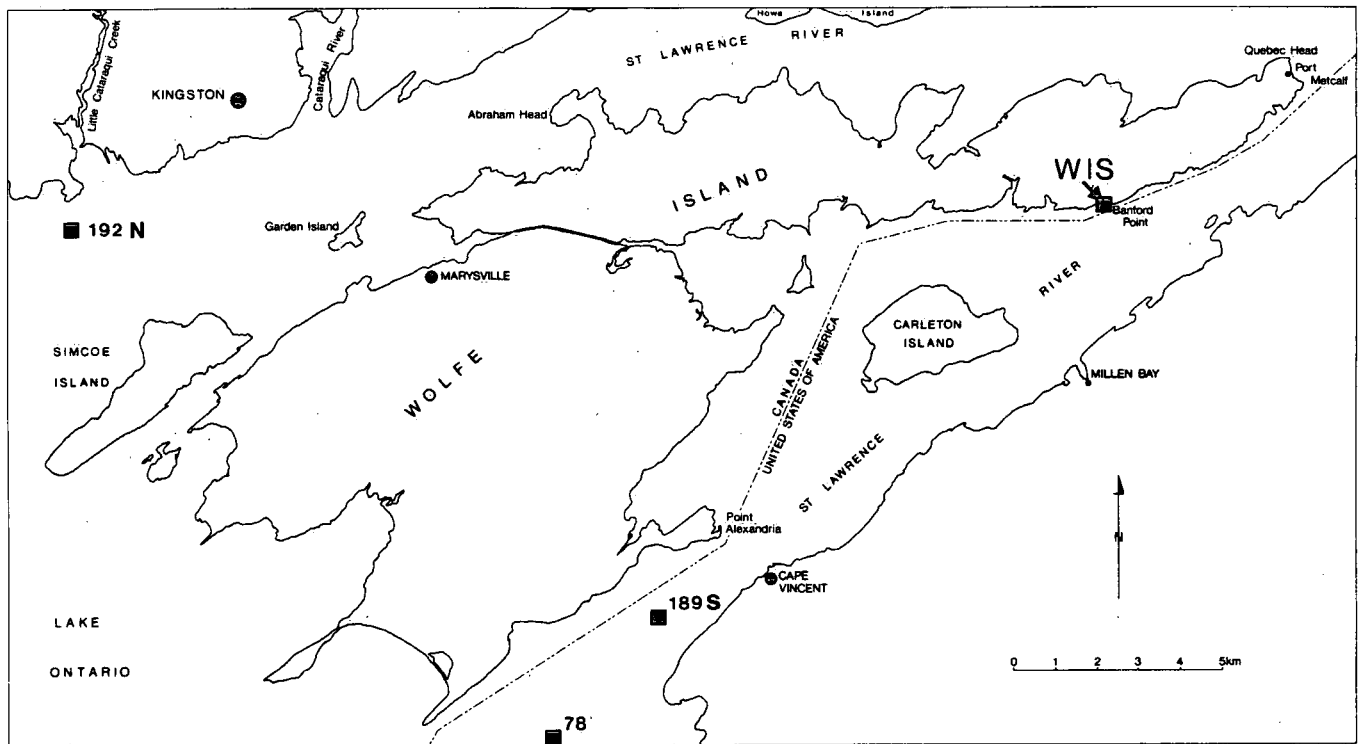


Figure 1. Sampling station locations. (WIS designates Wolfe Island station.)

This suspended sediment sampling program started in April 1982. Sampling frequency was once a month. Each time a suspended sediment sample was collected, a whole water sample was also taken in two 1-L, precleaned glass bottles (analytical methods from the *Analytical Methods Manual Update 1982* [Environment Canada, 1983]). Data in this report cover the period from April 1982 to December 1984.

RESULTS AND DISCUSSION

Organochlorine Pesticides and PCBs

The organochlorine pesticides (OCs) routinely measured in samples collected at Wolfe Island are listed in Table 1. Detection limits were as follows: 0.4 ng/L in water (9.0 ng/L for PCBs) and 4 ng/g in sediments (90 ng/g for PCBs). The OC results for water and suspended sediments will be examined separately.

In Whole Water

Three of the 18 organochlorine pesticides routinely measured in whole water samples were detected in more than 40% of the samples (Appendix A, Table A-1). They are α - and

γ -BHC and dieldrin. Their respective mean concentrations for the period 1982/84 were 5.8 ng/L, 1.0 ng/L, and 0.4 ng/L (Table 2). These concentrations were about half those found at the mouth of the Niagara River, where levels of 10.5 ng/L for α -BHC, 2.1 ng/L for γ -BHC, and 0.6 ng/L for dieldrin were reported for the period 1980/81 (Kuntz and Warry, 1983).

In addition to these compounds, PCBs, α - and γ -chlordane, p,p'-DDE, and heptachlor epoxide were found in more than 40% of the samples collected from the Niagara River at Niagara-on-the-Lake (NOTL) in 1980/81 (Kuntz and Warry, 1983). The volume of water collected was the same (2 L) in both cases, but the detection limit (0.1 ng/L) was lower for NOTL samples. It should be noted that α - and γ -chlordane, p,p'-DDE, and heptachlor epoxide present at NOTL were at concentrations below or near the detection limit of Wolfe Island samples. As the Niagara River is an important contributor of OCs to Lake Ontario (Warry and Chan, 1981; Oliver and Nicol, 1984), it is not surprising to find some of them present in low concentrations at Wolfe Island. In the lake, contaminants can be removed from the water column by volatilization, uptake by aquatic organisms, and settling of the particles on which the pesticides are adsorbed (Robinson, 1973).

The Niagara River, however, is not the only source of OCs to Lake Ontario. Atmospheric loading accounts for an appreciable input (Strachan and Huneault, 1979). Also, the Bay of Quinte (Frank *et al.*, 1980; Fox and Joshi, 1984) and the Oswego (Holdrinet *et al.*, 1978; Scudato and DelPrete, 1982) and the Black rivers (Collin, 1980) are possible sources, not to mention many other minor point and

Table 1. Organochlorines and Polyaromatic Hydrocarbons Measured at Wolfe Island Station, 1982/84

Whole water and suspended sediments	
Organochlorine pesticides	
p,p'-DDT	
o,p'-DDT	
p,p'-DDE	
p,p'-DDE	
p,p'-Methoxychlor	
Heptachlor	
Heptachlor epoxide	
α-Endosulfan	
β-Endosulfan	
α-Chlordane	
γ-Chlordane	
α-BHC	
γ-BHC	
Mirex	
Aldrin	
Endrin	
HEOD (dieldrin)	
PCBs	
Araclor total	
Suspended sediments	
Polyaromatic hydrocarbons	
Pyrene	
Fluorene	
Indene	
1,2,3,4-Tetrahydronaphthalene	
1-Methylnaphthalene	
2-Methylnaphthalene	
β-Chloronaphthalene	
Acenaphthalene	
Quinoline	
Acenaphthene	
Phenanthrene	
Fluoranthene	
Chlorobenzenes	
1,3-Dichlorobenzene	
1,2-Dichlorobenzene	
1,4-Dichlorobenzene	
1,3,5-Trichlorobenzene	
1,2,3-Trichlorobenzene	
1,2,4-Trichlorobenzene	
1,2,3,4-Tetrachlorobenzene	
Pentachlorobenzene	
Hexachlorobenzene*	

* Also analyzed in whole water sample.

Table 2. Organochlorine Pesticide and PCB Concentrations (occurrence >40%) at Wolfe Island, 1982/84

Parameters	N	Occurrence		St. dev.	Range
		(%)	Mean		
Whole water (ng/L)					
α-BHC	32	94	5.8	3.3	DL - 13.8
γ-BHC	32	88	1.0	0.6	DL - 2.5
Dieldrin	32	41	0.4	0.3	DL - 1.6
Suspended sediments (ng/g)					
PCBs	30	93	162	78	DL - 360
tDDT	30	90	18	13	DL - 58
Dieldrin	30	83	9	7	DL - 29
α-BHC	30	53	5	5	DL - 29

Note: Values equal to detection limit are included in calculation as half detection limit.

non-point sources. All these possible inputs and the recent success of large volume sampling methods (McCrea *et al.*, 1985; Biberhofer and Stevens, 1985) lead one to suspect that more OCs are present in the south channel of the St. Lawrence River than were detected by this study.

To illustrate the validity of this assumption, the results from a large volume water sample (36 L) collected off the shore of Wolfe Island at station No. 78 of the surveillance program (Fig. 1) are presented along with the levels measured at Wolfe Island during October 1983 (Table 3). PCBs, tDDT, methoxychlor, endrin, α- and γ-chlordane, and heptachlor epoxide were found using the large volume sampler at concentrations below the detection limit permitted by the analytical method used for Wolfe Island samples.

Table 3. Comparison of Organochlorine Concentrations (ng/L) Found at Station No. 78 of the Surveillance Program and at Wolfe Island in October 1983

Parameter	No. 78	Wolfe Island
α-BHC	4.83	4.9
γ-BHC	1.16	0.5
Heptachlor epoxide	0.333	<DL
α-Chlordane	0.010	<DL
γ-Chlordane	0.026	<DL
Dieldrin	0.538	<DL
Endrin	0.093	<DL
Mirex	<DL	<DL
Methoxychlor	0.052	<DL
tDDT	0.175	<DL
PCBs	0.430	<DL

Note 1: Source of station No. 78 data: Biberhofer and Stevens, 1985.

Note 2: Detection limit for Wolfe Island data: 9.0 ng/L for PCBs and 0.4 ng/L for OCs.

The presence of BHC compounds at the Wolfe Island station can be explained by their extensive use as fungicides and seed dressing (Martin and Worthing, 1974). The presence of BHC compounds in the whole water samples is attributed to both their higher solubility (α -BHC, 1.21 to 2.03 mg/L; γ -BHC, 7.52 mg/L at 25°C) (United States Environmental Protection Agency, 1979) and their continued use. The Niagara River (Kuntz and Warry, 1983) and atmospheric inputs (Strachan and Huneault, 1979) constitute the main sources to Lake Ontario. α -BHC was found in higher concentrations (5.8 ng/L) than γ -BHC (1.0 ng/L). This is likely due to photochemical conversion, which can, under certain environmental conditions, transform commercial lindane products (>90% γ -BHC) (United States Environmental Protection Agency, 1979) to α -BHC (Malaiyandi *et al.*, 1982; United States Environmental Protection Agency, 1979). γ -BHC can also be isomerized to α -, β -, and δ -BHC by biological processes (Benezet and Matsumura, 1973; United States Environmental Protection Agency, 1979).

The insecticides aldrin, dieldrin, and DDT were used extensively in Ontario from 1950 to 1969, the year they were banned (Harris and Miles, 1975). Biotransformation of aldrin into dieldrin (United States Environmental Protection Agency, 1979) and the high persistence of the latter account for the occurrence of dieldrin in water samples 15 years after the ban. Dieldrin is ubiquitous in the Lake Ontario basin (Harris and Miles, 1975). The levels measured at Wolfe Island range from non-detectable to 1.6 ng/L. The mean concentration of this compound is close to the detection limit, as 60% of the results were reported as less than 0.4 ng/L, and the value measured in Lake Ontario off the shore of Wolfe Island in October 1983 was 0.583 ng/L (Biberhofer and Stevens, 1985).

DDT was found very rarely in Wolfe Island whole water samples. Intensive use of this pesticide was associated with tobacco production areas located mainly in the Lake Erie basin (Frank *et al.*, 1974). The infrequent occurrence of DDT may be due to insufficiently sensitive analytical methods as Biberhofer and Stevens reported a concentration of 0.175 ng/L at station No. 78 (Fig.1) in 1985.

No clear seasonal variation was observed in any of the parameters measured.

With only three years of data, large fluctuations in standard deviations, and many values below the detection limit, it was difficult to establish trends for these parameters.

Five of the α -BHC values exceeded the IJC objective of 10 ng/L (International Joint Commission, 1978). The objectives for aldrin, dieldrin, and PCBs are one order of

magnitude lower (1.0 ng/L) (International Joint Commission, 1978). Dieldrin concentrations were above this value on three occasions. The only result for aldrin and the two for PCBs are not in compliance with the objective. The origin of these elevated concentrations is not clear.

In Suspended Sediments

In suspended sediments the situation is slightly different (Appendix A, Tables A-2 and A-3). As in the water samples, α -BHC and dieldrin were detected in more than 40% of the samples, but γ -BHC concentrations were below the detection limit of 4.0 ng/g. The levels of α -BHC (6 ng/g) were only half as high as those reported at NOTL for the period 1979/81 (Kuntz and Warry, 1983), while dieldrin concentrations (9 ng/g) were more than two times higher.

PCBs were found in 93% of the samples. A mean of 162 ng/g was measured (1982/84). The mean was around four times lower than at NOTL (1979/81), but quite close to the values found near Cape Vincent in 1981 (200 ng/g) and upstream near Kingston (190 ng/g) (Merriman, 1985; Table 4). PCBs were introduced in Canada in 1929 and used in electrical equipment and other products. Since 1977 they have been restricted to electrical equipment only (Durham and Oliver, 1983). They are widely distributed in the Lake Ontario basin. Mean bottom sediment levels of 57 ng/g were reported by Frank *et al.* (1979) for Lake Ontario. The Niagara River (Kuntz and Warry, 1983; Fox

Table 4. Organochlorine Pesticide and PCB Concentrations (ng/g) Found at Stations 189S and 192N in June 1981

Parameters	Bottom sediments		Suspended sediments	
	189S	192N	189S	192N
α -BHC	<	<	2	<
γ -BHC	<	<	<	<
Heptachlor	<	<	<	<
Aldrin	<	<	<	<
Heptachlor epoxide	<	<	<	<
γ -Chlordane	<	<	3	7
α -Chlordane	<	<	5	<
α -Endosulfan	<	<	<	<
p,p'-DDE	3	45	16	14
Dieldrin	<	<	14	4
Endrin	<	<	<	<
o,p'-DDT	<	<	<	<
p,p'-TDE	<	11	<	20
p,p'-DDT	<	<	9	<
β -Endosulfan	<	<	<	<
Mirex	<	9	6	6
p,p'-Methoxychlor	<	<	<	<
PCBs	10	310	200	190

< = Below detection limit.

Source: Merriman, 1985.

et al., 1983; Durham and Oliver, 1983) and the Bay of Quinte (Frank *et al.*, 1979) are important sources. Inputs via wet and dry precipitation are also considered important (Eisenreich *et al.*, 1981).

DDT was also found in suspended sediment samples from Wolfe Island. It was not surprising to find this compound and its metabolites associated only with particulate matter because of its low solubility (0.0012 ppm) (United States Environmental Protection Agency, 1980). Total DDT (tDDT) was found in 90% of the samples at a mean concentration of 18 ng/g. The oxidized form, p,p'-DDE, was the more common form (87%), although the reduced form, p,p'-DDE, was also found (43%). The presence of p,p'-DDT was detected in three samples. A concentration of 9 ng/g was also measured in samples collected near Cape Vincent (station 189S) in 1981 (Merriman, 1985). Since p,p'-DDT is the predominant form found in technical DDT (around 77%) (United States Environmental Protection Agency, 1980), it is possible that there may be a source near the south channel. Because of the stability of the compound, however, it is more likely that the source is old sediment deposits.

In contrast to the whole water sample data, where few compounds were detected less than 40% of the time, α -chlordane (33%), mirex (33%), and β -endosulfan (20%) were found in suspended sediments (Appendix A, Table A-3).

Chlordane is a soil insecticide that was introduced to Canada in 1940 (Harris and Miles, 1975). Its use increased markedly in 1970 when aldrin, dieldrin, and heptachlor were banned (Frank *et al.*, 1979). Since 1977, use of this product has also been prohibited. α -Chlordane concentrations range from detection limit to 27 ng/g (Appendix A, Table A-3), but most values remained close to the detection limit. In 1981, at station 189S (Fig. 1), values of 3 ng/g for γ -chlordane and 5 ng/g for α -chlordane were detected in suspended sediments (Merriman, 1985).

Mirex was first reported in Lake Ontario fish samples collected from the Bay of Quinte in 1973 (Kaiser, 1974). Subsequently, a sediment study conducted by Holdrinet *et al.* (1978) identified two sources of the chemical to Lake Ontario: the Niagara and Oswego rivers. They also determined that a discharge to the Oswego River occurred at the beginning of the sixties. The substance probably began entering the Niagara River around the same period, the late fifties or early sixties (Pickett and Dossett, 1979). Mirex is still being released by both rivers. Concentrations of 12 ng/g were reported for the period 1979/81 at NOTL by Kuntz and Warry (1983). In their 1979 study, Scudato and DelPrete (1982) concluded that the Oswego River is

still a source of mirex and will be for many years. In 1981 it was found that this insecticide is also widespread in suspended sediments of the international section of the St. Lawrence River at concentrations from 2 to 6 ng/g (Merriman, 1985). The highest concentrations were found upstream from Kingston and near Cape Vincent (stations 192N and 189S, respectively [Fig. 1]). A bottom sediment survey conducted along the international section of the St. Lawrence River in 1975 did not find mirex in any of the samples (detection limit = 1.0 ng/g) (Kuntz, 1985). The following year, Holdrinet *et al.* (1978) found no mirex residues in a series of suspended sediment samples taken from the St. Lawrence River between Lake Ontario and Quebec City (detection limit = 1.0 ng/g).

Biological samples, however, give different information. After the discovery of the product in fish from the Bay of Quinte (Kaiser, 1974), mirex was also found in adult herring gulls (*Larus argentatus*) at Pigeon Island in 1975 (Mineau *et al.*, 1984) and by the New York State Department of Environmental Conservation in several different fish species collected between Carleton Island and Massena in 1976 (Mirex Task Force, 1977). Karl Suns, of the Ontario Ministry of Environment, also reported mirex in spottail shiners (*Notropis hudsonius*) at Cornwall from 1979 to 1983 (Suns *et al.*, 1985). Since the main current in the Kingston basin of Lake Ontario, the nearest source to the St. Lawrence River, is a counterclockwise gyre (Pickett and Bermick, 1977; Simons, 1975), it may have prevented detectable levels of mirex from reaching the St. Lawrence River until the late seventies. Food chain concentration and mobility may explain the earlier presence of mirex and the more extended distribution in biological organisms than in sediments.

α - and β -Endosulfan were detected in 12% and 20% of the samples respectively. Results from a 1977 sediment survey led Frank *et al.* (1979) to suspect a spill of endosulfan in the Niagara basin of Lake Ontario. This spill, plus use of this compound by tobacco growers until 1977, could explain its presence in Lake Ontario. However, no endosulfan was found in either bottom or suspended sediments at stations 189S or 192N (Table 4) in 1981 (Merriman, 1985).

Chlorobenzenes

The presence of chlorobenzenes (CBs) in Lake Ontario has been reported by many authors: Oliver and Nicol, 1982; Fox *et al.*, 1983; and Biberhofer and Stevens, 1985. Most of these studies were undertaken at or near the mouth of the Niagara River because sources in that area were well known. Each isomer of chlorobenzene (same as in Table 1 plus 1,2,4,5-tetra) occurred in more than 70% of the suspended sediment samples collected weekly at NOTL in 1980

(Kuntz, 1984). Atmospheric inputs of CBs are restricted to hexachlorobenzene (HCB) (Strachan and Edwards, 1984). According to Oliver and Nicol (1982), the distribution pattern for the different CB compounds in the bottom sediments suggests a source of these compounds at the eastern end of Lake Ontario. The results from Wolfe Island samples also show distributions and concentrations that are different from those of the Niagara River. Four of the nine CBs regularly analyzed were detected in more than 40% of the samples. These were mainly highly chlorinated CBs (Table 5). The manufactured isomers (lower chlorinated) were virtually absent, except for 1,2-di, which was found in 40% of the samples (Appendix A, Table A-4). The mean concentration over the period 1982/84 of 1,2-di (137 ng/g) almost reached the level reported at NOTL in 1980 (148 ng/g, N = 28) (Kuntz and Warry, 1983). It should be noted, however, that with the exception of the period July 1983 to May 1984, all analyses for 1,2-di were below detection limits. Therefore it does not appear likely that these high values are real. Solvent interference in the analysis is suspected to be the cause of these anomalies. The isomer that has the widest usage, i.e., 1,4-di, was not detected in any of the samples. The higher chlorinated CB concentrations were lower than those at NOTL. The mean values of these CBs at Wolfe Island for the period 1982/84 were 32 ng/g for 1,2,4-tri, 14 ng/g for 1,2,3,4-tetra, 11 ng/g for penta, and 13 ng/g for hexa compared to 61 ng/g, 71 ng/g, 58 ng/g, and 94 ng/g respectively at NOTL in 1980 (Kuntz and Warry, 1983).

Table 5. Chlorobenzene Concentrations (ng/g, occurrence >50%) in Suspended Sediments at Wolfe Island, 1982/84

Parameters	N	Occurrence (%)	Mean	St. dev.	Range
1,2,4-Tri	28	54	32	44	DL - 131
1,2,3,4-Tetra	28	64	14	20	DL - 95
Penta	28	57	11	13	DL - 56
Hexa	28	89	13	11	DL - 54

Note: Values below detection limit are included in calculation as half detection limit.

The presence of the higher chlorinated benzenes can be explained by the fact that they have a greater tendency to become associated with suspended sediments, while the lower chlorinated benzenes are more soluble and volatile (Oliver, 1984). According to Oliver (1984), "the bulk of CBs entering Lake Ontario from the Niagara River are lost from the lake by volatilization."

The available information is too fragmentary to establish a real trend. However, the three highly chlorinated CBs showed lower concentrations in 1984 (Appendix A, Table A-4) than in the two previous years.

Hexachlorobenzene was the only CB analyzed in whole water samples. Concentrations remained below detection limits (0.4 ng/L) except for two occasions when values slightly above the detection limit were reported.

Polyaromatic Hydrocarbons

The polyaromatic hydrocarbons (PAHs) analyzed in suspended sediment samples collected at Wolfe Island are listed in Table 1. The majority were not detected at a detection limit of 50 ng/g. The exceptions were fluoranthene, β -chloronaphthalene, and acenaphthalene, which were detected on several occasions. These values could be the result of interference in the analyses.

Loading Estimates

To estimate the quantity of organics leaving Lake Ontario, it is necessary to calculate the loading. Since the information needed for these calculations is fragmentary in both time and space, the following assumptions were made:

- (1) The south channel is homogeneous in regard to the parameters for which loading is estimated.
- (2) The north channel has concentrations similar to the south channel.
- (3) The yearly mean values for each parameter calculated from 6 to 12 monthly values are representative of the whole year.

Loadings of suspended sediments were obtained from the product of the yearly mean parameter concentration (mg/kg), the yearly mean discharge (cfs), the yearly mean sediment concentration, and a transformation coefficient (8.937×10^{-4}) to obtain the loading in kilograms per year. A similar procedure was followed for the calculation of water loading: yearly mean parameter concentration ($\mu\text{g/L}$) was multiplied by the yearly mean flow (cfs) and the transformation coefficient (8.937×10^{-1}). The calculations were performed on parameters detected in more than 40% of the samples collected between 1982 and 1984. Values below detection limit were included as half the detection limit.

Discharge data were obtained from Cornwall. A lag time of nine days was used to approximate the travel time from Wolfe Island. Discharge data were not adjusted for the contribution (1%) (Casey and Salbach, 1974) from the tributaries that flow into the St. Lawrence River between Wolfe Island and Cornwall.

Loading estimates for the water fraction are more similar to those of NOTL in 1980/81 (Kuntz and Warry, 1983) than to those for suspended sediments (Table 6). The reason for this difference is due not only to lower organic concentrations in sediments but also to lower concentrations of suspended sediments (1982/84 mean of 1.4 mg/L at Wolfe Island compared to a mean of 8.9 mg/L at NOTL for 1979/82) (Kuntz, 1984).

Table 6. Organochlorine Pesticide, PCB, and Chlorobenzene Loading Estimates (occurrences >40%) from Lake Ontario to the St. Lawrence River, 1982/84

Parameters	1982	1983	1984	Mean
By whole water (kg/a)				
α -BHC	1410	1674	1129	1404
γ -BHC	356	165	220	247
Dieldrin	75	60	172	102
By suspended sediments (kg/a)				
PCBs	83	48	38	56
tDDT	14	3	4	7
Dieldrin	3	2	3	3
α -BHC	3	1	1	2
1,2,3-Tri	2	12	10	8
1,2,3,4-Tetra	9	6	1	5
Penta	7	5	1	4
Hexa	9	4	2	5

Note: Values reported as below detection limit were included in calculation as half detection limit.

Estimates of the chlorinated pesticide and PCB loading to Lake Ontario were reported by Strachan and Edwards (1984). These estimates for tDDT, PCBs, dieldrin, and tBHC, together with output estimates to the St. Lawrence River determined by this study, are presented in Table 7. Various inputs, such as municipal and industrial wastewater

discharge and runoff from non-point sources, together with various outputs through uptake by emigrating aquatic organisms and volatilization, must be taken into account when calculating a budget for these substances in Lake Ontario. Unfortunately, all the data necessary to estimate these processes are not available. Nevertheless, a simple comparison of the data presented in Table 7 shows a difference of 82% for tDDT, 98% for PCBs, 58% for dieldrin, and 76% for tBHC between combined inputs from the Niagara River and precipitation and outputs to the St. Lawrence. Assuming a state of equilibrium for each compound and negligible losses via emigrating biota, Table 7 data suggest that most of tDDT, PCBs and tBHC remain in Lake Ontario or are volatilized.

CONCLUSIONS

Three organochlorine pesticides (α - and γ -BHC and dieldrin) were detected in more than 40% of the whole water samples collected at Wolfe Island between 1982 and 1984. The presence of other compounds, however, is suspected as sampling techniques using larger volumes of water have detected more organochlorine compounds in nearby Lake Ontario.

In suspended sediments, PCBs, tDDT, dieldrin, and α -BHC occurred in more than 50% of the samples. The concentrations were much lower, however, than those reported for the Niagara River at NOTL. Generally, the concentrations of these contaminants corresponded well to the results from a WQB/OR survey of the same area completed in 1981. Mirex and α -chlordane were detected in 33% of the samples and β -endosulfan in 20%.

Higher chlorinated CBs were found at Wolfe Island more often than lower chlorinated CBs. The distribution pattern for CBs appears to be very different from what was observed at NOTL.

Table 7. Loading Estimates of Organic Input to Lake Ontario from Literature, and Output from Wolfe Island, 1982/84

Parameters	Input estimates from Niagara River and precipitation (kg/a)				Total	Whole water† output estimates to St. Lawrence River (kg/a)	Difference (%)
	Water*	Suspended sediments*	Air*				
tDDT	60	60	150	270	50‡	82	
PCBs	1000	1000	2300	4300	100§	98	
Dieldrin	100	10	130	240	100	58	
tBHC	2300	9	4500	6809	1650	76	

* Data from Strachan and Edwards, 1984.

† Whole water = dissolved and suspended sediment fraction.

‡ Estimated value = half detection limit.

§ Estimated value = 0.4 ng/L.

Loading estimates suggest that most of the PCBs, tDDTs and tBHCs entering Lake Ontario remain in the lake or are volatilized.

RECOMMENDATIONS

- (1) The collection of samples for organic analyses at Wolfe Island should be continued so that the trends may be followed and the loadings estimated.
- (2) Collection of larger volumes of samples and preservation with dichloromethane or on-site extraction with a counter-current extractor (Goulden and Anthony, 1985) should be implemented in order to improve detection limits of most organic compounds.
- (3) A series of surveys on the north and south channels of the St. Lawrence River should be undertaken to evaluate similarity and also to determine the representativeness of the Wolfe Island station.
- (4) The main current pattern in the Kingston basin should be identified in cooperation with the National Water Research Institute (NWRI) to evaluate the potential influence of the Bay of Quinte and the Black River on the Wolfe Island station and the St. Lawrence River.
- (5) A study of organic contamination on the international section of the St. Lawrence River should be planned and executed in 1987 to determine the trend of the main pollutants and for comparison with the 1975, 1977, and 1981 study data.
- (6) Future analyses should include other organic compounds, such as pentachlorophenol (PCP), which has been reported in the Bay of Quinte (Fox and Joshi, 1984).
- (7) A statistical method to produce better estimates of loading should be developed.
- (8) The accuracy of the sampling frequency currently employed should be evaluated statistically.

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REFERENCES

- Benezet, H.J., and F. Matsumura. 1973. Isomerization of γ -BHC to α -BHC in the environment. *Nature*, 243:480-81.
- Biberhofer, J., and R.J.J. Stevens. 1985. Organochlorine contamination in ambient waters of Lake Ontario. Water Quality Branch, Ontario Region, Inland Waters Directorate, Environment Canada, Burlington, Ont. Draft rep.
- Casey, D.J., and S.E. Salbach. 1974. IFYGL stream materials balance study. In Proc. 17th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res., pp. 668-81.
- Collin, R.L. 1980. Inplace toxics in the waters of New York. In Proc. Conf. Toxic and Hazardous Chemicals, Central New York Water Quality Management Program, pp. 75-85.
- Connell, D.W., and G.J. Miller. 1984. *Chemistry and Ecotoxicology of Pollution*. New York: John Wiley and Sons, pp. 162-227.
- Durham, R.W., and B.G. Oliver. 1983. History of Lake Ontario contamination from the Niagara River by sediment radiodating and chlorinated hydrocarbon analysis. *J. Great Lakes Res.*, 9(2):160-68.
- Eisenreich, S.J., B.B. Looney, and J.D. Thornton. 1981. Airborne organic contaminants in the Great Lakes ecosystem. *Environ. Sci. Technol.*, 51:30-38. (Cited in Strachan and Edwards, 1984.)
- Environment Canada. 1983. *Analytical Methods Manual Update 1982*. Water Quality Branch, Inland Waters Directorate, Ottawa, Ont.
- Fox, M.E., J.H. Cary, and B.G. Oliver. 1983. Compartmental distribution of organochlorine contaminants in the Niagara River and the western basin of Lake Ontario. *J. Great Lakes Res.* 9(2): 287-94.
- Fox, M.E., and S.R. Joshi. 1984. The fate of pentachlorophenol in the Bay of Quinte, Lake Ontario. *J. Great Lakes Res.*, 10(2):190-96.
- Frank, R., A.E. Armstrong, R.G. Boelens, H.E. Braun, and C.W. Douglas. 1974. Organochlorine insecticide residues in sediment and fish tissues, Ontario, Canada. *Pestic. Monit. J.*, 7:165-80.
- Frank, R., R.L. Thomas, M. Holdrinet, A.L.W. Kemp, and H.E. Braun. 1979. Organochlorine insecticides and PCB in surficial sediments (1968) and sediment cores (1976) from Lake Ontario. *J. Great Lakes Res.*, 5(1):18-27.
- Frank, R., R.L. Thomas, M.V.H. Holdrinet, and V. Damiani. 1980. Note PCB residues in bottom sediments collected from the Bay of Quinte, Lake Ontario 1972-73. *J. Great Lakes Res.*, 6(4): 371-76.
- Goulden, P.D., and D.H.J. Anthony. 1985. Design of a large sample extractor for the determination of organics in water. NWRI Contribution Number 85-121. National Water Research Institute, Burlington, Ont.
- Harris, C.R., and J.R.W. Miles. 1975. Pesticide residues in the Great Lakes region of Canada. *Residue Rev.*, 57:27-79.
- Holdrinet, M. Van Hove, R. Frank, R.L. Thomas, and J.L. Helging. 1978. Mirex in the sediments of Lake Ontario. *J. Great Lakes Res.*, 4(1): 69-74.
- International Joint Commission. 1978. Great Lakes Water Quality Agreement of 1978. International Joint Commission, Canada and the United States.
- Kaiser, K.L.E. 1974. Mirex, an unrecognized contaminant of fishes from Lake Ontario. *Science*, 185:523-25.
- Kuntz, K.W. 1984. Toxic contaminants in the Niagara River, 1975-1982. Tech. Bull. No. 134, Water Quality Branch, Ontario Region, Inland Waters Directorate, Environment Canada, Burlington, Ont.

- Kuntz, K.W. 1985. Contaminants in bottom sediments of the St. Lawrence River in June 1975. Water Quality Branch, Ontario Region, Inland Waters Directorate, Environment Canada, Burlington, Ont. Int. rep.
- Kuntz, K.W., and N.D. Warry. 1983. Chlorinated organic contaminants in water and suspended sediments of the lower Niagara River. *J. Great Lakes Res.*, 9(2):241-48.
- Malaiyandi, M., K. Muzika, and F.M. Benoit. 1982. Isomerization of γ -hexachlorocyclohexane to its α -isomer by ultra-violet light irradiation. *J. Environ. Sci. Health*, A17:299-311. (Cited in Strachan and Edwards, 1984.)
- Martin, J., and C.R. Worthing, eds. 1974. *Pesticides Manual*, 4th ed. British Crop Protection Council. Lavenham, U.K.: Lavenham Press Ltd. (Cited in Strachan and Edwards, 1984.)
- McCrea, R.C., J.D. Fisher, and K.W. Kuntz. 1985. Distribution of organochlorine pesticides and PCBs between aqueous and suspended sediment phases in the lower Great Lakes region. *Water Pollut. Res. J. Can.*, 20(1):67-77.
- Merriman, J. 1985. Organic contaminants in bottom and suspended sediments of the international section of the St. Lawrence River. Water Quality Branch, Ontario Region, Inland Waters Directorate, Environment Canada, Burlington, Ont. Unpub. rep.
- Mineau, P., G.A. Fox, R.J. Norstrom, D.V. Weseloh, D.J. Hallett, and J.A. Ellenton. 1984. Using the herring gull to monitor levels and effects of organochlorine contamination in the Canadian Great Lakes. In *Toxic Contaminants in the Great Lakes*, ed. J.O. Nriagu and M.S. Simmons, pp. 426-52. New York: John Wiley and Sons.
- Mirex Task Force. 1977. Mirex in Canada, a Report of the Task Force on Mirex, April 1, 1977, to the Environmental Contaminants Committee of Fisheries and Environment Canada and Health and Welfare Canada. Tech. rep. 77-1. Fisheries and Environment Canada and Health and Welfare Canada, Ottawa, Ont.
- Oliver, B.G. 1984. Distribution and pathways of some chlorinated benzenes in the Niagara River and Lake Ontario. *Water Pollut. Res. J. Can.*, 19(1):47-57.
- Oliver B.G., and K.D. Nicol. 1982. Chlorobenzenes in sediments, water and selected fish from Lakes Superior, Huron, Erie and Ontario. *Environ. Sci. Technol.*, 16(8):532-36.
- Oliver, B.G., and K.D. Nicol. 1984. Chlorinated contaminants in the Niagara River 1981-1983. *Sci. Total Environ.*, 39:57-70.
- Pickett, R.L., and S. Bermick. 1977. Observed resultant circulation of Lake Ontario. *Limnol. Oceanogr.*, 22:1071-76.
- Pickett, R.L., and D.A. Dossett. 1979. Mirex and the circulation of Lake Ontario. *J. Phys. Oceanogr.*, 9(5):441-45.
- Robinson, J. 1973. Dynamics of pesticide residues in the environment. In *Environmental Pollution by Pesticides*, ed. C.A. Edwards, p. 459. London: Plenum Press. (Cited in Connell and Miller, 1984.)
- Scudato, R.J., and A. DelPrete. 1982. Lake Ontario sediment-mirex relationships. *J. Great Lakes Res.*, 8(4):695-99.
- Simons, T.J. 1975. Verification of numerical models of Lake Ontario. II. Stratified circulations and temperature changes. *J. Phys. Oceanogr.*, 5:98-110.
- Strachan, W.M.J., and H. Huneault. 1979. Polychlorinated biphenyls and organochlorine pesticides in Great Lakes precipitation. *J. Great Lakes Res.*, 5(1):61-68.
- Strachan, W.M.J., and C.J. Edwards. 1984. Organic Pollutants in Lake Ontario. In *Off-prints from Contaminants in the Great Lakes*, ed. J.O. Nriagu and M.S. Simmons, pp. 239-64. New York: John Wiley and Sons.
- Suns, K., G.E. Crawford, D.D. Russel, and R.E. Clement. 1985. Temporal Trends and Spatial Distribution of Organochlorine and Mercury Residues in Great Lakes Spottail Shiners (1975-1983). Ontario Ministry of the Environment, Rexdale, Ontario.
- United States Environmental Protection Agency. 1979. Water-related Environmental Fate of 129 Priority Pollutants, Vols. 1 and 2, EPA-440/4-79-029a and EPA-440/4-79-029b. Office of Water Planning and Standards, Washington, D.C.
- United States Environmental Protection Agency. 1980. Ambient Water Quality Criteria for DDT. EPA-440/5-80-038. Office of Water Planning and Standards, Washington, D.C.
- Warry, N.D., and C.H. Chan. 1981. Organic contaminants in the suspended sediments of the Niagara River. *J. Great Lakes Res.*, 7(4):394-403.

APPENDIX A

ORGANOCHLORINE OCCURRENCE AT WOLFE ISLAND, 1982/84

Table A-1. Organochlorine Pesticide Concentrations (ng/L, occurrence >40%) in Whole Water at Wolfe Island

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Mean
α-BHC (94%)													
1982	—	—	—	8.8	6.7	5.4	5.2	6.9	6.4	7.3	1.0	5.0	5.9
1983	4.9	3.1	3.5	13.8	<0.4	<0.4	6.0	5.4	4.3	4.9	10.6	6.3	6.9
1984	5.8	6.7	3.4	6.3	5.1	—	4.2	2.7	3.6	3.0	4.1	4.5	4.5
γ-BHC (88%)													
1982	—	—	—	2.3	1.4	1.8	1.6	2.5	1.3	1.2	<0.4	1.0	1.5
1983	1.1	1.3	1.0	1.3	<0.4	0.5	<0.4	0.7	<0.4	0.5	0.6	0.6	0.7
1984	0.6	0.7	1.2	1.3	0.9	—	0.8	0.8	0.8	0.6	0.9	9.0	0.9
Dieldrin (41%)													
1982	—	—	—	<0.4	0.5	0.5	<0.4	0.6	<0.4	<0.4	<0.4	<0.4	0.3
1983	<0.4	<0.4	0.5	0.5	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.3
1984	<0.4	<0.4	1.6	<0.4	0.6	—	1.1	0.5	0.7	1.1	0.5	0.8	0.7

Table A-2. Organochlorine Pesticide and PCB Concentrations (ng/g, occurrence >50%) in Suspended Sediments at Wolfe Island

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Mean
tDDT (90%)													
1982	—	—	—	29	58	36	—	13	18	33	42	23	32
1983	6	18	26	—	11	14	6	<4	<4	13	11	16	11
1984	28	27	29	27	20	—	11	<4	4	7	9	7	16
PCBs (93%)													
1982	—	—	—	110	360	200	—	100	310	130	160	170	190
1983	330	200	110	—	120	<90	230	170	200	150	140	130	170
1984	170	140	230	150	120	—	200	<90	90	130	130	120	140
Dieldrin (83%)													
1982	—	—	—	<4	<4	21	—	<4	10	5	6	6	7
1983	<4	17	4	—	16	<4	6	5	8	4	7	6	7
1984	9	9	22	29	18	—	17	4	6	7	8	7	12
α-BHC (53%)													
1982	—	—	—	<4	<4	29	—	5	10	6	5	4	8
1983	5	7	6	—	9	13	<4	<4	<4	<4	<4	<4	5
1984	5	<4	10	8	<4	—	9	<4	<4	5	<4	<4	4

Table A-3. Organochlorine Pesticide Concentrations (ng/g, occurrence >20% and <50%) in Suspended Sediments at Wolfe Island

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Mirex (33%)												
1982	—	—	—	10	10	<4	—	<4	<4	<4	7	6
1983	12	<4	<4	—	<4	<4	<4	<4	<4	<4	<4	7
1984	8	5	6	5	<4	—	<4	<4	<4	<4	<4	<4
α -Chlordane (33%)												
1982	—	—	—	<4	<4	21	—	<4	27	16	9	9
1983	<4	<4	<4	—	6	<4	<4	<4	<4	<4	<4	<4
1984	5	4	8	7	17	—	<4	<4	<4	<4	<4	<4
β -Endosulfan (20%)												
1982	—	—	—	<4	<4	<4	—	4	19	15	5	5
1983	5	<4	<4	—	<4	<4	<4	<4	<4	<4	<4	<4
1984	<4	<4	<4	<4	<4	—	<4	<4	<4	<4	<4	<4

Table A-4. Chlorobenzene Concentrations (ng/g, occurrence >40%) in Suspended Sediments at Wolfe Island

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Mean
1,2-Di (40%)													
1982	—	—	—	—	—	<50	—	<50	<50	<50	<50	<50	—
1983	<50	<50	<50	—	<50	<50	480	370	660	260	280	370	—
1984	220	150	330	180	100	—	<50	<50	<50	<50	<50	<50	—
1,2,4-Tri (54%)													
1982	—	—	—	—	—	<5	—	<5	6	<5	<5	8	4
1983	9	<5	<5	—	16	25	39	25	147	<5	62	131	42
1984	88	62	125	80	37	—	<5	<5	<5	<5	<5	<5	37
1,2,3,4-Tetra (64%)													
1982	—	—	—	—	—	50	—	26	11	19	16	7	22
1983	7	9	<5	—	44	95	10	9	11	<5	5	30	20
1984	<5	6	8	10	<5	—	<5	<5	<5	<5	<5	<5	4
Penta (57%)													
1982	—	—	—	—	—	37	—	22	7	13	10	7	16
1983	16	<4	<4	—	28	56	10	11	21	<4	<4	23	16
1984	<4	7	6	7	<4	—	<4	<4	<4	<4	<4	<4	3
Hexa (89%)													
1982	—	—	—	—	—	8	—	54	9	21	19	11	20
1983	38	<4	<4	—	15	16	16	15	18	8	11	12	14
1984	9	11	6	9	5	—	7	<4	9	7	8	8	7

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