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Trace Organic Contaminants in Sediment of the International Section of the St. Lawrence **River, 1981** 

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J.C. Merriman



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## **TECHNICAL BULLETIN NO. 148**

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

(Disponible en français sur demande)



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## Abstract

Bottom and suspended sediment was collected from the St. Lawrence River between Kingston and Cornwall in July 1981 by the Water Quality Branch, Ontario Region. Samples were analyzed for organochlorine pesticides, PCBs, chlorobenzenes and organic carbon. Particle size distribution was determined on bottom sediment.

This report summarizes the concentration and distribution of the trace organic contaminants and compares findings with other available historical data. Total PCBs were compared with the Ontario Ministry of Environment dredged material guideline for open water disposal.

## Résumé

Des sédiments de fond et en suspension ont été prélevés dans le fleuve Saint-Laurent, entre Kingston et Cornwall, en juillet 1981 par la Direction de la qualité des eaux, Région de l'Ontario. Les échantillons ont été analysés en vue de déceler la présence de pesticides organochlorés, de BPC, de chlorobenzènes et de carbone organique. La granulométrie des sédiments de fond a été déterminée.

Le présent rapport résume la concentration et la répartition des contaminants organiques à l'état de traces et compare les résultats avec d'autres données chronologiques existantes. Les BPC totaux ont été examinés en fonction des recommandations du ministère de l'Environnement de l'Ontario pour les matériaux dragués en vue de leur élimination en eaux libres.

# Trace Organic Contaminants in Sediment of the International Section of the St. Lawrence River, 1981

J.C. Merriman

#### INTRODUCTION

The international section of the St. Lawrence River has been the subject of frequent environmental monitoring since 1964 with the establishment of the International Lake Ontario-St. Lawrence River Water Pollution Board by the International Joint Commission (IJC) (International Lake Erie Water Pollution Board and the International Lake Ontario-St. Lawrence River Water Pollution Board, 1969). Most of the work in the early years reported by the Commission concentrated on the physical, chemical and bacteriological quality of the river (IJC, 1965; 1968; 1970a,b, 1976).

From the mid-1970s emphasis has been on toxic chemicals, in particular, trace organic contaminants. Work carried out by both Environment Canada and the Ontario Ministry of Environment has shown that there are areas of concern for various organic contaminants in the down-stream section of the river on both the Canadian and the American sides. Lindane and  $\alpha$ -BHC have been found to be widespread in St. Lawrence River water, whereas PCBs have been detected in water near the mouth of the Grass River (Chan, 1980). Wong (1981) estimated contaminant loadings for PCBs, organochlorine pesticides, PAHs and chlorobenzenes from the city of Cornwall. Work carried out by

the Ontario Ministry of Environment has shown PCBs in bottom sediment in the Cornwall area and at the mouth of the Grass River to exceed dredge spoil guidelines (IJC, 1982).

In 1981, the Water Quality Branch, Ontario Region, carried out a sediment survey on the international section of the St. Lawrence River, extending from Lake Ontario to the Cornwall area, to determine the concentration and distribution of organic contaminants in both the bottom and the suspended sediment. This report summarizes the data and compares concentrations of contaminants with other historical data in the study area, Lake Ontario and the Niagara River.

#### METHODOLOGY

Sampling sites are shown in Figure 1, and locations and dates are given in Table 1. Ten stations were sampled for suspended sediment. Bottom sediment samples were collected at seven of these sites. Sampling locations were selected to give an overview of sediment chemistry. One site, station 84 on the Grass River, was selected to provide further information on PCBs at this location which has been cited in the literature as a problem area.

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Figure 1. St. Lawrence River sampling stations, 1981.

Table 1. St. Lawrence River Sampling Locations

Station	Date	Bottom sediment	Suspended sediment	Latitude	Longitude	
75N	81-06-17	X	X	45°02'28''	74° 36' 52''	
75S	81-06-20		х	45° 19′ 43′′	74° 36′ 43′′	
78	81-06-18	х	X	45°01'22''	74°41′03′′	
84	81-06-19	x	х	44° 58' 46''	76° 46′ 36″	
98	81-06-22	х	х	44° 56' 57''	75°03′48′′	
136	81-06-23		х	44° 35' 59''	-75° 39' 15''	
158N	81-06-25		х	44° 22' 32''	75°55'48''	
158S	81-06-24	х	x	44° 21′ 20′′	75° 54' 29''	
189	81-06-26	х	x	44°08′56′′	76°20/18''	
1 <b>92</b>	81-06-27	X	X	44° 12' 20''	76°.32′30′′	

#### **Bottom Sediment**

Bottom sediment samples were collected using a Shipek sampler. The top 3 cm of the sample was removed from the middle of the bucket, placed in a solvent-washed glass jar with foil-lined caps, and frozen. On receipt in the laboratory, the sample was thawed. Any excess water was decanted from the jar and the sample was homogenized.

A 5- to 10-g portion of the homogenized sediment was extracted with 1:1 hexane-acetone. The extract was filtered, then partitioned with water and subsequently extracted with benzene. The combined extracts were dried, reduced in volume and cleaned on a gel permeated chromatographic column. Further cleanup was done on a silica gel column from which two fractions were obtained. Each fraction was analyzed by gas liquid chromatography using two columns, one packed and one capillary. A complete description of analytical methodologies may be found in the *Analytical Methods Manual* (Environment Canada, 1979).

Particle size analysis on bottom sediment was determined using the sieve and sedigraph method, which provides percentages for gravel, sand, silt and clay. Samples were freeze-dried and gently broken up with a mortar and pestle. All particles large enough to block the sedigraph suction tube (0.80 mm) were removed. The sample was then dispersed in a Calgon suspension and automatic analysis was done with the sedigraph. Results were processed with SIZDIST, a FORTRAN IV computer program (Sandilands and Duncan, 1980). A more detailed description of the methodology may be found in Duncan and LaHaie (1979).

#### Suspended Sediment

Suspended sediment samples were collected using two Westfalia separators. Water was pumped through each centrifuge at a rate of 6 L+min<sup>-1</sup> using a March 5C-MD submersible magnetic drive pump. A Teflon hose encased in stainless steel was used as a transfer line between the pump and the centrifuge. On average, 7200 L of water was centrifuged to collect each sample.

Sediment was removed from the centrifuge bowls by scraping the sediment from the walls of the four-chamber bowl with a Teflon scraper. The sediment-water slurry was then pressure-filtered through a  $5 \mu m$  Teflon filter. The filter was dried in a desiccator. Sediment was then removed from the filter and homogenized using a mortar and pestle. The analytical methodology for the suspended sediments was the same as that described for bottom sediment.

#### **RESULTS AND DISCUSSION**

#### **Bottom Sediment**

Seven stations were sampled for bottom sediment. Flow conditions were too fast at three sites for any accumulation to occur; thus no bottom sediment samples could be obtained at those locations.

Analytical results are presented in Table 2. Of the 29 contaminants analyzed, half were found to be below the detection level, while another 20% were detected only once in trace amounts. Variables that were not detected include  $\alpha$ -BHC, lindane, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin,  $\alpha$ -chlordane,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, p,p'-DDT, o,p'-DDT, methoxychlor and 1,2,3-trichlorobenzene. Parameters that were found in quantifiable amounts included DDE, TDE, mirex, total PCBs and chlorobenzenes.

#### $\Sigma DDT$ and Metabolites

Neither p,p'-DDT nor o,p'-DDT were found in the bottom sediment samples. The use of DDT was restricted in 1972. The degradation product of DDT, p,p'-DDE, was

Parameter	75N	78	84	98	158S	189	192
α-BHC	<1	<1	<1	<1	<1	<1	<1
Lindane	<1	<1	<1	<1	<1	<1	<1
Heptachlor	<1	<1	<1	<1	<1	<1	<1
Heptachlor epoxide	<1	<1	<1	<1	<1	<1	<1
Aldrin	<1	<1	<1	<1	· <1	<1	<1
Dieldrin	<1	<1	<1	<1	<1	<1	<1
Endrin	<1	<1	<1	<1	<1	<1	<1
$\gamma$ -chlordane	<1	<1	<1	<1	<1	<1	3
α-chlordane	<1	<1	<1	<1	<1	<1	<1
à-endòsülfan	<1	<1	<1	<1	<1	<1	<1
$\beta$ -endosulfan	<1	<1	<1	<1	<1	<1	<1
p,p'-DDT	<1	<1	<1	<1	<1	<1	1
o,p'-DDT	<1	<1	<1	<1	<1	<1	<1
p,p'-DDE	8	6	<1	5	6	3	45
p,p'-TDE	2	<1	<1	<1	<1	<1	11
$\Sigma$ DDT + metabolites	10	6	<1	5	6	3	56
Methoxychlor	<1	<1	<1	<1	<1	<1	<1
Mirex	<1	<1	<1	<1	<1	<1	9
Total PCBs	80	850	8740	80	20	10	310
1,3-Dichlorobenzene	5	<1	10	9	<1	5	15
1,4-Dichlorobenzene	<1	9	<1	<1	6	<1	<1
1,2-Dichlorobenzene	5	3	7	6	3	2	15
1,3,5-Trichlorobenzene	1	1	<1	<1	<1	<1	1
1,2,4-Trichlorobenzene	<1	<1	<1	<1	<1	<1	<1
1,2,3-Trichlorobenzene	<1	<1	<1	<1	<1	<1	3
1,2,4,5-Tetrachlorobenzene	<1	<1	<1	<1	<1	<1	2
1,2,3,4-Tetrachlorobenzene	<1	<1	<1	<1	<1	<1	1
Pentachlorobenzene	<1	<1	<1	<1	<1	<1	2
Hexachlorobenzene	4	13	<1	<1	<1	1	11
Total chlorobenzenes	15	26	17	15	9	8	50

Table 2. Concentration of Organic Contaminants in St. Lawrence River Bottom Sediment (µg·kg<sup>-1</sup>)

found in six of the seven samples with the highest concentration of 45  $\mu$ g·kg<sup>-1</sup> at station 192. Concentrations at this site were five times higher than the next highest concentration.

TDE was found in two of seven samples. Detections occurred at opposite ends of the river at station 192 near Kingston and at station 75N, downstream from Cornwall. Concentrations of p,p'-DDE and p,p'-TDE at station 192 were higher than those found in most of the Niagara River bottom sediment samples with the exception of two sites located near point source inputs (Kuntz, 1984).

When DDT and its metabolites are summed, station 192 clearly stands out as having a higher concentration (56  $\mu$ g\*kg<sup>-1</sup>) than the rest of the stations where concentrations ranged from 3 to 10  $\mu$ g\*kg<sup>-1</sup> (Fig. 2). Many organic contaminants have been shown to sorb onto finer particulate material, and differences in sorption within these finer fractions (i.e. silt and clay) have been found to be related to differences in organic carbon content (Karickhoff *et al.*, 1979). Particle size analysis and organic carbon content at station 192 show high percentages of clay and organic carbon in relation to other stations sampled (Table 3). This may partially account for elevated concentrations found at this site.

Another possible explanation for higher concentrations at station 192 may be that the location is influenced by point sources. Computed water transport models show that the direction of water movement may be in a westerly direction at this station (Simons, 1975). This model, however, has not been verified for the eastern end of Lake Ontario. If this is in fact correct, point sources from the Kingston area may be transported and deposited in the vicinity of station 192, resulting in the higher concentrations. Pickett and Dossett (1979) found that the spread of mirex from sources in the Niagara and Oswego rivers did conform to Lake Ontario currents recorded during 1972-73. Since very little is known about circulation patterns in the eastern end of Lake Ontario, mirex concentrations in bottom sediments may be a useful tool in addition to the regular techniques used to determine circulation patterns.

Analysis of bottom sediments (Thomas and Mudroch, 1979) from previously dredged small craft harbours in the



Figure 2. St. Lawrence River bottom sediment:  $\Sigma DDT$  and metabolites ( $\mu g \cdot kg^{-1}$ ).

Station	Gravel	Sand	Silt	Clay	Organic carbon
75N	0	39.2	32.6	28.2	4.1
78	0	45.3	35.1	19.6	3.6
84	0	13.1	48.9	38.0	5.3
98	0	23.6	58.5	17.9	3.9
158C	0	61.8	18.4	19.8	3.9
189	0	75.9	14.3	9.8	2.3
192	0	48.7	17.7	33.6	7.6

Table 3. Particle Size Distribution and Organic Carbon Content of St. Lawrence River Bottom Sediment (%)

general vicinity of station 192 show that the concentrations of DDT were approximately three times higher at 192 than those found in the harbours. Unfortunately, there were no data available on contaminant levels in the bottom sediment of the small craft harbours prior to dredging.

Historical data for Lake Ontario bottom sediment showed a mean concentration for depositional zones to be  $62 \ \mu g \cdot kg^{-1}$  for DDT (Frank *et al.*, 1979). This is in good agreement with what was found at station 192.

#### Mirex

The only detection of mirex in bottom sediments was at station 192 (9  $\mu$ g·kg<sup>-1</sup>). Holdrinet *et al.* (1978) found mirex in the bottom sediment of Lake Ontario from industrial point sources located on the Niagara and Oswego rivers. Concentrations in the eastern end of Lake Ontario were found to range from 8 to 22  $\mu$ g·kg<sup>-1</sup> at seven sites.

Mirex levels at station 192 fall within the range found in 1976 by Holdrinet.

#### Total PCBs

Concentrations of total PCBs are quite variable throughout the St. Lawrence River (Fig. 3). Stations 189 and 136 are the only two stations with concentrations below the Ontario Ministry of Environment (MOE) guideline of 50  $\mu$ g·kg<sup>-1</sup> for dredged material. Station 78 with a concentration of 850  $\mu$ g·kg<sup>-1</sup> indicates that there are point sources in the Cornwall area. Data collected by the Ministry of Environment and Environment Canada from the Cornwall area also indicate elevated levels of PCBs (IJC, 1982; Wong, 1981; Wong and Marsalek, 1981).

The Grass River (station 84) has been recognized as a source of total PCBs to the St. Lawrence River for several years (Chan, 1980; IJC, 1982). An extremely high concentra-



Figure 3. St. Lawrence River bottom sediment: total PCBs ( $\mu g \cdot k g^{-1}$ ).

tion of 8740  $\mu$ g·kg<sup>-1</sup> was found in the bottom sediment of this river (Fig. 3). This source as well as sources from Cornwall contributes to the transboundary pollution of Lake St. Francis in the province of Quebec (Sloterdijk, 1983).

A total PCB concentration of  $310 \ \mu g \cdot k g^{-1}$  was found at station 192 upstream from Kingston. This is well over the MOE guideline and is almost three times higher than levels of PCBs found in the bottom sediment of small craft harbours in the area (Thomas and Mudroch, 1979). All three small craft harbours had been dredged previously dating back to 1968.

Frank et al. (1979) reported PCBs in the bottom sediment of eastern Lake Ontario to be in the range of 20-260  $\mu$ g·kg<sup>-1</sup>. He also found PCBs in the range of 2-100  $\mu$ g·kg<sup>-1</sup> in the Adolphus Basin from his Bay of Quinte study (1980). Concentrations from these surveys appear to be lower than those found at station 192 (310  $\mu$ g·kg<sup>-1</sup>). One possible explanation for this difference is in the sample treatment. In both studies by Frank, the bottom sediments were freeze-dried, whereas in the Water Quality Branch survey, the bottom sediments were frozen and then submitted wet for analysis. It is conceivable that in the freeze-drying process, the more volatile forms of PCBs were lost, resulting in somewhat lower concentrations. Station 192 is also located in the vicinity of both the Kingston Township sewage treatment outfall and the Dupont discharge, which could also account for the elevated concentrations found at this site.

#### Chlorobenzenes

Chlorobenzenes were found in relatively low concentrations in the St. Lawrence River bottom sediment. Di, tri, tetra, penta and hexachlorobenzenes were detected at station 192. Dichlorobenzenes were detected at all stations sampled, ranging from a low of 7  $\mu$ g·kg<sup>-1</sup> at station 189 to a high of 30  $\mu$ g·kg<sup>-1</sup> at station 192.

Tri, tetra and pentachlorobenzenes were virtually absent in the bottom sediment of the river except for traces found at station 192, while hexachlorobenzene was found at stations 192 and 78 in concentrations of 11  $\mu$ g·kg<sup>-1</sup> and 13  $\mu$ g·kg<sup>-1</sup>, respectively. Hexachlorobenzenes have been found in surface runoff from the city of Cornwall (Wong, 1981). This is the likely source for the hexachlorobenzenes found at station 78, which had the highest concentration found for the seven sites sampled. Chlorobenzene concentrations in the St. Lawrence River bottom sediment were found to be significantly lower than those found in the Lake Ontario (Oliver and Nicol, 1982) and the Niagara River (Kuntz, 1984).

With the exception of station 192, concentrations of total chlorobenzenes tended to increase in a downstream direction (Fig. 4). The lowest levels were found at stations 189 and 158 with concentrations of 8 and 9  $\mu$ g·kg<sup>-1</sup>, respectively. Downstream concentrations were in the range of 15-26  $\mu$ g·kg<sup>-1</sup>. Station 192 had a concentration of 50  $\mu$ g·kg<sup>-1</sup>, almost twice as high as the next highest station.



Figure 4. St. Lawrence River bottom sediment: total chlorobenzenes (µg·kg<sup>-1</sup>).

Particle size analysis data show that station 192 has the highest percent clay-sized fraction for all St. Lawrence River stations, suggesting that it is an excellent depositional area where contaminated sediments may settle. Higher concentrations at this site may indicate influence from a point source input as mentioned above. Although station 84 on the Grass River had a higher percent clay-sized fraction than station 192, total chlorobenzenes do not appear to be accumulating in bottom sediment, as a concentration of 17  $\mu$ g·kg<sup>-1</sup> was found at this site.

#### **Suspended Sediment**

Ten sites were sampled for suspended sediment. Results of analyses are given in Table 4. A total of eight of 28 variables analyzed were found to be below the detection limit. These included lindane, heptachlor, heptachlor epoxide, aldrin,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, o,p'-DDT and methoxychlor. Three variables,  $\alpha$ -BHC, endrin and 1,2,4-trichlorobenzene, were detected only once, and in trace amounts.

#### Dieldrin

Dieldrin concentrations found in the suspended sediment at the ten stations sampled ranged from non-detactable levels at stations 84 and 78 to a high of 14  $\mu$ g·kg<sup>-1</sup> at station 189S. These concentrations are quite similar to those found in streams flowing into Lake Ontario (Frank *et al.*, 1981) and those found in the suspended sediment of the Niagara River (Warry and Chan, 1981; Kuntz and Warry, 1983).

#### Chlordane

Both  $\alpha$  and  $\gamma$  isomers of chlordane were found in the suspended sediment of the St. Lawrence River. Concentrations ranged from non-detectable levels to  $6 \,\mu g \cdot kg^{-1}$ at station 158S for  $\alpha$ -chlordane, while concentrations of  $\gamma$ -chlordane varied from non-detectable to 7  $\mu g \cdot kg^{-1}$ at station 192. Neither of the isomers were detected in the Grass River. Suspended sediment data compared well with those for tributaries flowing into Lake Ontario (Frank *et al.*, 1981) and for the Niagara River at Niagara-on-the-Lake (Kuntz and Warry, 1983).

#### $\Sigma DDT$ and Metabolites

Stations 189 and 78 had p,p'-DDT concentrations of 9 and 16  $\mu g \cdot k g^{-1}$ , respectively. p,p'-DDT was found in six of 15 suspended sediment samples collected in the Niagara River in 1981 (Kuntz, 1984). The degradation product of p,p'-DDT, p,p'-DDE, which is also very persistent, was found at all stations, ranging from a low of 7  $\mu g \cdot k g^{-1}$ to a high of 18  $\mu g \cdot k g^{-1}$ . Its prevalence throughout the river indicates the widespread use of DDT in the past. Concentrations of p,p'-TDE ranged from non-detectable levels at three stations to a high of 20  $\mu g \cdot k g^{-1}$  at station 192. Levels were almost twice as high at 192 compared with the next highest concentration found at 158N.

Total DDT and its metabolites ranged from a low of 11  $\mu$ g·kg<sup>-1</sup> at station 98 to a high of 34  $\mu$ g·kg<sup>-1</sup> at station 192. Station 78 at Cornwall had a concentration of 33  $\mu$ g·kg<sup>-1</sup> (Fig. 5).

Parameter	75N	755	78	84	98	136	158N	1585	189	192
α-BHC	<1	<1	<1	<1	<1	<1	<1	<1	2	<1
Lindane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor epoxide	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Aldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	3	11	<1	<1	11	5	12	5	14	4
Endrin	<1	<1	<1	<1	<1	<1	<1	<1	6	<1
γ-chlordane	2	2	2	<1	2	2	4	4	· 3	7
α-chlordane	<1	2	<1	<1	2	3	3	6	5	<1
α-endosulfan	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
β-endosulfan	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
p,p'-DDT	<1	<1	16	<1	<1	<1	<1	<1	9	<1
o,p'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
p,p'-DDE	10	10	13	18	7	12	10	15	16	14
p,p'-TDE	4	6	4	<1	4	<1	11	8	<1	20
$\Sigma DDT + metabolites$	14	16	33	18	11	12	21	23	25	34
Methoxychlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Mirex	3.	2	2	<1	2	4	<1	6	6	6
Total PCBs	30	200	20	1800	50	110	100	150	200	190
1,3-Dichlorobenzene	<1	25	49	28	<1	28	<1	30	24	51
1,4-Dichlorobenzene	<1	22	<1	22	27	17	<1	18	<1	<1
1,2-Dichlorobenzene	11	22	31	15	<1	13	14	.30	36	29
1,3,5-Trichlorobenzene	11	4	11	2	<1	8	9	9	8	2
1,2,4-Trichlorobenzene	<1	<1	5	<1	<1	<1	<1	<1	<1	<1
1,2,3-Trichlorobenzene	5	· <1	<1	4	<1	4	6	4	6	4
1,2,4,5-Tetrachlorobenzene	3	4	<1	1	3	3	3	3	3	3
1,2,3,4-Tetrachlorobenzene	1	1	2	1	<1	2	2	2	<1	2
Pentachlorobenzene	1	1	1	1	<1	2	2	19	3	2
Hexachlorobenzene	10	3	27	1	3	6	4	8	6	4
Total chlorobenzenes	42	82	126	75	30	83	40	123	86	97

Table 4. Concentration of Organic Contaminants in St. Lawrence River Suspended Sediment ( $\mu g \cdot k g^{-1}$ )



Figure 5. St. Lawrence River suspended sediment:  $\Sigma$ DDT and metabolites ( $\mu g \cdot k g^{-1}$ ).

Mirex

Mirex was found to be widespread in suspended sediments throughout the St. Lawrence River. It was found at all but two stations, 158N and the Grass River. Concentrations ranged from 2 to  $6 \,\mu g \cdot k g^{-1}$  and appeared to decrease in concentration in a downstream direction, probably the result of a dilution effect (Fig. 6). The only known sources of mirex are from tributaries flowing into Lake Ontario. Concentrations in the St. Lawrence River are lower than those found at Niagara-on-the-Lake. From 1979 to 1981 the mean concentration of mirex was  $12 \,\mu g^{-1} kg^{-1}$  based on 70 suspended sediment samples (Kuntz and Warry, 1983).

#### Total PCBs

Total PCBs decreased in a downstream direction (Fig. 7). Upstream concentrations were 190 and 200  $\mu$ g·kg<sup>-1</sup> at station 192 and 189, respectively, and de-



Figure 6. St. Lawrence River suspended sediment: mirex ( $\mu g \cdot kg^{-1}$ ).



Figure 7. St. Lawrence River suspended sediment: total PCBs ( $\mu g \cdot k g^{-1}$ ).

creased to a low of 20 and 30  $\mu$ g·kg<sup>-1</sup> at station 78 and 75 in the Cornwall area. A very high total PCB concentration of 1800  $\mu$ g·kg<sup>-1</sup> was found in the Grass River. As stated earlier, documented sources are responsible for these elevated levels. High levels of total PCBs are evident downstream from the confluence of the Grass and St. Lawrence rivers at station 75S where a concentration of 200  $\mu$ g·kg<sup>-1</sup> was found. With the exception of station 84, St. Lawrence River total PCBs in suspended sediment are much lower in concentration than what has been found in the Niagara River. Kuntz and Warry (1983) reported a mean of 718  $\mu$ g·kg<sup>-1</sup> at Niagara-on-the-Lake between 1979 and 1981.

#### Chlorobenzenes

Chlorobenzenes were found to be widespread in the suspended sediment (Fig. 8). Di, tri, tetra, penta and hexachlorobenzenes were found at all stations with the exception of station 98 where only di and hexachlorobenzene were quantified. Concentrations for all the chlorobenzenes were much lower than those reported in the Niagara River (Kuntz, 1984).

Dichlorobenzene concentrations ranged from a high of 80  $\mu$ g·kg<sup>-1</sup> at stations 192 and 78 to a low of 11  $\mu$ g·kg<sup>-1</sup> at station 75. There was no discernible spatial variation. Trichlorobenzene concentrations ranged from non-detectable at station 98 to a high of 16  $\mu$ g·kg<sup>-1</sup> at stations 75N and 78. Tetrachlorobenzene concentrations were lower than tri and dichlorobenzene levels. Concentrations ranged from non-detectable at station 98 to a high of 5  $\mu$ g·kg<sup>-1</sup> at five stations. Hexachlorobenzene concentrations were found to be near or below the detection level, with the exception of station 158C where a concentration of 19  $\mu$ g·kg<sup>-1</sup> was found. This suggests that there is a point source discharge in the vicinity of Alexandria.

Hexachlorobenzene concentrations ranged from a low of 1  $\mu$ g\*kg<sup>-1</sup> in the Grass River to a high of 27  $\mu$ g\*kg<sup>-1</sup> at station 78. With the exception of station 78, all concentrations found were 20  $\mu$ g\*kg<sup>-1</sup> or less. Point sources from Cornwall are suspected to be the cause of the elevated hexachlorobenzene levels at station 78. Studies conducted in Cornwall have shown that hexachlorobenzene was found in institutional, industrial and residential surface runoff samples (Wong, 1981).

#### CONCLUSIONS AND RECOMMENDATIONS

Concentrations of organic contaminants in bottom and suspended sediment were found to be highly variable. Certain patterns emerged from the data that did indicate consistently higher concentrations of specific locations. Extremely high levels of total PCBs remain a problem in the Grass River (station 84). This situation should be monitored on a regular basis because of the transboundary transport of this contaminant and its international implications.

High concentrations of total PCBs were found in the bottom sediment at station 78 near Cornwall. In addition, this site showed elevated levels of chlorobenzenes in both



Figure 8. St. Lawrence River suspended sediment: total chlorobenzenes ( $\mu g \cdot k g^{-1}$ ).

bottom and suspended sediment as well as high concentrations of DDT and its metabolites in suspended sediment. Further investigation is required to determine the extent and sources of contaminants in that area.

Station 192 exhibited the highest concentrations in bottom sediment compared with the other stations for most variables analyzed. For some parameters, the concentrations were higher than background levels in Lake Ontario. Additional surveys are necessary to find out the distribution and source of contamination. Verification of numerical models developed to simulate currents during stratified conditions in the eastern end of Lake Ontario would aid in the interpretation of transport and fate of contaminants from known point source inputs.

Sediment quality data are a very useful component in determining the transport and fate of contaminants, detecting point source influences, and also in determining changes of contaminant concentrations over time. It is important that criteria and guidelines be developed for trace organics in sediment so that their environmental significance can be better assessed.

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#### REFERENCES

- Chan, C.H. 1980. St. Lawrence River water quality surveys, 1977. Sci. Ser. No. 113, Inland Water's Directorate, Water Quality Branch, Burlington, Ontario.
- Duncan, G.A., and G.G. LaHaie. 1979. Size Analysis Procedures used in the Sedimentology Laboratory, National Water Research Institute. Hydraulics Division, National Water Research Institute, Burlington, Ontario.
- Environment Canada. 1979. Analytical Methods Manual. Inland Waters Directorate, Water Quality Branch, Ottawa.
- Frank, R., R.L. Thomas, M.V.H. Holdrinet, and V. Damiani. 1980. PCB residues in bottom sediments collected from the Bay of Quinte, Lake Ontario 1972–73. J. Great Lakes Res., 6(4): 371–376.
- Frank, R., R.L. Thomas, M.V.H. 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, R.K. McMillan, H.E. Braun, and R. Dawson, 1981. Organochlorine residues in suspended solids collected from the mouths of Canadian

streams flowing into the Great Lakes 1974-1977. J. Great Lakes Res., 7(4): 363-381.

- Holdrinet, M.V.H., R. Frank, R.L. Thomas, and L.J. Hetling. 1978. Mirex in the sediments of Lake Ontario. J. Great Lakes Res., 4(1): 69-74.
- International Joint Commission. 1965. First interim report on the Pollution of Lake Erie. Lake Ontario and the international section of the St. Lawrence River.
- International Joint Commission. 1968. Second interim report on the pollution of Lake Erie, Lake Ontario and the international section of the St. Lawrence River.
- International Joint Commission. 1970a. Third interim report on the pollution of Lake Érie, Lake Ontario and the international section of the St. Lawrence River.
- International Joint Commission. 1970b. Pollution of Lake Erie, Lake Ontario and the international section of the St. Lawrence River.
- International Joint Commission. 1976. International Joint Commission Water Quality Board fourth annual report, Appendix B, Windsor, Ontario.
- International Joint Commission, 1982. Report on Great Lakes Water Quality, Great Lakes Water Quality Board, Windsor, Ontario.
- International Lake Erie Water Pollution Board and the International Lake Ontario – St. Lawrence River Water Pollution Board. 1969. Report to the International Joint Commission on Pollution of Lake Erie, Lake Ontario and the international section of the St. Lawrence River. Vol. 3.
- Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res., 13: 241-248.
- Kuntz, K.W. 1984. Toxic contaminants in the Niagara River 1975– 1982. Tech. Bull. No. 134, Inland Waters Directorate, Water Quality Branch, Ontario Region, Burlington, Ontario.
- 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): 241-248.
- 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): 532-536.
- Pickett, R.L., and D.A. Dossett. 1979. Mirex and the circulation of Lake Ontario. J. Phys. Oceanogr., 9(2): 441-445.
- Sandilands, R.G., and G.A. Duncan. 1980. SIZDIST-A computer program for size analysis. Hydraulics Division Tech. Note, Rep. No. 80-08, National Water Research Institute, Burlington, Ontario.
- Simons, T.J. 1975. Verification of numerical models of Lake Ontario. II. Stratified circulations and temperature changes. J. Phys. Oceanogr., 5: 98-100.
- Sloterdijk, H. 1983. Toxic substances in Lake St. Francis sediments. Presented at the 10th Aquatic Toxicity Workshop, Halifax, November 1983.
- Thomas, R.L., and A. Mudroch. 1979. Small craft harbours sediment survey Lakes Ontario, Erie and Lake St. Clair 1978. Great Lakes Biolimnology Laboratory, Burlington, Ontario.
- 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.
- Wong, J. 1981. Persistent toxic substances in urban runoff from the city of Cornwall. Unpublished report, National Water Research Institute, Burlington, Ontario.
- Wong, J., and J. Marsalek. 1981. Persistent toxic substances in urban runoff. Presented at the SWMM Model Users Group Meeting, Niagara Falls, September 1981.

