

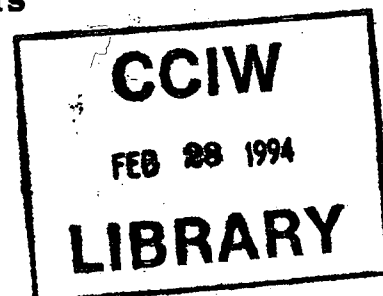
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# **NATIONAL WATER RESEARCH INSTITUTE**

at the

**Canada Centre for Inland Waters**



## **ST. LAWRENCE RIVER TRACE ORGANIC CONTAMINANTS STUDY PART IV, 1989-90 and SUMMARY.**

M.E. Comba<sup>1</sup>, V.S. Palabrica<sup>1</sup>, S.M. Backus<sup>2</sup> and K.L.E. Kaiser<sup>1</sup>

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<sup>1</sup> Nearshore/Offshore Interactions Project, National Water Research Institute, Burlington, Ontario, L7R 4A6.

<sup>2</sup> Backus Consulting, 39 Puritan Court, Stoney Creek, Ontario, L8E 4K9.



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## **EXECUTIVE SUMMARY**

- The principal mechanism for pollutant transport in the St. Lawrence River is water and suspended particulate matter.
- Average rates of water flow and suspended particulate matter concentration have remained relatively constant over the long term. Therefore, observed decreases in water and suspended particulate matter contaminant concentrations are a direct response to reduced inputs.
- Bottom sediments are temporary sinks and sources as the physical conditions in the river do not accommodate their long term storage.
- Rates of hydrophobic contaminant discharge are positively correlated with the discharged amounts of particulate organic carbon (POC) and dissolved organic carbon (DOC).
- The reduction in contaminant loadings is most pronounced for Lake Ontario.
- Contaminant behaviour and partitioning are similar to those in the Great Lakes connecting channels. The amount of contaminant sorbed to suspended particulates is positively correlated to POC concentrations. The linearity of the correlations is weakened through river dynamics, compound grouping and a critical level of SPM (POC) necessary to affect adsorption.
- Contaminant loadings carried by the St. Lawrence River enter the foodchain of the St. Lawrence estuary with the elevated bioaccumulation factors mostly due to the high lipid levels in the marine biota.

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# ST. LAWRENCE RIVER TRACE ORGANIC CONTAMINANTS STUDY PART IV, 1989-90 and SUMMARY .

M.E. Comba<sup>1</sup>, V.S. Palabrica<sup>1</sup>, S.M. Backus<sup>2</sup> and K.L.E. Kaiser<sup>1</sup>

## ABSTRACT

*Prior to 1985, sources, fate and transport of organic contaminants in the St. Lawrence River were virtually unknown. The impact of Lake Ontario on the St. Lawrence corridor was thought to be minimal, since most chemicals were expected to settle to the lake's bottom on the premise they would become permanent deposits. Preliminary investigations, and in particular the observation of Mirex (which was only known to occur in Lake Ontario) in 1985 St. Lawrence River suspended particulate matter led to the Nearshore Offshore Interactions Project (NOI) undertaking an extensive five-year study of organic contaminant processes and interactions in the St. Lawrence River/Estuary system. The objectives of this study were to determine loadings, resident times, rates of transport, bioaccumulation and behaviour within the river and estuary for some of the more widely used organochlorine compounds. In studying these processes it was important to examine certain aspects of the river's physical and seasonal variations that might contribute to contaminant behaviour, but more importantly could have substantial effects on the measurement of contaminants. This final report compiles experimental and analytical data on work undertaken by NOI in the St. Lawrence River, Canada, including data for samples collected during 1989, 1990, with comments on processes governing transport and behaviour of the measured contaminants. The flux and concentration levels are compared with previous years and presented along with individual tabulations of contaminant concentrations. Material in this report should eventually appear in published form, and prior right to publication is reserved. Enquiries concerning the contents of this report should be addressed to K.L.E. Kaiser, Project Chief, NOI.*

## INTRODUCTION

The Laurentian Great Lakes are the world's largest freshwater resource and consist of five major lakes joined together by inter-connecting channels. Water from the Great Lakes drains from Lake Ontario, through the St. Lawrence River and discharges into the Gulf of St. Lawrence to the Atlantic Ocean. The Great Lakes-St. Lawrence drainage basin covers roughly 400,000 square miles (1,000,000 km<sup>2</sup>) with a population of over 50 million inhabitants residing in two Canadian provinces

and eight American states. Due to an extensive industrial, agricultural and municipal base within the drainage basin, water quality and local habitat are often directly impacted with many detrimental effects, related to the release of man-made chemicals.

The St. Lawrence River alone spans 500 km between Kingston, Ontario and Quebec City, Quebec. Lake Ontario is the single dominant hydrodynamic force, discharging over 60% of the river's annual flow. Annual rates of water and suspended particulate matter discharge have remained relatively constant since the river flow has been regulated by dams as far downstream as Montreal, since 1958. From there on, the Ottawa River is the major tributary influence and can constitute up to 50% of the unregulated inputs. On average the Ottawa River contributes 15-20 % of the total St. Lawrence River discharge, except during spring when run-off values may approach 30 %. The volume of the St. Lawrence River is estimated to be approximately 8-10 km<sup>3</sup> of which the three riverine lakes (St. Francois, St. Louis and St. Pierre) make up 2-3 km<sup>3</sup>. This river volume is roughly a fortieth of the annual St. Lawrence River discharge (405 km<sup>3</sup>) and ignoring mixing, requires only ~9 days for replenishment. It is for this reason, together with the shallow depths, that most waterborne contaminants do not undergo any long term retention, and ultimately are exported to the St. Lawrence estuary.

The estuary begins at Québec City and covers a further distance of 500 km into the Gulf of St. Lawrence and the Atlantic Ocean. The estuary is divided into three geochemical zones (upper, middle and lower) determined through ratios of fresh and saline water. The water of the upper and middle estuaries is brackish because of the advection mixing of the "salt wedge" during each ebb and flood cycle of the semi-diurnal tide. The upper and middle estuaries are distinguished from each other by their significant difference in suspended particulate matter concentration. Elevated concentrations of 100-200 mg/l (maximum turbidity zone) are prominent in the upper estuary which rapidly decrease to about 10 mg/l in the middle estuary, and decline to less than 1 mg/l in the deep saline waters (300 m) of the lower estuary in the Laurentian Trough.

During transit downriver, a contaminant's behaviour can be significantly influenced by numerous physical processes and the presence of any organic surfaces or phases in the transporting compartments. For hydrophobic pollutants, the exchange rate between recipient environmental compartments

is more than often affected by the different amounts of dissolved and particulate carbon present. Consequently, processes such as sedimentation, consumption, depuration, metabolism, resuspension and evaporation impart spatial and temporal variations to contaminant concentrations. In enormous rivers like the St. Lawrence, the combination of compartmental effects and dilution complicates the measurement and interpretation of contaminant concentrations. However, despite the low concentrations, the distribution, fate and consequences of anthropogenic contaminants are important (R.J. Allan, 1989) and can have substantial biological impacts on fishes and mammals downstream of their discharge (Martineau et al., 1987; Gagnon et al., 1989; Muir et al., 1990; and Comba et al., 1993).

## EXPERIMENTAL

### Sample Collection

#### *General*

Sample collection was performed with the research vessel C.S.S. *Limnos* from June 28 to July 4/89 for stations 29, 41, 44, 252, 243 and 257 with stations 112 and 28 sampled on July 16 and 19, respectively. In 1990 sample collections took place between June 25 and June 30. A detailed chronology of information and sampling events can be found in the cruise reports (TOD, 1989, 1990). The sampling procedures, if not specified here, were those used in earlier collections (Comba et al., 1989a, 1989b, and 1990). The sampling locations have been previously documented (Comba et al., 1989b) except 1989 stations at 41A, 41B and 41C (Figure 1) in western Lake St. Francois at respective geographical coordinates of Latitude W. and Longitude N. 45°03'37", 74°31'54", 45°03'05", 74°32'00", and 45°02'22", 74°32'06".

Organic contaminant concentrations were determined on suspended particulate samples collected by centrifugation as well as for the centrifuged water. Sampling locations and amounts of suspended particulate matter are given in Table 1 with the rates of river flow used to calculate contaminant flux given in Table 2. Values of flux are in metric units. Contaminant levels were also evaluated with respect to higher values of pH. Concurrent experiments were performed to evaluate dynamics of contaminant adsorption/desorption properties related to centrifugal force and the effects of DOC on contaminant partitioning. As for previous sample collections, a second stage centrifuge for capture of suspended particles lost by the first stage centrifugation step was employed. Findings from these experiments will be reported separately. The measurements reported here complement other data reports conducted in conjunction with this project. These include organic contaminants in

the water column (Kaiser et al., 1990b; Lum and Kaiser, 1986; Lum et al., 1987; Comba and Kaiser, 1990a, 1990b; Comba et al., 1989a, 1989b, 1990, and 1993), sediments (Kaiser et al., 1990a) toxicity effects (Kaiser et al., 1988), contaminants in biota, (Gagnon et al., 1989; Metcalfe and Charlton, 1990) and inorganic contaminants in water and particulate (Lum et al., 1989).

In 1989 suspended particulate matter (SPM) in bulk water samples was collected from the separation bowls of Westfalia centrifuges (CA) operated at 9800 rpm with water flow rates of 6 l/min. Most samples were taken with the vessel at anchor, however, due to navigation restrictions the 1989 stations 600 (Lake St. Louis) and 28 (Lake Ontario) had to be pumped into large holding tanks and processed onboard. Centrifuged sample sizes ranged between 1200 to 12,000 litres. Sampling depths were 8 metres, except station 600, which was sampled at 2 m, a depth corresponding to the midpoint of non mixed Ottawa river water based on conductivity measurements (uncorrected) of 80  $\mu$ S (Siemens). In 1990 a 5 m sampling depth was used for water collection. During both surveys the Westfalia centrifugate was continuously collected in a receiving reservoir and resampled at a flow rate of 1 l/min. The centrifugate was recentrifuged with a Beckman J2-21 centrifuge at 20,000 rpm equipped with a JCF-Z continuous flow rotor (40,000 g force). Suspended particulate matter was collected (CB) from recentrifuged water volumes between 500-1000 l which were placed in 500 ml clean glass jars and stored at 4°C until analysis.

#### *Sediment Samples*

Surficial sediment samples in the riverine lakes were taken in July 1989 with a mini-Shipek sampler. The top 5 cm of these samples were used for analyses. The core samples were collected between 1985 and 1990 with a benthos corer (7 cm diameter). The samples were extruded and sectioned into 1 cm slices, for analyses. Sample chronology and geographical positions are reported in Table 3.

#### *Water samples*

Two hundred litre Westfalia and Beckman continuous flow centrifuged water samples were extracted (APLE) with an aquatic phase liquid-liquid extractor (McCrea and Fisher, 1984). The solvent, dichloromethane, was continuously pumped from the bottom of the extraction drum to a spray bar, which dispersed the solvent into the water sample. The pump was turned on giving an effective recirculating rate of approximately 12 l/min for 60 minutes and turned off to allow the solvent to settle out of the sample water; 40 minutes later, the solvent was drained back into the original amber solvent bottles. A layer of sample water was included during the draining process to minimize the volatilization of the solvent.

Contaminant levels reported here were extracted at ambient pH. In 1990 the neutral phase was re-extracted for

**Table 1. Concentration (mg/l) of suspended particulate matter (CA) in St. Lawrence River water 1989 and 1990.**

Station *	Year	Volume Processed (l)	ppm	Latitude (N)	Longitude (W)
28	1989	1,800	1.9	44° 07' 16"	76° 22' 08"
29	1989	12,960	1.3	44° 38' 19"	75° 35' 57"
29	1990	9,720	1.1		
41 a	1989	1,200	1.9	45° 03' 37"	74° 31' 54"
41 b	1989	1,200	1.9	45° 03' 05"	74° 32' 00"
41 c	1989	1,200	2.9	45° 02' 22"	74° 32' 06"
44	1989	11,160	0.91	45° 11' 23"	73° 46' 17"
44	1990	8,640	1.3		
600	1989	1,200	2.4	45° 20' 27"	74° 00' 12"
252	1989	10,440	3.2	45° 24' 27"	73° 46' 17"
252	1990	2,610	4.5		
243	1989	9,000	5.7	45° 58' 43"	73° 10' 36"
112	1989	5,040	9.0	46° 14' 02"	72° 45' 50"
112	1990	2,160	13		
257	1989	4,200	10	46° 30' 00"	72° 14' 12"
257	1990	4,680	6.9		

\* see figure 1 for locations.

**Table 2. Average flow data (m<sup>3</sup>/s) in the St. Lawrence River from June 26 - 30, 1989 and June 25-30, 1990.**

Year	Location and Flow (m <sup>3</sup> / s)									
	Lake Ontario	Saunders Dam	Beauharnois Turbine	Cateau control structure	Riviere des Mille Iles	Riviere des Prairies	Ste. Anne	Vaudreuil	LaSalle Channel	Quebec City
1989	8037 <sup>a</sup>	7782 <sup>b</sup>	6812 <sup>c</sup>	700 <sup>c</sup>	160 <sup>c</sup>	1009 <sup>c</sup>	465 <sup>c</sup>	263 <sup>c</sup>	8640 <sup>c</sup>	9985 <sup>d</sup>
1990	7924 <sup>a</sup>	8004 <sup>b</sup>	7700 <sup>c</sup>	800 <sup>c</sup>	160 <sup>c</sup>	1000 <sup>c</sup>	430 <sup>c</sup>	240 <sup>c</sup>	9000 <sup>c</sup>	10,800 <sup>d</sup>

(a) International St. Lawrence River Board of Control, Water Resources Branch, Guelph, Ontario.

(b) Seaway Authority, Cornwall, Ontario.

(c) Water Resources Branch, Longueuil, Quebec.

(d) Estimated.



**Table 3. Sediment sampling stations for mirex in the St. Lawrence riverine lakes.**

Lake	Latitude N	Longitude W	Sample type	Date
St. Francois	45-11-19	74-19-27	core	02-10-85
	45-13-15	74-12-16	core	02-10-85
	45-14-06	74-13-42	core	17-07-90
St. Louis	45-13-45	73-55-44	core	03-10-85
	45-24-43	73-49-39	core	03-10-85
	45-26-52	74-03-02	core	03-10-85
	45-24-28	73-46-18	core	20-06-87
	45-22-32	73-46-17	shipek	01-07-89
	45-22-17	73-49-10	shipek	01-07-89
	45-21-48	73-49-48	shipek	01-07-89
	45-20-28	73-52-30	shipek	01-07-89
	45-20-35	73-52-32	shipek	01-07-89
	45-19-43	73-53-06	shipek	01-07-89
St. Pierre	46-07-41	72-56-56	core	13-10-85
	46-11-21	72-53-47	core	13-10-85
	46-14-02	72-45-46	core	23-06-87
	46-14-20	72-46-39	shipek	16-07-89
	46-16-09	72-43-11	shipek	16-07-89

both centrifugation steps, upon adjustment of the pH to >10 with 50% w/w NaOH (Anachemia), which had been pre-extracted with hexane.

#### Sample Preparation

##### *Suspended particulate*

Subsamples of homogenized freeze-dried suspended particulate were extracted with 3 x 50 ml portions of dichloromethane using an Ultra-Turrax homogenizer. Each sample was placed in a 300 ml Erlenmeyer flask, coupled to a ground glass adapter on the homogenizer which positioned the probe 1 mm above the flask bottom. Each 50 ml extraction was performed for five minutes. The three combined extracts were passed through sodium sulphate and rinsed with 50 ml of hexane. The sample extract was concentrated to 8 ml with a rotary evaporator.

An additional 20 ml of hexane was added to the concentrated sample and reduced to 8 ml again. The extract was transferred to a 15 ml-centrifuge tube with 2 x 2 ml hexane rinses. The samples were concentrated to approximately 1 ml by atmospheric evaporation prior to column chromatographic fractionation.

##### *Water samples*

Methylene chloride extracts from the 200 l water samples (APLE) were concentrated to 200 ml with a 12 stage Snyder condenser and further concentrated to 50 ml by rotary evaporation. The 50 ml extracts were passed through sodium sulphate and rinsed with 50 ml of hexane. Samples were reduced to 8-10 ml in hexane and concentrated to a final volume of 1-2 ml in hexane as stated previously for SPM.

## Sample Clean-Up

### *Column chromatography*

Glass columns 300 x 1 cm prewashed with acetone, toluene, and hexane were prepared by gravity settling through hexane to a height of 20 cm with activated silica gel. The prepared sample was added to the top of the silica gel column and eluted to the top of the bed. The sample container was rinsed twice with 2 ml of hexane and the above procedure repeated for each addition. Another 46 ml of hexane was then added to the column and the eluent allowed to chromatograph through the silica gel column into a 250 ml round bottom positioned beneath the column. The flask was removed and labelled Fraction A. Another 250 ml round bottom flask was placed beneath the silica gel column, and eluted with 50 ml of (1:1) methylene chloride and hexane. The chromatographic eluent was labelled Fraction B.

To each fraction a volume of 0.5 ml toluene was added and the fraction concentrated to 2 to 3 ml on a rotary evaporator. The samples were transferred to centrifuge tubes with two 1 ml toluene rinses. The samples were allowed to evaporate to 1 ml and quantitatively adjusted to 1 ml with toluene; transferred to autosampler vials; capped with an aluminum foil liner and autosampler crimp cap and the liquid level recorded on the vial.

### *Mercury treatment of silica gel A fractions*

Sample extracts (fraction A) of sediment and suspended particulate were treated with mercury to remove organic sulphur. To each autosampler vial 0.5 ml of triple distilled mercury was added. The vial was capped and agitated on a vortex stirrer for five minutes. The extracts were allowed to stand overnight and the samples transferred to another autosampler vial, recapped and the liquid level recorded.

### *Silica gel (activated)*

Two hundred gram amounts of Silica Gel 60, 70 to 230 mesh, ASTM, as supplied by EM Science, was activated by heating for 24 hours at 350 °C and used without further treatment.

### *Freeze-drying*

Suspended sediments, in 500 ml jars were refrigerated at 4 °C and allowed to settle for a period of one week. The supernatant was carefully removed by suction using a disposable glass pipette attached to a water aspirator to approximately 1 cm above the suspended particulate layer. The jars were covered with a Mediwipe (McGaw Supply Limited Mississauga, Ontario) secured with an elastic band, frozen and then freeze-dried. Freeze-drying was performed with a Vitris 100-SRC sublimator

at a shelf temperature of 2 °C and a vacuum of 15-30 Torr for 72-100 h.

## MEASUREMENTS

### *Detection limits*

A description of detection limit terminology and appropriate detection limit values are given in the Appendix.

### *Percent organic matter*

Approximately 1 g of freeze-dried suspended sediment collected by centrifugation was weighed with a Mettler H 20T analytical balance into a pre-combusted porcelain crucible. The sample was combusted in a muffle furnace at 550 °C overnight or until it formed a white ash. The sample was allowed to cool inside the furnace and re-weighed to determine the amount of organic matter based on loss on ignition.

### *Chlorophyll*

Chlorophyll determinations were made in accordance with the procedure of Burnison, 1980. A 0.5-1 l volume of raw water was filtered through a pre-combusted 4.25 cm GF/F filter mounted on a minifilter head, under gentle water aspiration suction of 180 mm Hg. The residue collected was stored at -20 °C in a teflon-capped vial into which the loosely rolled filter paper was placed. Upon analysis the vial was brought to room temperature and 4 ml of reagent-grade dimethylsulfoxide (DMSO) was added and the vial resealed. It was warmed in a heating block (Temp-Block Module H2025-5, Scientific Products) at 65 °C for 10 minutes. The vial was removed, agitated thoroughly and the contents gravity filtered through a Nucleopore 0.2 µm membrane filter. The vial and filter were rinsed with 90% acetone, and the filtrate volumes brought to 10 ml with 90% acetone. Absorbance readings were taken in a 1-cm path length cuvette with a Bausch and Lomb Spectronic 20 at wavelengths of 750 and 664 nm. The extract was acidified with 10 µl of concentrated HCl and the absorbance measurements repeated after 5 minutes at 750 and 664 nm.

### *Particulate organic carbon and particulate organic nitrogen*

Raw water was gravity filtered through pre-combusted, pre-weighed GF/C filters mounted on a minifilter head and the volume of collected filtrate recorded. The filtered particulate was sequentially rinsed with deionized water, 2-5 ml of 0.1N H<sub>2</sub>SO<sub>4</sub>, and again with deionized water, and stored at 4 °C in a petri dish. The filter papers were analyzed by the National Laboratory for Environmental Testing (Burlington, Ontario) using a Perkin-Elmer Model 2400 CHN Analyzer and NAQUADAT method No. 06901. The procedure uses thermal combustion of the sample to form gases that are separated by chromatography and quantitated with a thermal conductivity detector.

#### *Dissolved organic carbon*

At each river station, one litre of raw water was collected and filtered through a pre-weighed, pre-combusted 4.25 cm diameter glass fibre (GF), GF/C (1.2  $\mu$ ) filter media, using a Millipore filtering device and a vacuum pump. The first 100 ml of each filtrate was discarded, and the next 20 ml volume transferred into a hypovial, its pH adjusted between 2 - 4 with dilute nitric acid. The hypovial was then capped, labelled and stored at 4°C. Dissolved organic carbon was determined with a Beckman Model 915B total organic carbon analyzer equipped with an infrared detector sensitized for CO<sub>2</sub>. The inorganic carbon was removed by sparging with a stream of CO<sub>2</sub>-free nitrogen prior to syringe injection of the liquid sample. The injected sample was combusted at a temperature of 950 °C in the presence of an oxidizing catalyst.

#### *Organochlorine pesticides*

Organochlorine levels were quantitated by averaging their dual capillary column responses for each silica gel fraction. Fraction A contained the PCB components, pentachlorobenzene, hexachlorobenzene, heptachlor, aldrin and mirex. Fraction B contained,  $\alpha$ ,  $\beta$  and  $\gamma$  BHC, heptachlor epoxide,  $\alpha$  and  $\gamma$  chlordane,  $\alpha$  and  $\beta$  endosulfan, endrin, dieldrin, o,p and p,p-DDE, o,p and

p,p-DDD, o,p and p,p DDT. Estimates of contaminant flux were evaluated by grouping associated compounds and summing the individual contaminant concentrations [ $\Sigma$ ]. Contaminant groupings included  $\Sigma$  HCB (pentachloro and hexachlorobenzene),  $\Sigma$  aldrin (aldrin, endrin, dieldrin),  $\Sigma$  BHC ( $\alpha$ ,  $\beta$ ,  $\gamma$ ),  $\Sigma$  chlordane (heptachlor, heptachlor epoxide,  $\alpha$ ,  $\gamma$ ) and  $\Sigma$  DDT (o,p-DDE, p,p-DDE, o,p-DDD, p,p-DDD, o,p DDT, p,p-DDT).

#### *Polysaccharides*

One litre of centrifuged water was rotary evaporated to between 20 and 50 ml. The final volume was recorded and stored in a 50 ml glass hypovial with an aluminum cap and teflon seal. Polysaccharide sample concentrations were measured against a series of glucose standards at an absorbance of 485 nm and a cell length of 1 cm. A Bausch and Lomb Spectronic 20 spectrophotometer was used.

#### *Statistical Analyses*

The statistical data presented were obtained using SPSS<sup>®</sup> for Windows<sup>™</sup>. Bivariate correlations for linear relationship were computed as Pearson coefficients ( $r$ ) with a two-tailed level of significance and confidence interval of 95 %.

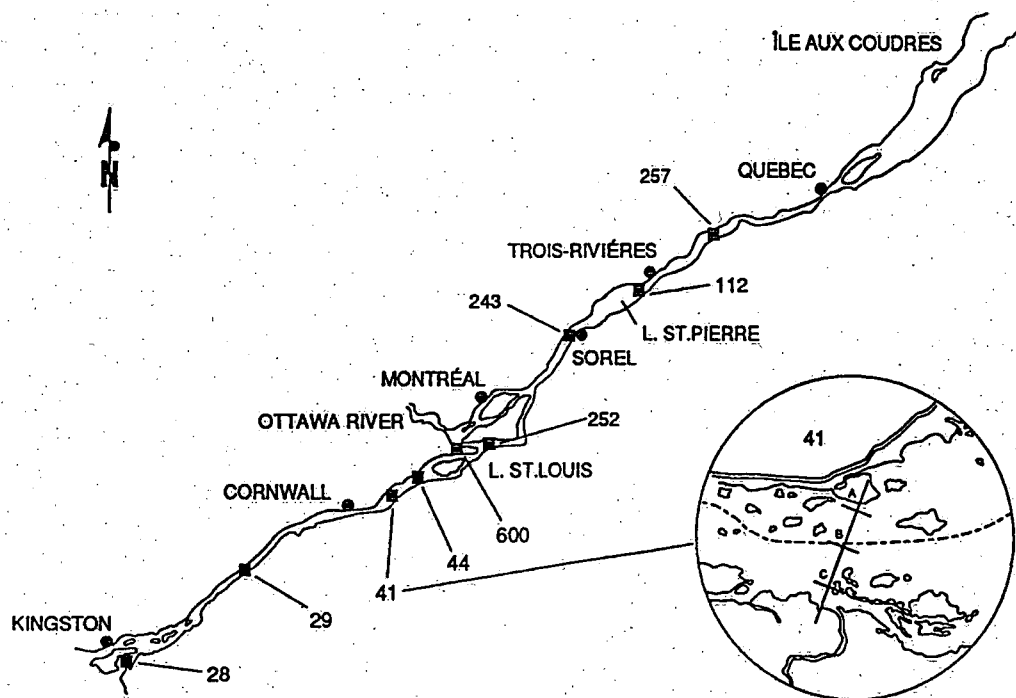


Figure 1. Sampling sites in the St. Lawrence River 1989 and 1990.

### *Polychlorinated biphenyls*

Polychlorinated biphenyls (PCB) were measured as individual congeners based on the dual capillary column procedure established at the 1985 PCB Workshop in Grosse Ile, Michigan (Mullin, 1985). Initial quantitation of PCB congeners was carried out using the primary Green Bay (GB) Mass Balance PCB Standard (Swackhamer, 1988) obtained through the University of Minnesota. The GB PCB standard is a mixture of Aroclors 1232, 1248 and 1262 (items #E107, #E108 and #E130) from the Quality Assurance Branch, U.S. EPA, Cincinnati, Ohio, in a ratio of 25:18:18. Individual congener concentrations were calibrated by Mullin (Mullin, 1985) for this specific PCB standard.

A second primary PCB standard (NOI Standard) was prepared using purchased Aroclor solutions of 200  $\mu\text{g ml}^{-1}$  1016, 1221, 1242, 1254, and 1262 (Supelco 4-8701; 4-8705; 4-8706; 4-8707; 4-4810) at ratios of 1:1:1:1:1 and reconstituted in hexane to a concentration of 1  $\mu\text{g ml}^{-1}$ . The NOI PCB standard was calibrated with the primary Green Bay standard and verified using individual laboratory standards (120), NRC CLB-1 chlorinated biphenyl marine reference, the Canadian Wildlife Service, (CWS) pooled herring gull egg standard and the four Integrated Atmospheric Deposition Network quality assurance mixtures.

PCB values reported here are given as total PCB based on the sum of the congener measurements.

### *Sample Quantitation and Quality Assurance*

Extracts were analyzed by dual capillary column gas chromatography utilizing electron capture detectors and a HP 5890 gas chromatograph. Two fused silica high performance capillary columns (i) 30 m HP-5 (Hewlett Packard) and (ii) 30 m DB-1 (Chromatographic Specialties, Brockville) with 0.25 mm internal diameter and 0.11  $\mu\text{m}$  phase thickness were employed. Samples were injected automatically (2  $\mu\text{l}$ ) into a split/splitless injector (250 °C) operated with a splitless hold time of 0.2 minutes. Initial chromatography conditions were 65 °C, isothermal for two minutes, 10 °C/minute to 110 °C, 3 °C/minute; final temperature 280 °C; 5 minute isothermal hold. The carrier gas was hydrogen.

Quantitation of organochlorine pesticides was based on dual column confirmation with less than 30% variance between mean values. Quantitative assurance was ascertained by verification with performance standards, compliance with specified fractionation procedures and continuous monitoring with method spikes. Quantitative values were assigned according to response factors based on instrument performance standards and retention time match for the compounds of concern. Acceptance windows were  $\pm 0.05$  minutes on both columns. Quantitation

procedures and standard reliability were checked regularly through quality control samples and participation in CAPCO Interlaboratory quality assurance studies. Conditions not meeting specified criteria or NOI protocol are not reported. Quantitated contaminant levels are assigned reliability qualifiers and archived in the NOI - Project data base presently under development (EDAMS, 1991).

## RESULTS

### Particulate Matter

#### *Suspended particulate matter (SPM)*

Periodic concentration measurements made using large volume water samples during May 1985, June 1986, July 1987, 1990 and October 1985, 1988 ranged from a low of 0.38 mg/l in October 1985 to a high of 24.5 mg/l in May 1985, with a five year mean concentration of  $0.96 \pm 0.46$  mg/l for Lake Ontario and  $10.8 \pm 3.0$  mg/l at Quebec City. The tenfold increase in SPM concentration with seaward direction resulted in a mean flux of  $3900 \pm 900$  kt/a of riverborne suspended particulate matter being exported to the estuary (Figure 2).

#### *Particulate organic matter (POM)*

The percent of organic matter (% POM) in SPM (Figure 3) ranged between 27 % to 65 % at the outflow of Lake Ontario with the highest concentration observed in July, 1987 and the lowest in October 1985. The % POM in river SPM decreased sharply with easterly direction within a range of 8.6-17% at Quebec City.

#### *Particulate organic carbon (POC)*

POC was the major component of the riverborne organic particulate organic matter contributing up to 65 %-100 % of the POM and 4.6 % to 83 % of SPM composition (Figure 4). Concentrations of POC remained relatively constant throughout the river (Table 4), with concentrations that ranged between 0.090 and 0.73 mg C/l and had a mean concentration of  $0.40 \pm 0.14$  mg C/l. The increased flux of POC (Figure 5) with distance downstream, was just about double the amount discharged by Lake Ontario with a total calculated annual flux for discharged POC of  $199 \pm 66 \times 10^3$  t/a. The lesser amounts of discharged POC would imply that new in-stream additions of SPM are significantly lower in organic carbon content and are therefore mainly inorganic.

#### *Chlorophyll*

Concentrations of chlorophyll (a) (Figure 6) and total chlorophyll [chlorophyll pheo-pigments and degraded or inactive chlorophyll (a)] (Figure 7) were higher during the summer periods (1987, 1989) and lower in the fall (1985, 1988). Elevated levels of chlorophyll (a) were observed in each of the riverine lakes for periods of known primary production

(Munwair and Munwair, 1986).

The particulate C/N ratio (Figure 8) was calculated using the particulate organic nitrogen concentrations and particulate organic carbon concentrations shown in Table 4.

#### Water

##### *Dissolved organic carbon (DOC)*

In the St. Lawrence river the DOC fraction was 20:1 of the POC fraction, atypical of natural aquatic systems. DOC concentrations ranged from 3.1 to 13 mg/l (Table 5) with a mean discharge flux of  $2.1 \times 10^6$  t/a. This value was similar to the  $1.8 \times 10^6$  t/a measured by Pocklington and Tan, 1987, for bimonthly samples over a four year period. Although DOC flux values varied within stream we found no apparent increase in the amount of DOC between the Lake Ontario input and Quebec City's discharge. The largest in-stream variations of DOC flux were observed downstream of the Montreal sewage treatment outfall. The highest values were found prior to 1987 prior to the completion of primary and secondary treatment processes. The DOC flux rates estimated from these measurements contradict those of Pocklington and Tan, (1987), who reported a doubling of DOC flux based on published values for Lake Ontario DOC (Chan, 1980) and their measurements at Quebec City. The reason they calculated double the DOC flux was as a result of DOC measurements determined by two separate analytical procedures (digestion vs combustion). The digestion procedure was used to measure Lake Ontario DOC and the combustion at Quebec City. These methods have now been shown to produce different values for the same samples with particular emphasis on organic matter content. Overall, samples analyzed using combustion gave higher results than those by digestion (Koprivnjak et. al., Comba and Kaiser, unpublished data). It is not clear yet, as to which method accurately estimates the true DOC.

##### *Polysaccharides*

Polysaccharide concentrations (Table 6) in 1989 within the St. Lawrence River ranged from 0.02 to 1.2 ppm. Their corresponding proportions in DOC content ranged from 0.6 % to 16%.

##### Organochlorine contaminants

There were no remarkable differences between mean concentrations of PCB and or the other pesticides between 1989 and 1990 samples (Table 7). Concentrations of adsorbed pesticides were in the low parts per billion (dry weight) ranging from below detectable levels (BDL) to 24 ng/g in 1989 (Table 8) and BDL-14 ng/g in 1990

**Table 6. Polysaccharide concentrations in St. Lawrence River centrifuged water, 1989.**

Station	mg/l	% DOC
28	0.28	3.5
29	0.56	16
44	0.02	0.59
600	0.88	14
252	0.20	6.5
243	1.2	2.7
112	0.56	6.6
257	0.60	15

(Table 9) pesticides. PCB concentrations were somewhat higher, ranging from 65-780 ng/g in 1989 and 150-400 ng/g in 1990. Concentrations of organochlorine pesticides in centrifuged water were also similar between 1989 (Table 10) and 1990 (Table 9). Values in the low parts per trillion ranged from BDL-0.56 ng/l and BDL-0.95 ng/l respectively. The corresponding ranges in PCB concentration were 0.35-1.7 ng/l and 0.37-0.57 ng/l.

The 1989 and 1990 flux estimates for grouped organochlorines ( $\Sigma$ 's of BHC, aldrin, DDT, chlordane, HCB, PCB) and mirex in water and SPM are shown in figures 10 through 23. As there were no major differences in contaminant concentrations between years, then the 1989 and 1990 flux values were also similar. As in past surveys (Comba et al., 1989a, 1989b, 1990), all monitored contaminants exhibited internal flux variability. The consistent observation of intermittent increases of in-stream contaminant flux were interpreted to represent contaminant introduction from point sources, resuspended contaminated sediment, or both. This was concluded through the occurrence of mirex and pp-DDT. In the case of mirex, the only known significant origin was Lake Ontario; and therefore internal fluxes greater than observed inputs would be caused by resuspension of previously deposited materials. On the other hand, the increases in the  $\Sigma$ DDT included the measurement of pp-DDT. The observation of DDT's active ingredient which rapidly degrades to products of DDE and DDD, could only be interpreted as current inputs, even though the application of this compound was banned in the 1970's. The continued active usage of DDT in the St. Lawrence River watershed, and most notably in the Quebec corridor was reported as recently as 1991 (Pham et al., 1993).

**Table 4. Concentrations (mg/l) of particulate organic carbon (ppm C) and organic nitrogen (ppm N) in the St. Lawrence River, 1985-1990.**

Particulate organic carbon							Particulate organic nitrogen					
Station*	October 85	June 86	June 87	October 88	June 89	July 90	October 85	June 86	June 87	October 88	June 89	July 90
27		0.46	0.35	0.41				0.075	0.059	0.054		
28		0.48	0.38	0.33	0.33			0.077	0.063	0.043	0.046	
29		0.38	0.39		0.28	0.37		0.061	0.065		0.043	0.060
31		0.48	0.51					0.076	0.071			
32		0.49	0.55					0.078	0.087			
41	0.26	0.39	0.38	0.25			0.028	0.061		0.034		
44	0.33				0.18	0.23	0.034				0.025	0.031
51	0.19		0.36	0.090			0.022		0.054	0.008		
574(254)	0.28	0.48	0.33				0.023	0.075	0.054			
56	0.21	0.49					0.037	0.070				
252		0.48	0.37		0.19	0.30		0.075	0.058		0.029	0.049
22	0.22		0.38				0.024		0.045			
600					0.46						0.066	
251		0.46	0.47					0.067	0.058			
243		0.68	0.71	0.48	0.23			0.093	0.083	0.049	0.033	
95	0.36						0.033					
504			0.52						0.081			
112	0.37	0.62	0.48		0.43	0.51	0.033	0.089	0.059		0.061	0.090
255			0.61						0.080			
257					0.49	0.44					0.078	0.050
253		0.73	0.59	0.43				0.11	0.081	0.038		

\* For locations see references (Comba et al., 1989,1990).

Table 5. Concentration (mg/L) of dissolved organic carbon (DOC) during June in the St. Lawrence River.

Station <sup>a</sup>	27	28	29	41	44	51	252	22	600	251	243	504	112	255	257	253
1987	8.6	6.3	6.1	5.8		6.7	5.7	7.9		11	13	4.1	7.6	7.0		6.1
1989		8.1	3.6		3.4		3.1		6.3				8.5			
1990			4.3		4.2		3.4				4.4		4.2		4.0	

<sup>a</sup> For locations see references (Comba et. al., 1989,1990).

Table 7. Mean concentrations of organochlorines in water (ng/l) and SPM (ng/g) during 1989-1990.

	ΣBHC	ΣChlordane	ΣAldrin	ΣDDT	ΣHCB	ΣPCB	Mirex
Water 1989	0.65±0.43	0.041±0.063	0.12±0.20	0.082±0.16	0.010±0.008	0.97±0.48	0.003±0.003
Water 1990	0.84±0.40	0.029±0.046	0.12±0.56	0.076±0.060	0.073±0.14	0.48±0.07	0.001±0.001
SPM 1989	2.1±0.63	13±9.1	11±11	10±7.7	1.5±0.9	170±62	2.1±0.63
SPM 1990	1.4±1.1	10±5.8	13±6.4	8.0±3.1	2.8±1.9	250±100	1.4±1.1

**Table 8.** Concentration (ng/g, dry weight) of organochlorine contaminants in St. Lawrence River suspended sediment, 1989.

Station No.*	28	29	44	112	243	252	257	41A	41B	41C	600
Weight (g)	2.06	5.0	4.65	10.13	10.07	10.12	10.14	1.84	1.84	2.91	1.02
PCB	0.54	0.87	0.78	0.3	0.36	0.48	0.3	0.92	0.87	0.78	BDL
HCB	0.5	1.6	1.5	0.34	0.52	0.8	0.58	2.1	1.8	1.4	BDL
HEPTACHLOR	2.1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
ALDRIN	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
OP-DDE	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
PP-DDE	7.3	5.5	5.8	1.1	2.5	2.3	1.6	4.5	5.1	4.3	15
OP-DDT	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
PP-DDT	2.4	1.3	1.6	0.41	1.2	0.82	0.9	1.7	2.7	2.1	13
MIREX	1.5	1.7	1.6	0.19	0.74	0.59	0.38	BDL	1.6	1.6	BDL
A-BHC	1.6	3.4	2.8	1.5	0.79	1.7	1	1.5	1.7	0.74	2.6
B-BHC	1.8	4	7.6	1.3	1.3	6.6	0.56	3.7	5.5	BDL	3.2
G-BHC	1.9	3.2	6.7	1.3	1.2	0.97	0.88	BDL	BDL	BDL	BDL
HEPEPOXIDE	4.7	4.5	4.3	0.95	1.2	2.2	1.5	4.4	4.5	BDL	8.1
G-CHLORDANE	4.3	3.1	3.1	1.2	1.5	2.6	1.4	2.3	3.2	1.9	3.6
A-ENDOSULFAN	7.5	5.1	5.4	1.9	1.1	2.4	1.3	2.9	4.9	3.1	7.2
A-CHLORDANE	5.1	9.8	5.6	1.2	1.8	3.6	2.2	1.7	7.6	3.1	6.2
DIELDRIN	18	24	12	1.7	1.9	4.9	1.8	9.2	13	6.5	8.5
OP-DDD	19	7.8	3.7	1.2	1.7	3.5	1.8	3	7.1	3	6.9
ENDRIN	BDL	3.6	BDL	5.1	4.7	11	8.9	BDL	BDL	BDL	BDL
B-ENDOSULFAN	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
PP-DDD	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Total PCB	270	140	190	65	110	170	150	150	210	230	780

\* see figure 1 for locations.



**Table 9.** Concentrations of organochlorine contaminants in 1990 St. Lawrence River centrifuged water (ng/l) and suspended particulate matter (ng/g, dry weight) at 5 m depth.

DATE	June 26	June 27	June 29	June 28	June 30	June 26	June 27	June 29	June 28	June 30
GMT TIME (Z)	1714	1630	1100	1215	0115	1714	1630	1100	1215	0115
STATION	29	44	112	252	257	29	44	112	252	257
Sample amount	200 l	200 l	200 l	200 l	200 l	8 g	8 g	10 g	8 g	10 g
Water										
PECB	0.02	0.005	0.32	0.003	0.002	4.7	2.1	1.1	1.5	1.1
HCB	0.003	0.004	0.004	0.005	0.005	1.5	0.66	0.52	0.60	0.44
HEPTACHLOR	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
ALDRIN	BDL	BDL	0.004	BDL	0.01	BDL	BDL	0.93	BDL	BDL
OP-DDE	BDL	0.01	BDL	0.1	0.002	BDL	BDL	BDL	BDL	BDL
PP-DDE	0.005	0.004	0.004	0.002	0.003	BDL	BDL	BDL	BDL	BDL
OP-DDT	0.001	0.01	0.02	BDL	BDL	BDL	BDL	1.1	BDL	1.6
PP-DDT	BDL	BDL	BDL	BDL	0.15	BDL	BDL	0.37	4.5	2.2
MIREX	0.001	0.001	0.001	0.001	0.001	3.1	1.6	0.40	1.2	0.25
A-BHC	0.32	0.54	0.58	0.88	0.95	2.9	BDL	BDL	1.5	0.99
B-BHC	0.06	0.06	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
G-BHC	0.11	0.14	BDL	BDL	0.58	BDL	BDL	0.37	BDL	1.3
HEPEPOXIDE	0.02	0.03	BDL	BDL	0.05	2.1	1.3	0.77	1.3	0.70
G-CHLORDANE	0.005	0.01	BDL	BDL	0.06	1.9	2.0	0.60	1.2	0.85
A-ENDOSULFAN	BDL	0.01	BDL	0.07	BDL	5.9	BDL	BDL	BDL	BDL
A-CHLORDANE	BDL	0.01	BDL	0.04	BDL	2.9	2.5	0.86	1.7	1.0
DIELDRIN	0.05	0.07	0.14	BDL	0.17	14	BDL	0.99	3.8	1.1
OP-BDD	BDL	0.01	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
ENDRIN	BDL	0.03	BDL	BDL	BDL	8.3	9.9	BDL	4.0	BDL
B-ENDOSULFAN	BDL	BDL	BDL	BDL	BDL	2.6	BDL	BDL	BDL	BDL
PP-DDD	BDL	0.06	BDL	BDL	BDL	12	8.5	1.9	4.3	3.3
Total PCB	0.48	0.51	0.57	0.37	0.45	400	200	150	300	190

a See figures for locations.

**Table 10.** Concentration (ng/l) of organochlorine contaminants in St. Lawrence River centrifuged water (APLE) samples, June/July 1989.

Station No. *	28	29	41A	41B	41C	44	112	243	252	257	800
PCB	0.002	0.01	0.02	0.005	0.01	0.01	0.003	0.02	0.01	0.003	0.002
HCB	0.002	BDL	0.02	0.006	0.02	0.01	0.004	0.004	0.01	0.003	0.002
HEPTACHLOR	BDL	BDL	BDL	BDL	BDL	0.01	0.004	0.02	BDL	BDL	0.02
ALDRIN	0.002	BDL	BDL	0.01	BDL	BDL	0.01	BDL	0.06	0.004	BDL
OP-DDE	BDL	0.03	0.01	BDL	BDL	BDL	BDL	0.56	BDL	0.02	BDL
PP-DDE	0.013	0.02	0.02	0.01	0.02	0.005	0.005	0.01	0.02	0.004	0.002
OP-DDT	0.011	0.04	0.03	0.002	BDL	0.01	BDL	BDL	BDL	BDL	0.01
PP-DDT	0.01	0.32	0.01	0.03	BDL	BDL	BDL	BDL	BDL	0.008	BDL
MIREX	0.0003	0.004	0.007	0.001	0.01	0.001	0.001	0.001	0.003	0.0002	BDL
A-BHC	0.66	I	I	0.62	I	I	0.78	I	I	0.36	0.2
B-BHC	0.07	I	I	0.06	I	I	0.08	I	I	0.06	0.02
G-BHC	0.16	I	I	0.13	I	I	0.02	I	I	BDL	0.06
HEP EPOXIDE	0.03	I	I	0.02	I	I	0.06	I	I	0.01	0.01
G-CHLORDANE	0.01	I	I	BDL	I	I	0.04	I	I	BDL	BDL
A-ENDOSULFAN	0.02	I	I	0.01	I	I	BDL	I	I	0.02	0.01
A-CHLORDANE	0.01	I	I	0.01	I	I	0.04	I	I	0.01	BDL
DIELDRIN	0.08	I	I	0.12	I	I	0.14	I	I	0.08	BDL
OP-DDD	0.01	I	I	BDL	I	I	BDL	I	I	0.01	0.01
ENDRIN	0.03	I	I	0.01	I	I	BDL	I	I	BDL	0.04
B-ENDOSULFAN	0.01	I	I	BDL	I	I	0.45	I	I	0.03	BDL
PP-DDD	0.02	I	I	0.04	I	I	BDL	I	I	0.01	0.02
Total PCB	0.35	1.7	0.97	0.83	1.7	0.66	0.66	0.92	1.1	0.49	0.41

I = no result, chromatographic interference.

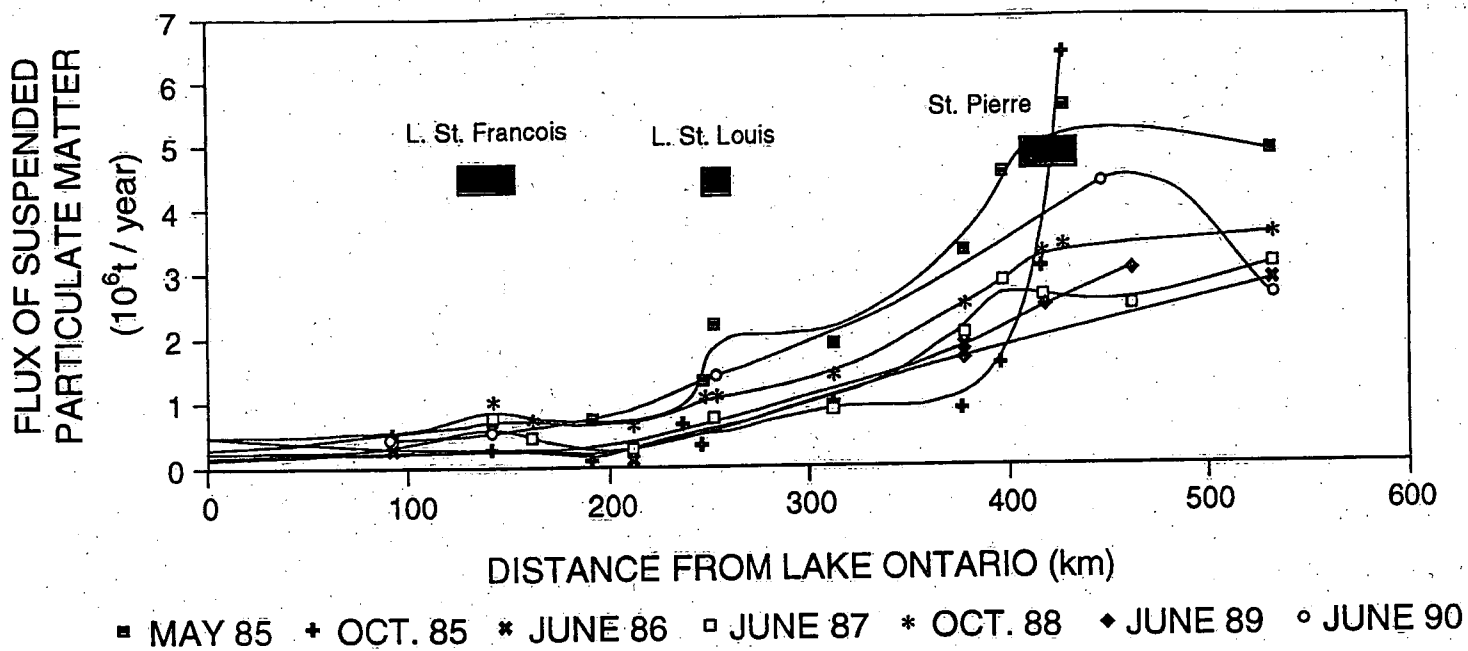


Figure 2. Flux ( $10^6$  t/a) of suspended particulate matter in the St. Lawrence River.

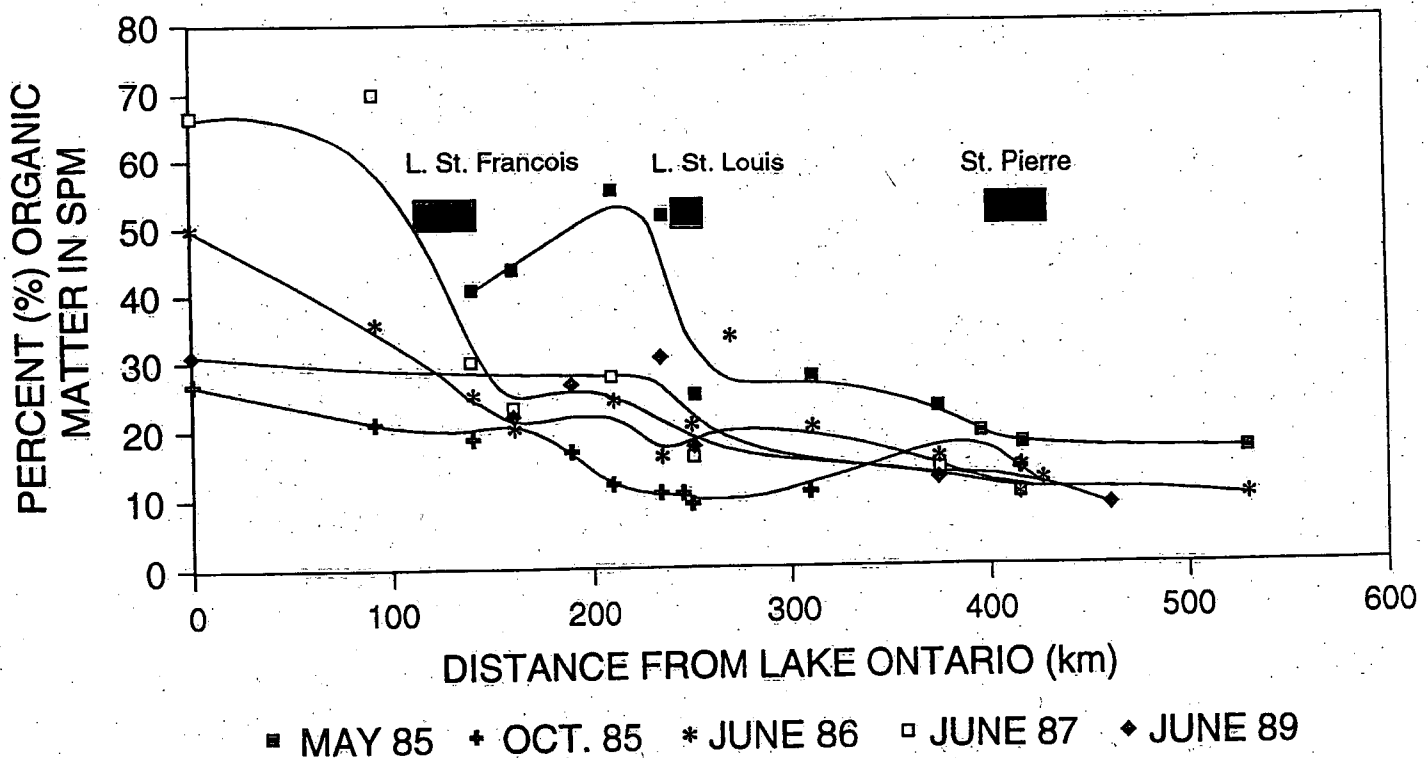


Figure 3. Percent (%) organic matter in St. Lawrence River suspended particulate matter.

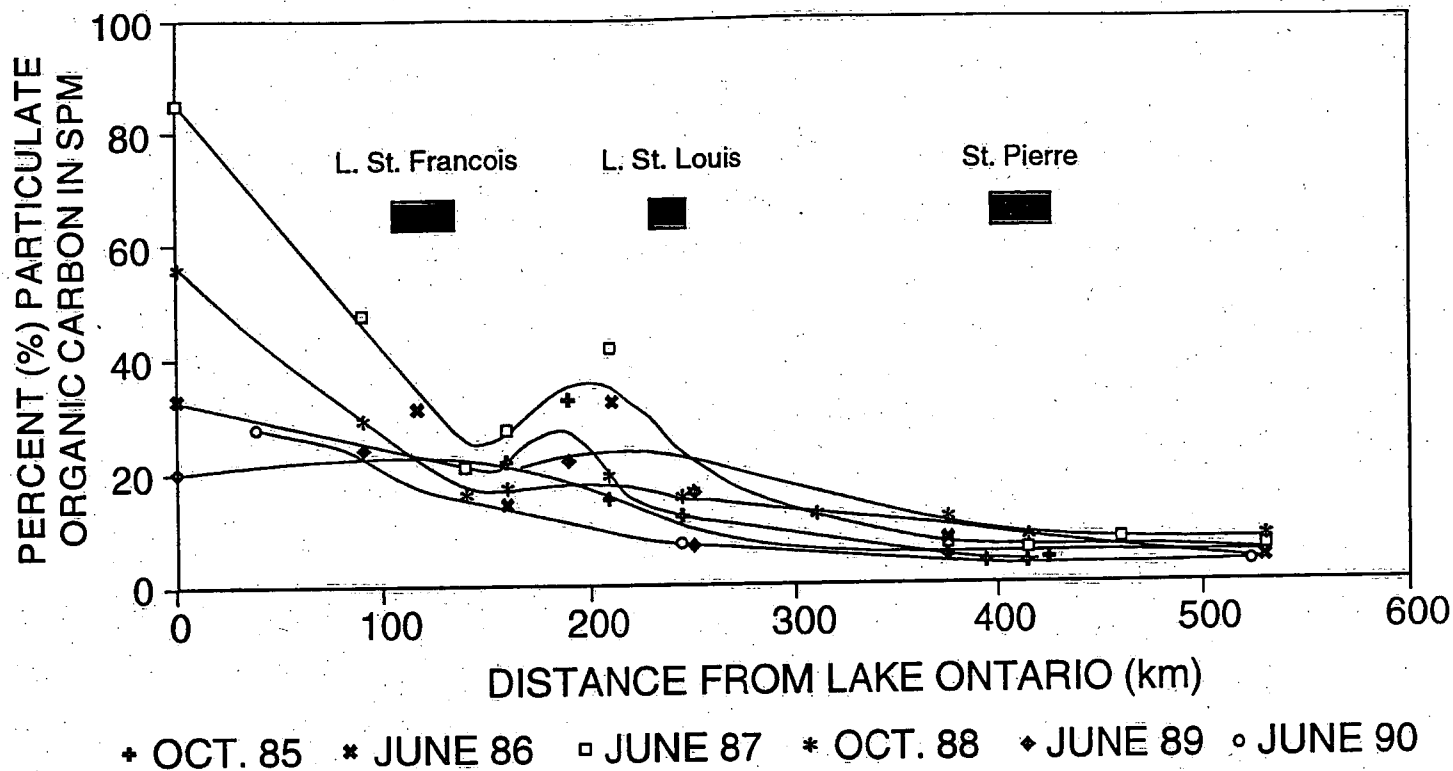


Figure 4. Percent (%) particulate organic carbon in St. Lawrence River suspended matter.

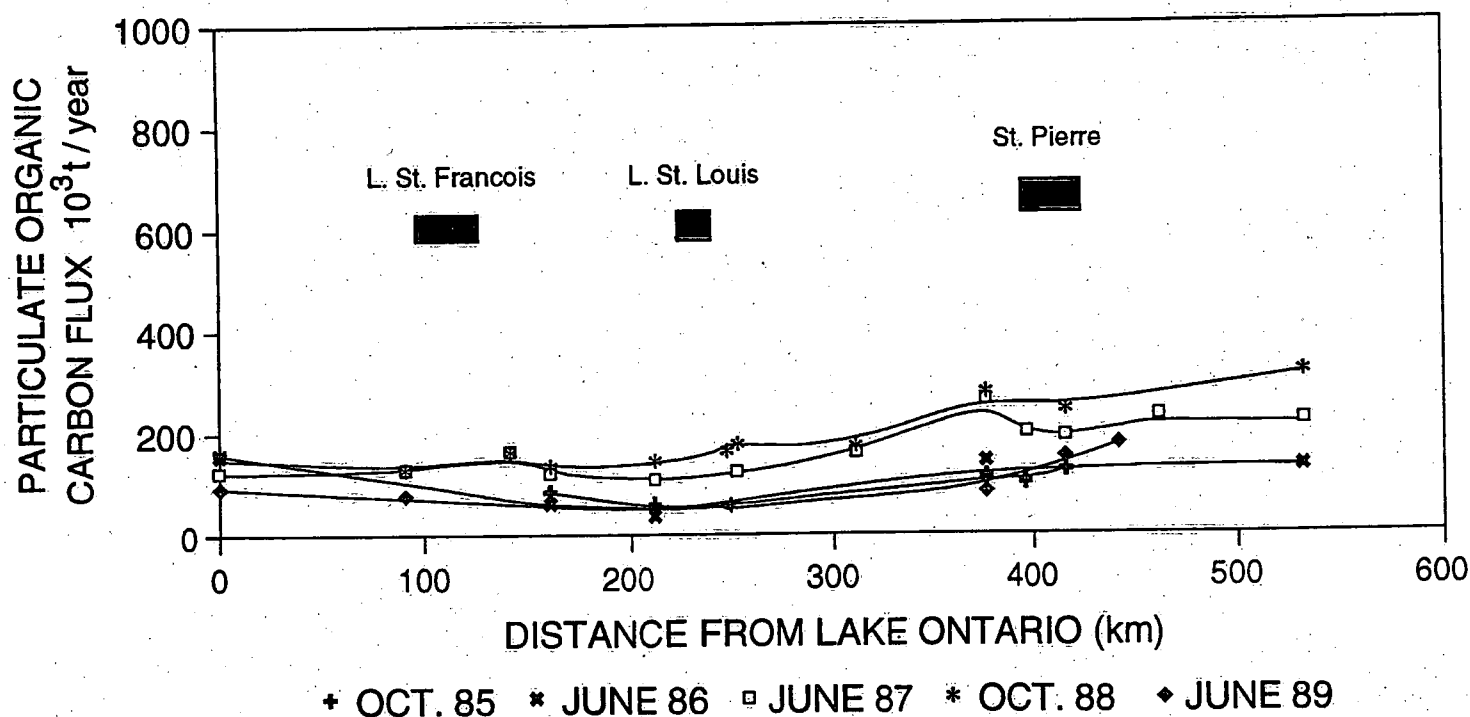


Figure 5. Flux ( $10^6$  t/a) of particulate organic carbon in St. Lawrence River suspended matter.

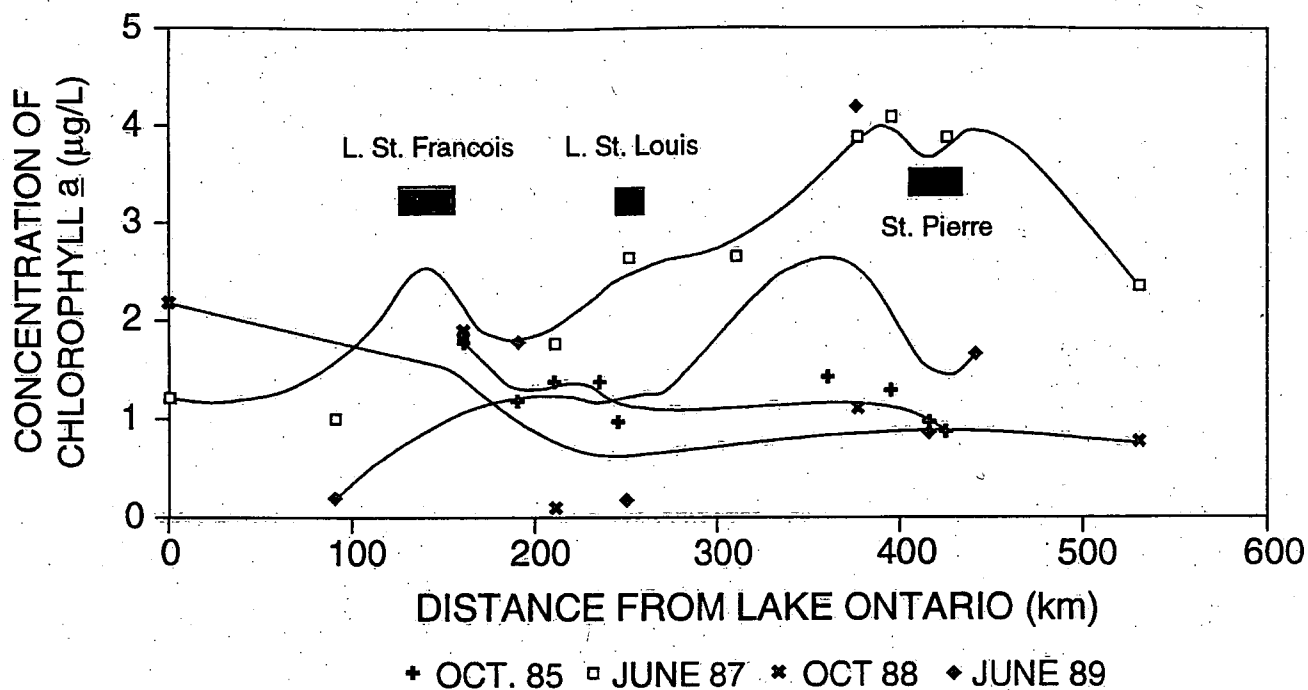


Figure 6. Concentration (ppm) of chlorophyll *a* in St. Lawrence River water.

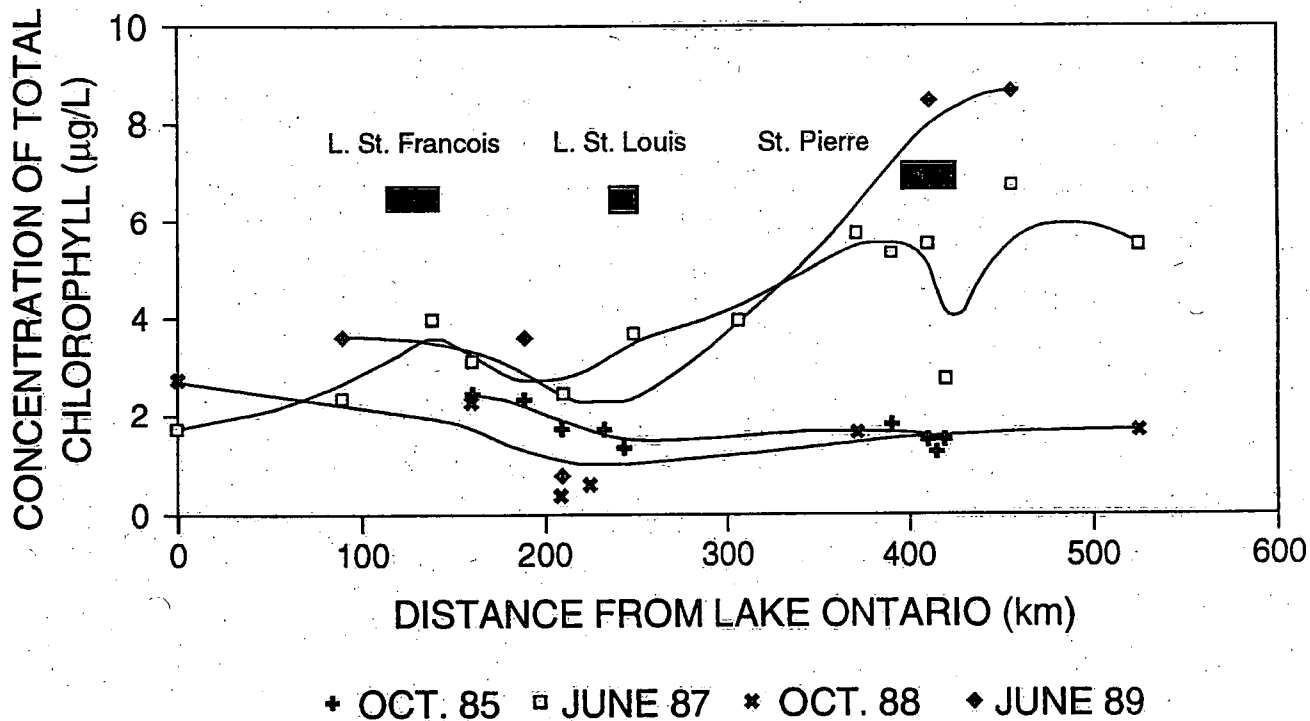
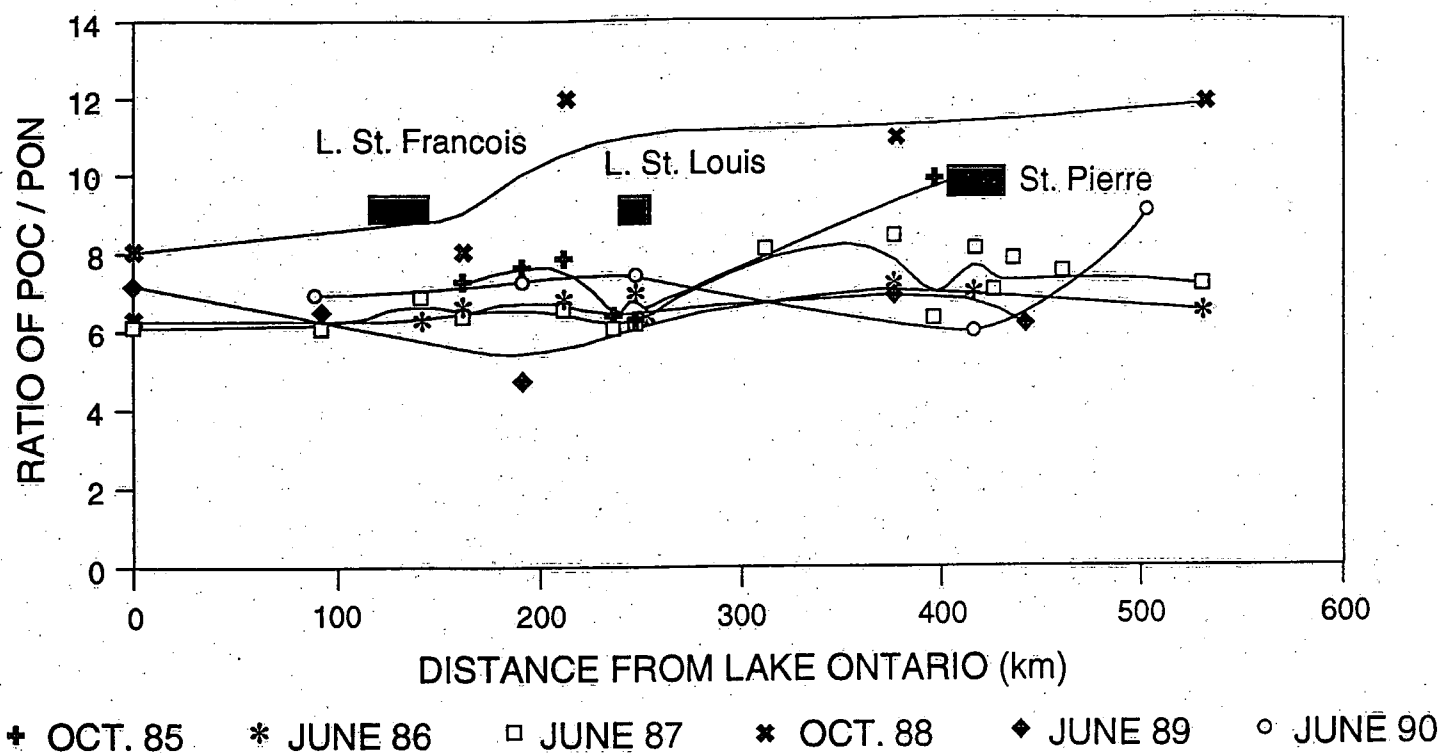
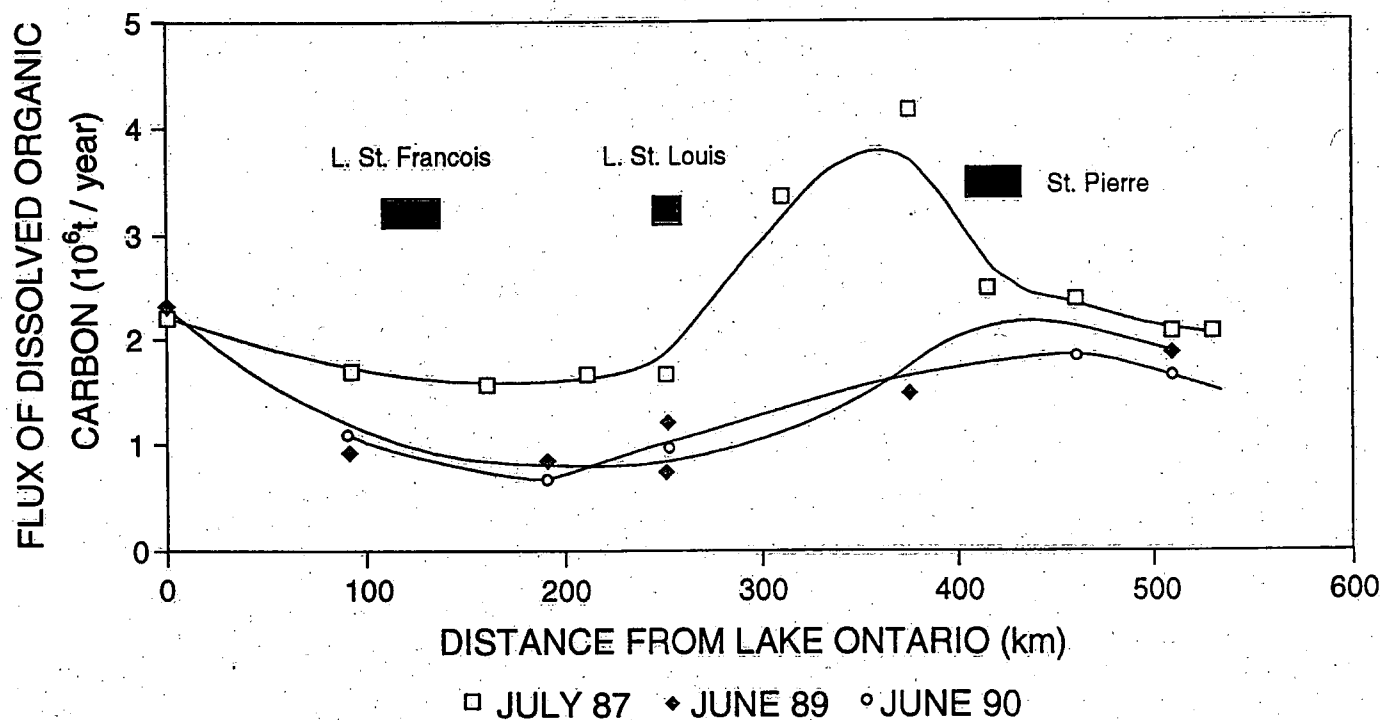


Figure 7. Concentration (ppm) of total chlorophyll in St. Lawrence River water.



**Figure 8.** Ratio of particulate organic carbon and particulate organic nitrogen (POC/PON) in St. Lawrence River suspended matter.



**Figure 9.** Flux ( $10^6$  t/a) of dissolved organic carbon (DOC) in St. Lawrence River.

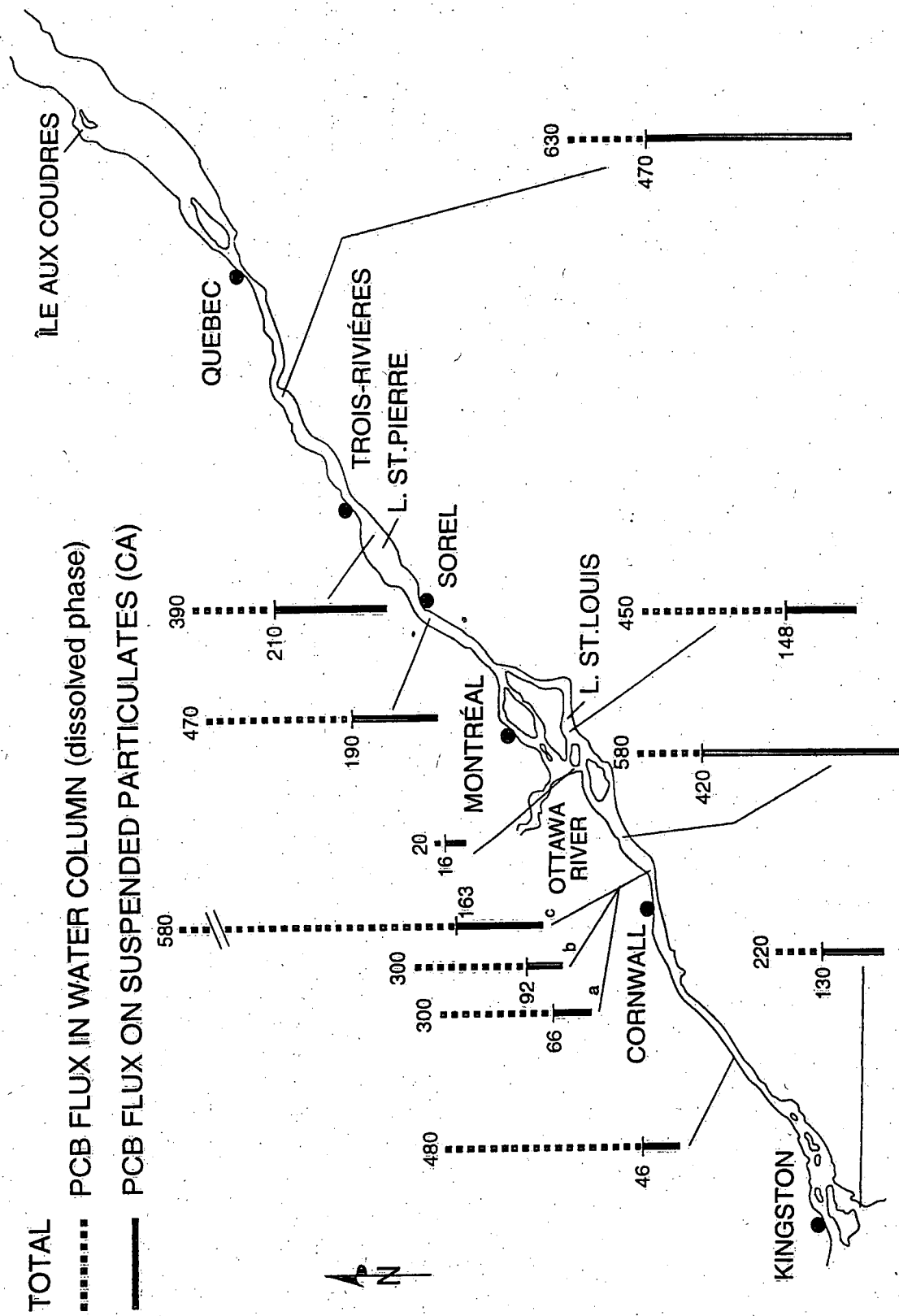


Figure 10. PCB flux (kg/a) in suspended particulates and water of the St. Lawrence River, June/July, 1989.

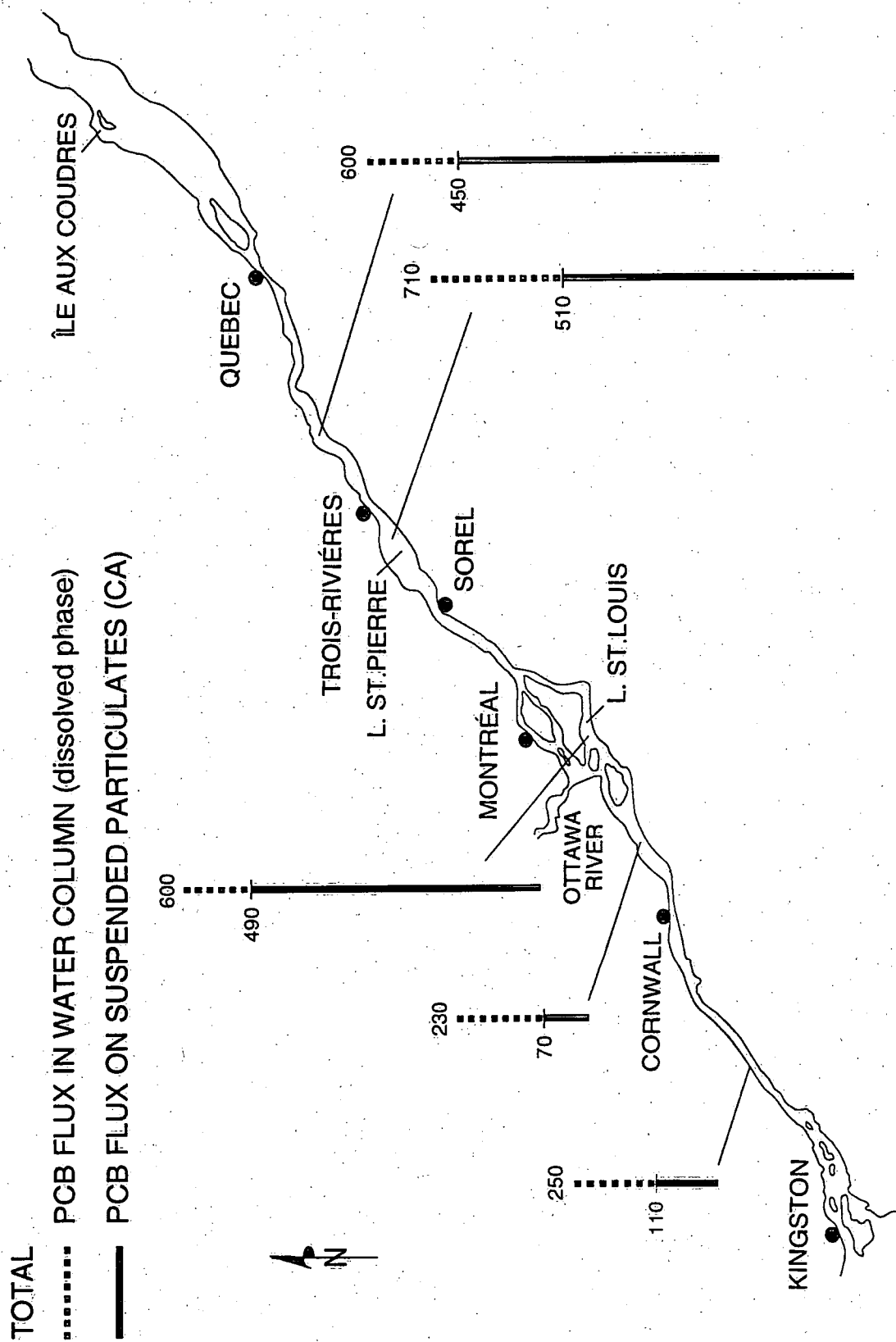


Figure 11. PCB flux (kg/a) in suspended particulates and water of the St. Lawrence River, June, 1990.



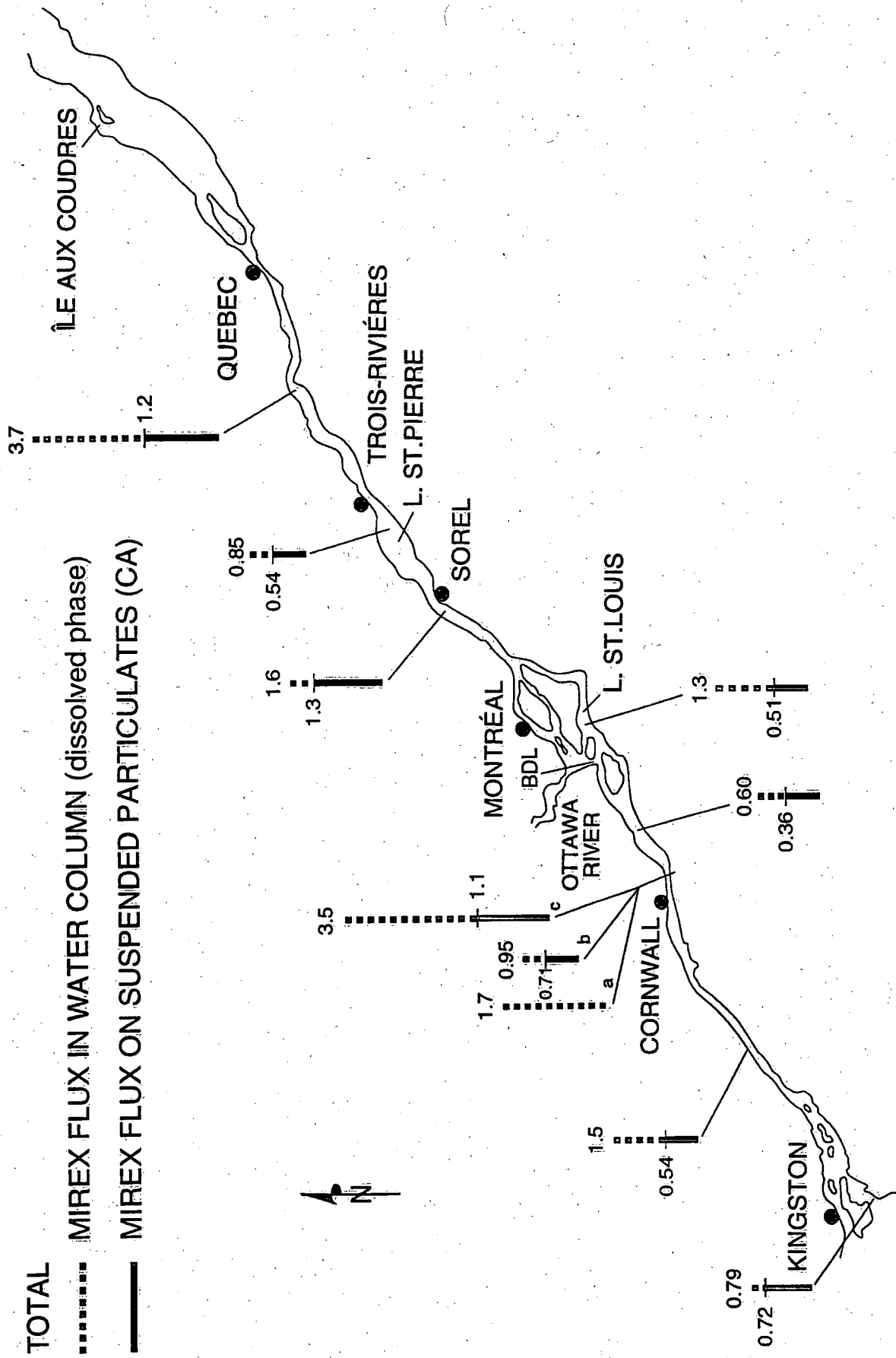


Figure 12. Mirex flux (kg/a) in suspended particulates and water of the St. Lawrence River, June/July, 1989.

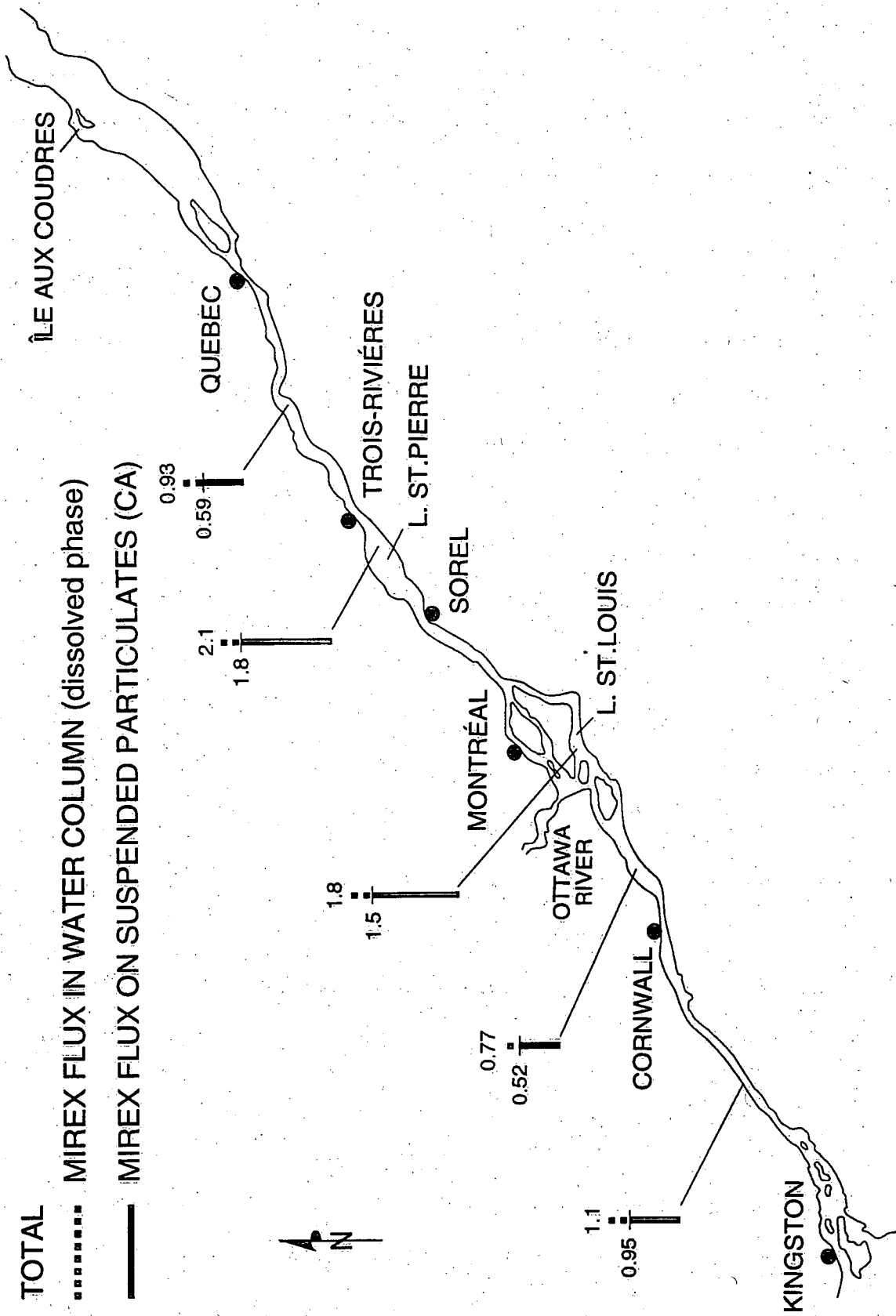
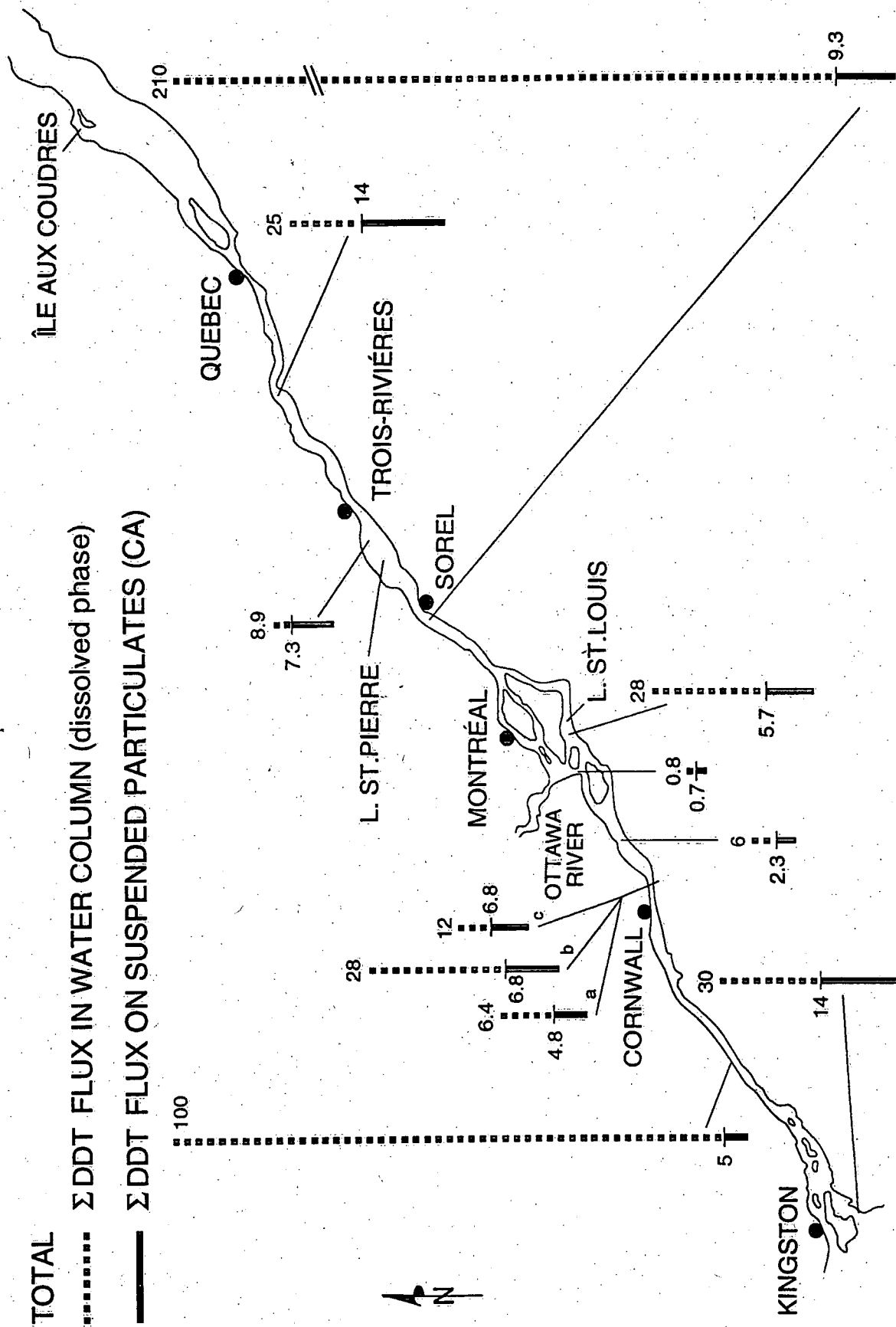


Figure 13. Mirex flux (kg/a) in suspended particulates and water of the St. Lawrence River, June, 1990.



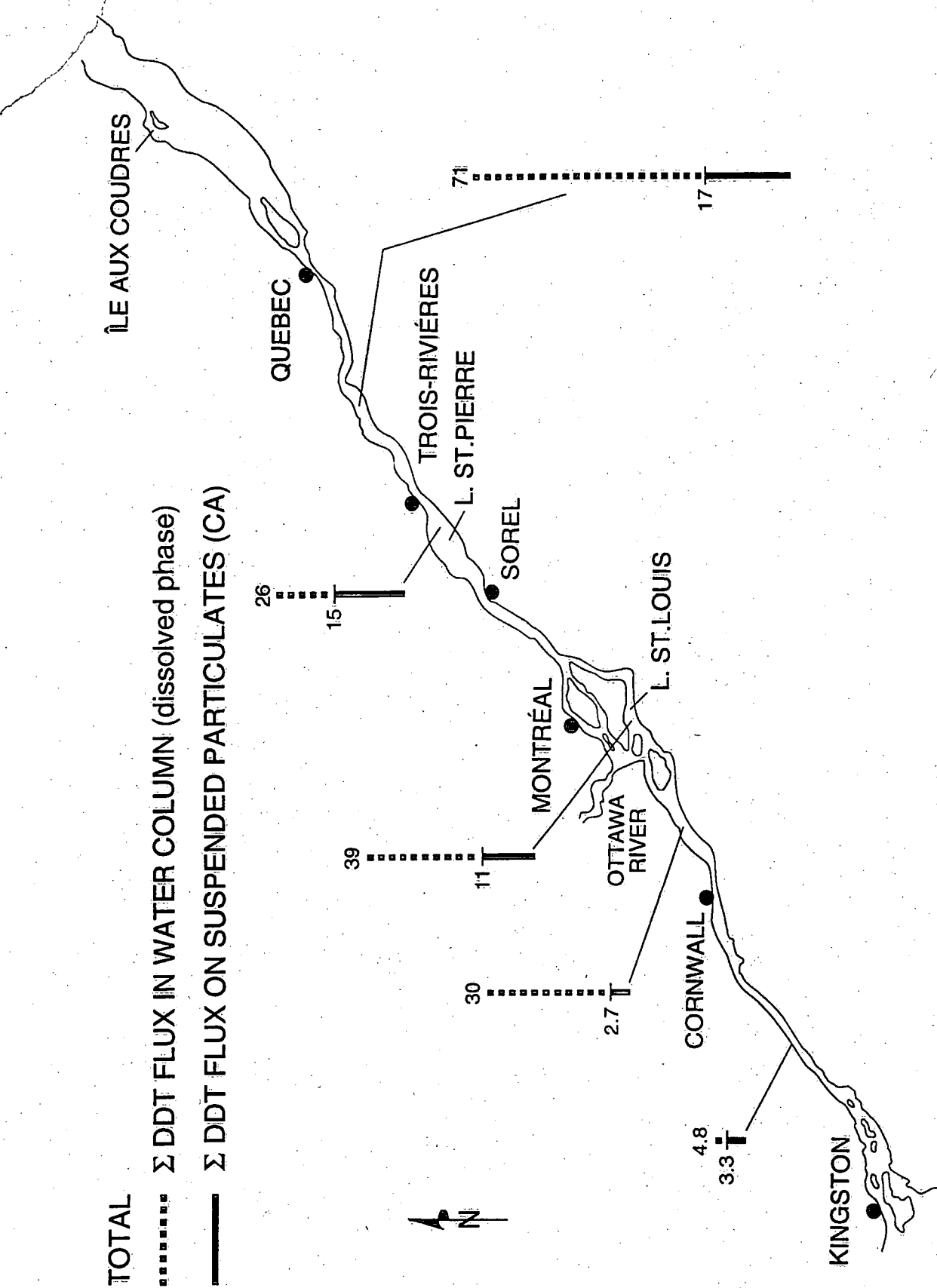


Figure 15.  $\Sigma$  DDT flux (kg/a) in suspended particulates and water of the St. Lawrence River, June, 1990.

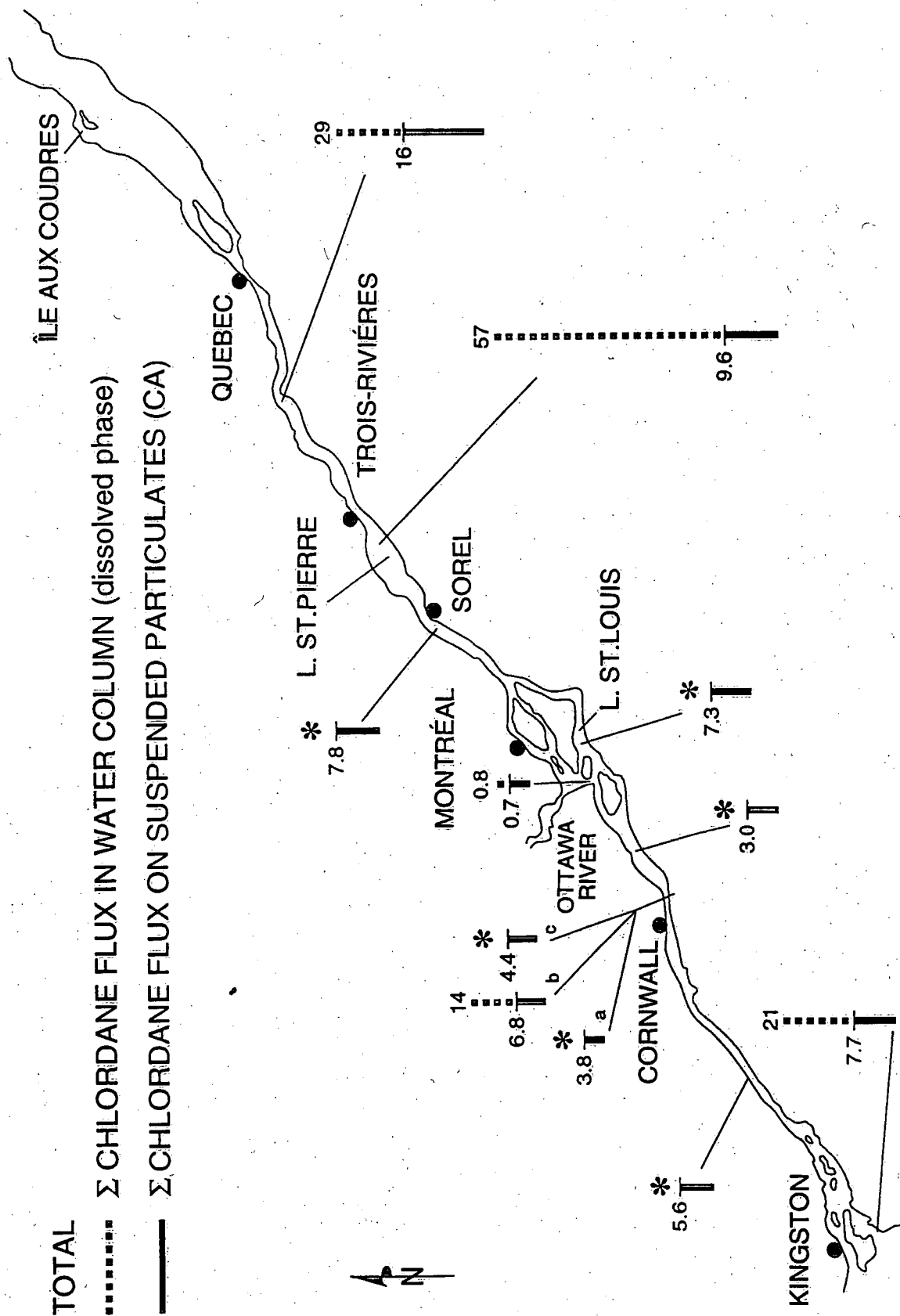


Figure 16. Σ Chlordane flux (kg/a) in suspended particulates and water of the St. Lawrence River, June/July, 1989.  
 (\* = interference)

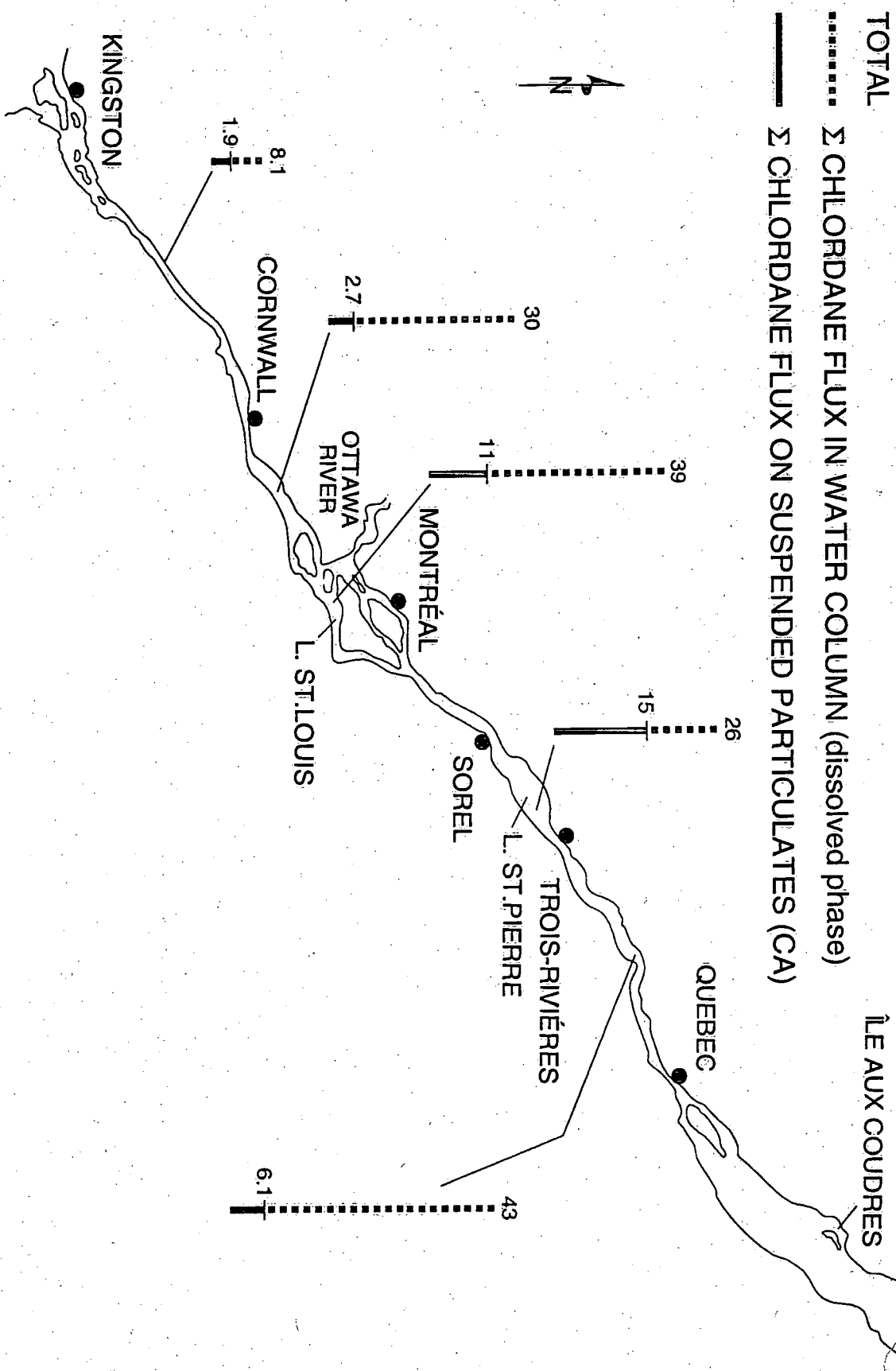
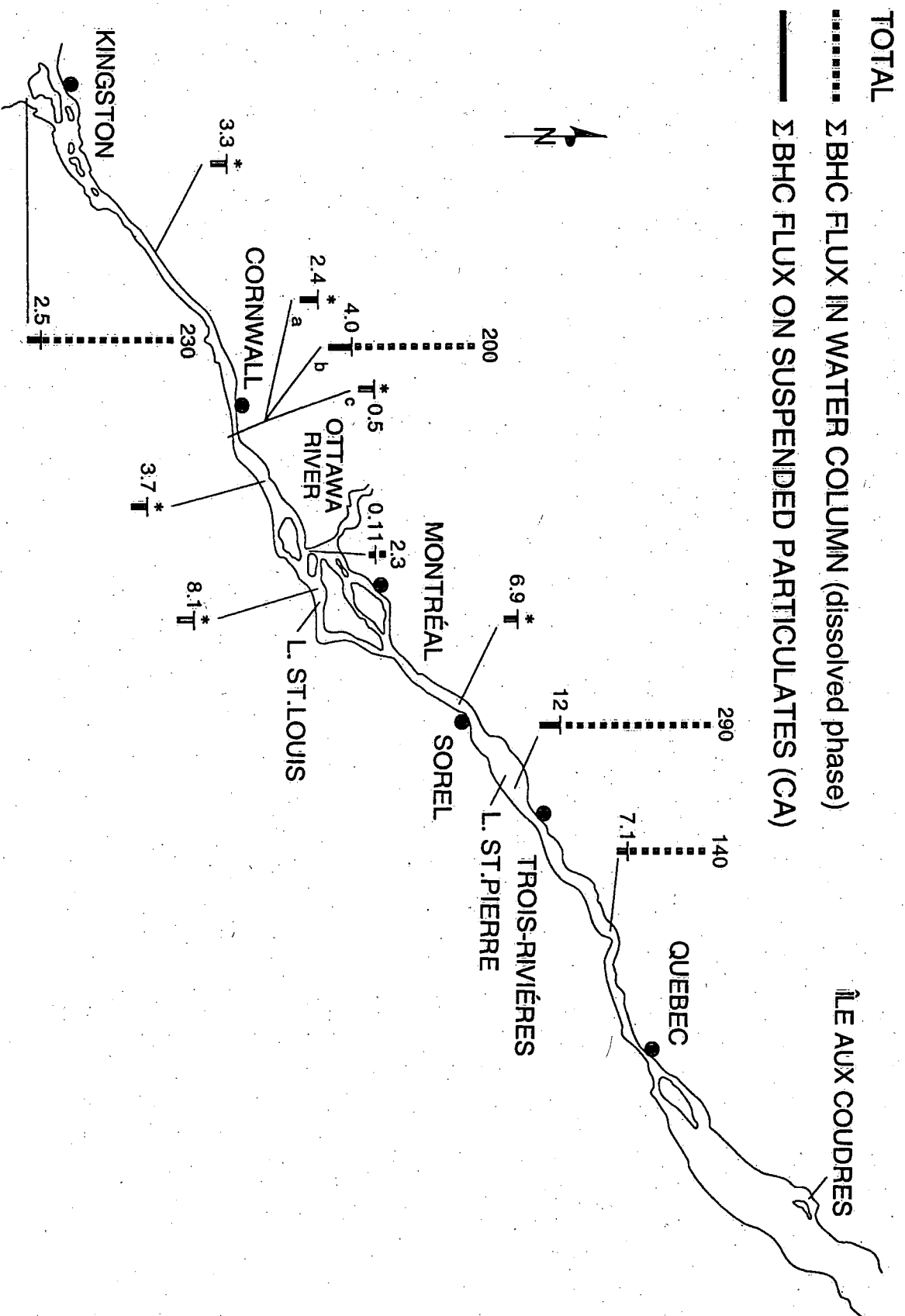


Figure 17.  $\Sigma$  Chlordane flux (kg/a) in suspended particulates and water of the St. Lawrence River, June, 1990.



**Figure 18.**  $\Sigma$  BHC flux (kg/a) in suspended particulates and water of the St. Lawrence River, June/July, 1989.  
 (\* = interference)

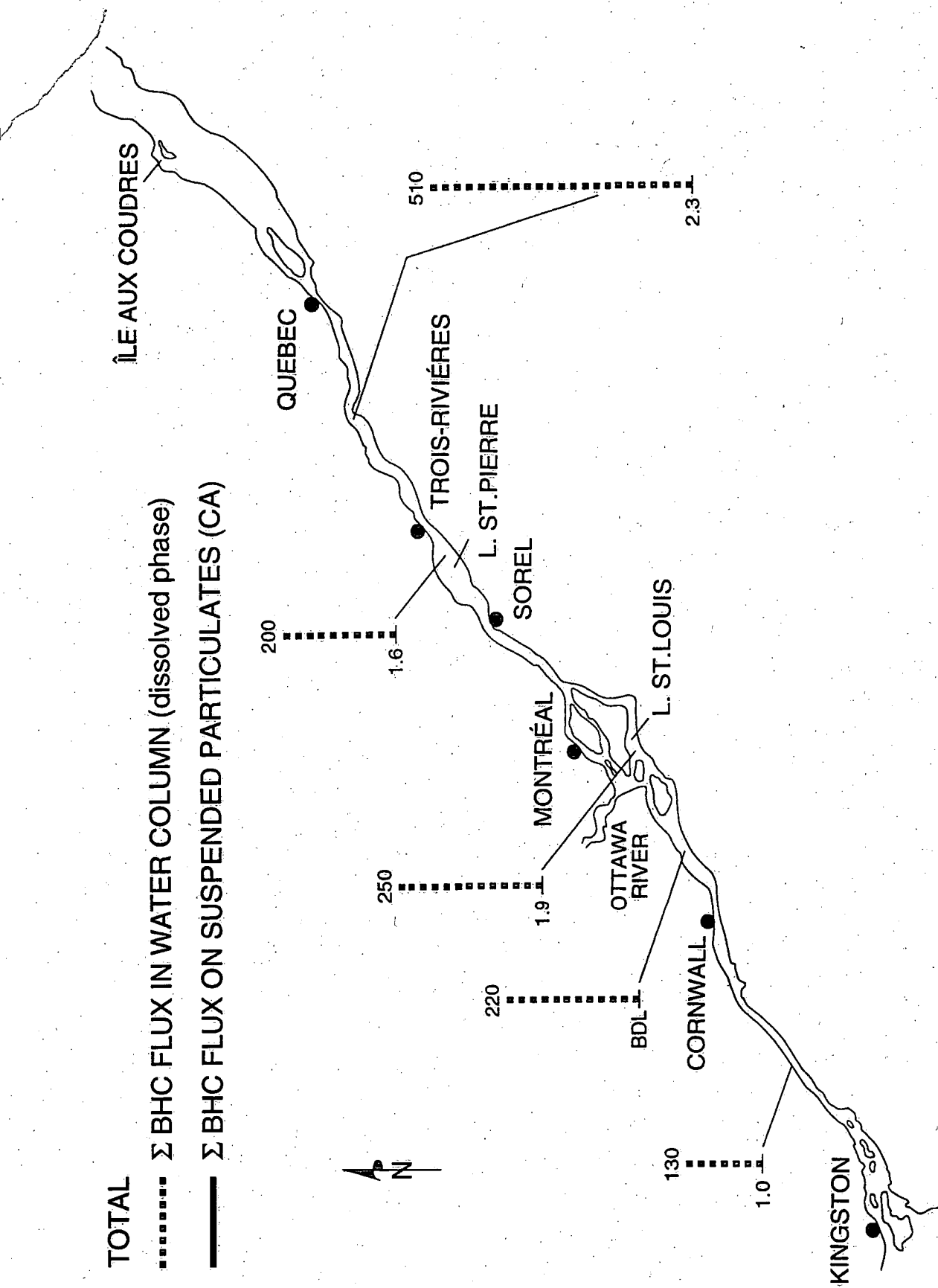


Figure 19.  $\Sigma$  BHC flux (kg/a) in suspended particulates and water of the St. Lawrence River, June, 1990.



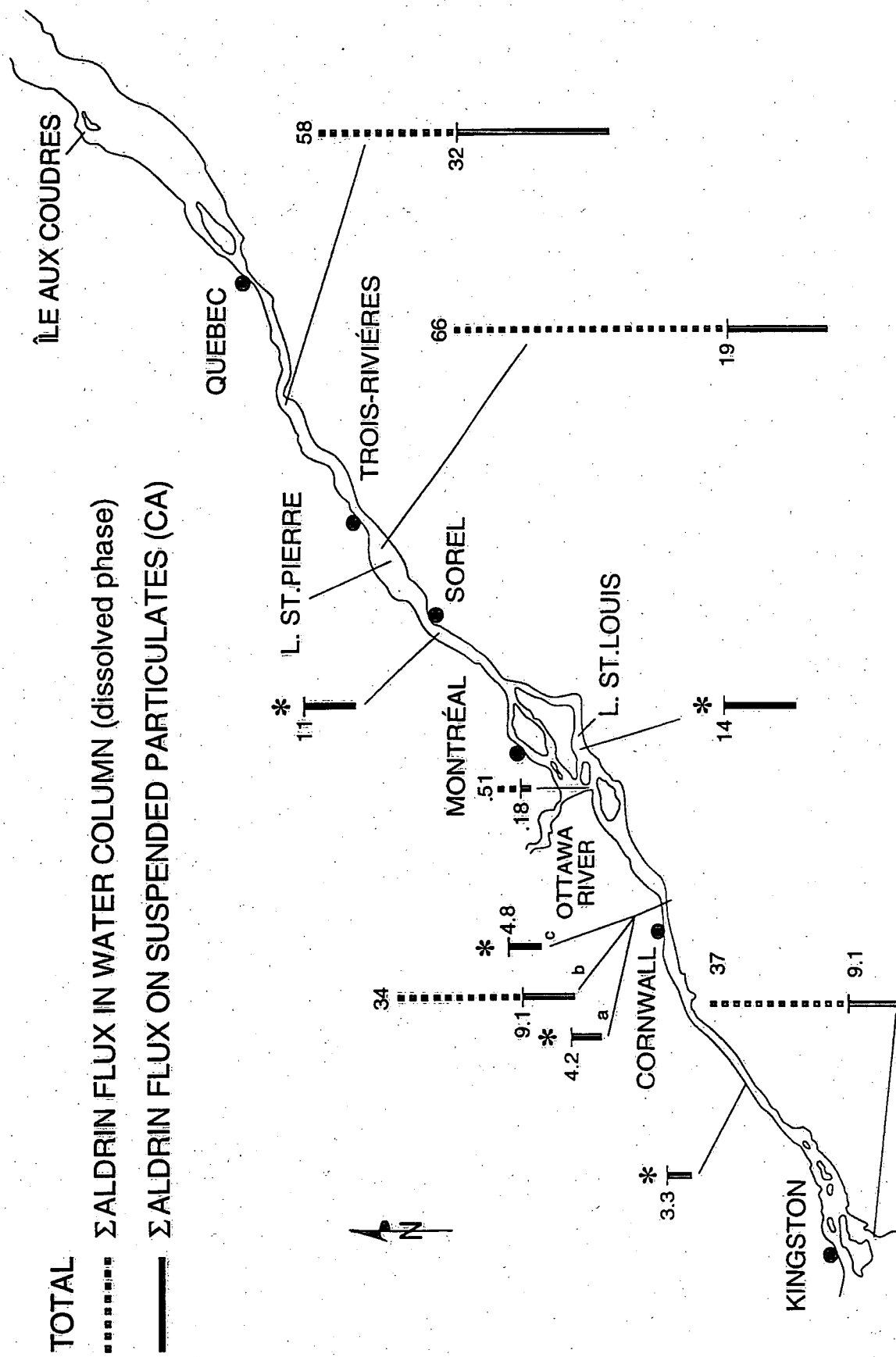


Figure 20.  $\Sigma$  Aldrin flux (kg/a) in suspended particulates and water of the St. Lawrence River, June/July, 1989.  
(\* = interference)

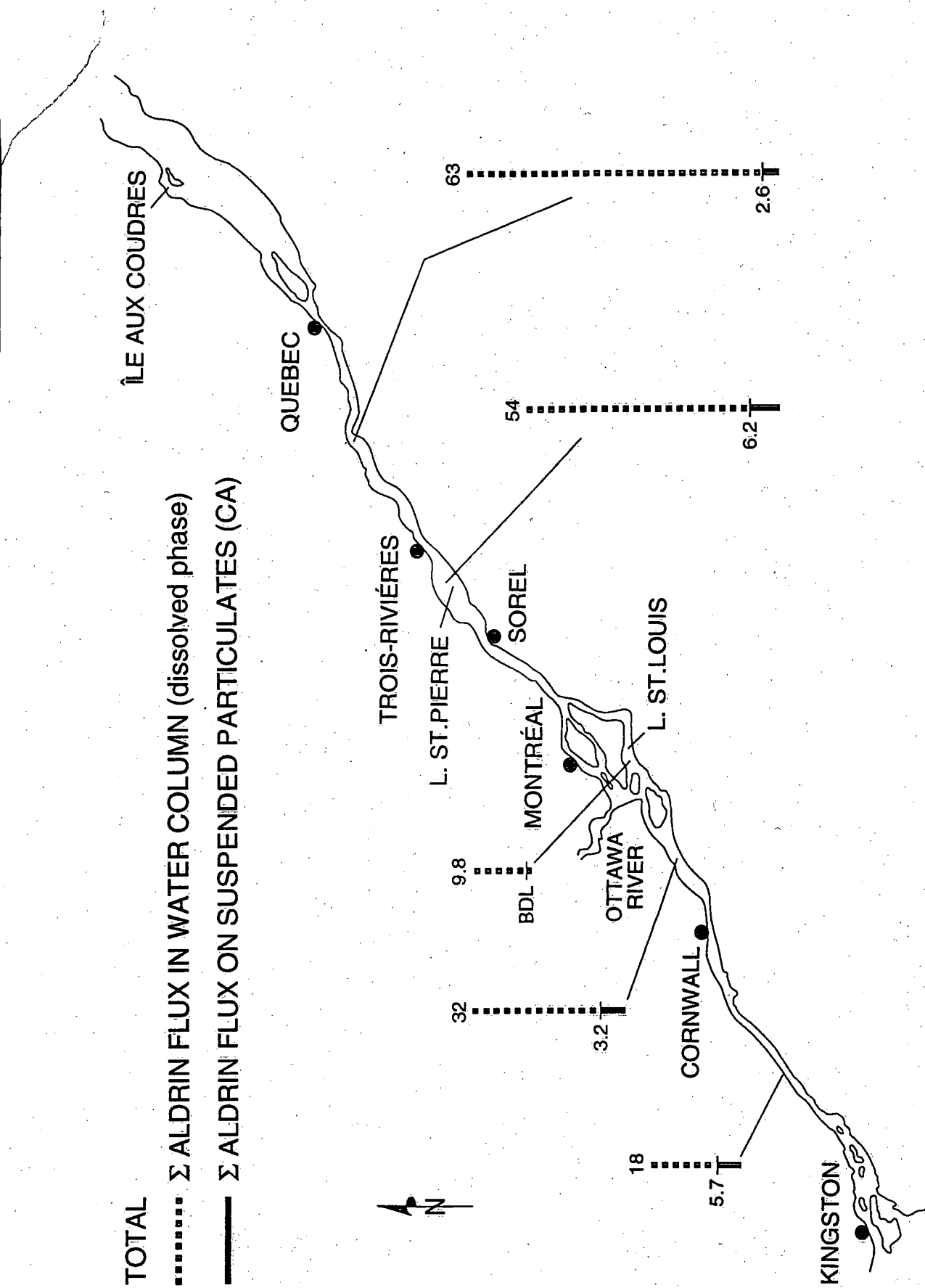


Figure 21.  $\Sigma$  Aldrin flux (kg/a) in suspended particulates and water of the St. Lawrence River, June, 1990.

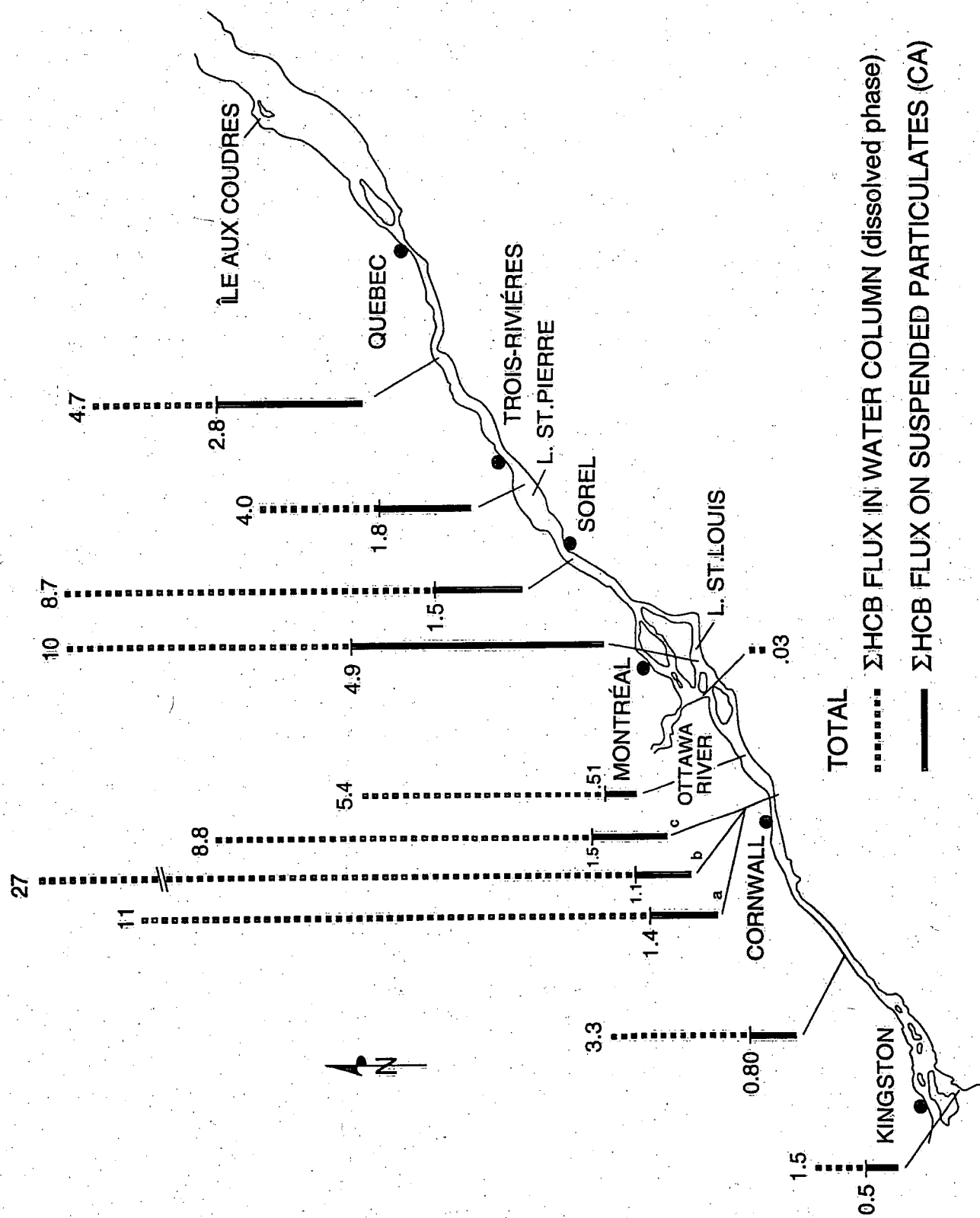


Figure 22.  $\Sigma$  HCB flux (kg/a) in suspended particulates and water of the St. Lawrence River, June/July, 1989.

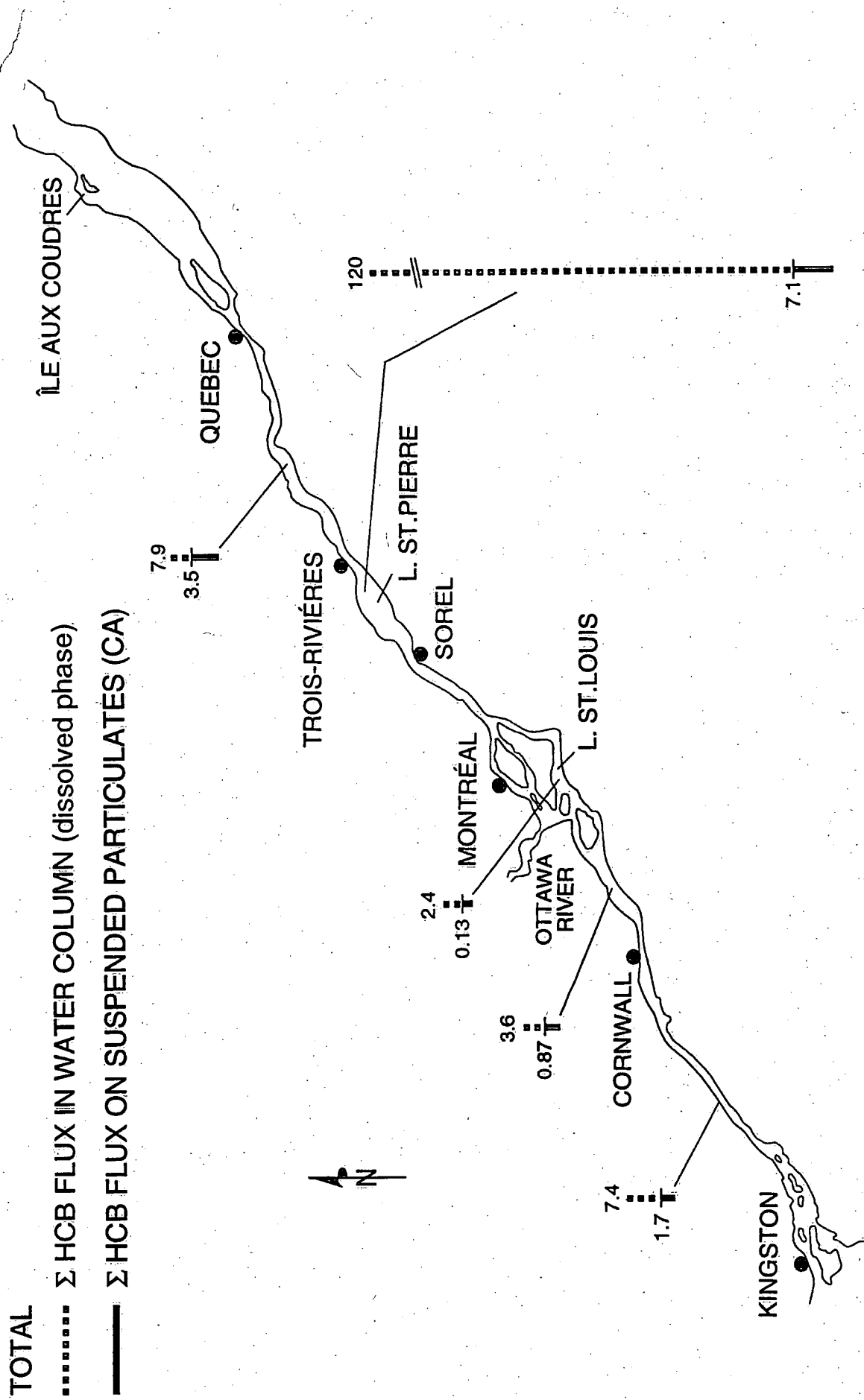


Figure 23.  $\Sigma$  HCB flux (kg/a) in suspended particulates and water of the St. Lawrence River, June, 1990.

## DISCUSSION

### Contaminant behaviour

The physical and chemical distributions of a contaminant between its surrounding environment is controlled by its behaviour and partitioning between the two principal transporting compartments, namely water and suspended particulate matter. The distinction between dissolved or adsorbed onto particulate is arbitrarily established through filtration/centrifugation limitations, which focus on a nominal particle size of approximately 0.4 and 1.0  $\mu\text{m}$ , respectively. Consequently, a considerable amount of submicron size particles (colloidal material), often composed of organic (humic) and inorganic (calcium carbonate) substances can be part of the dissolved fraction. Presently there is little knowledge as to which carbon phase (POC or DOC), if any, controls sorption-dissolution phenomenon, although organic surfaces and phases are thought to play an important role in such processes and subsequently in contaminant transport (Platford et al., 1985). Partitioning of hydrophobic compounds to solids has been shown to be statistically correlated to organic carbon content (Karickhoff et al., 1979; DiToro, 1985) and binding energy a function of the organic coating type (Knezovich et al., 1987). Bioavailability, toxicity, and rates of transfer were also reported to be influenced by the organic content of the receiving compartment. In water, the dissolved organic matter (DOM), and the colloidal content were reported to markedly influence bioavailability and partitioning (McCarthy and Black, 1988; Baker et al., 1986, Servos and Muir, 1989) and enhance the formation of mirex photoproducts in Lake Ontario surface waters (Mudambi and Hasset, 1988). Also, the dissolved organic carbon (DOC) fraction in the solute (Landrum et al., 1984, Comba and Kaiser, 1990) has been linked with many other observed binding and partitioning effects.

The detrital organic particles involved in contaminant interactions are for the most part carbohydrate and protein products from in-situ (autochthonous) and terrestrial (allochthonous) events. In the St. Lawrence River, the sources of particulate organic carbon in the summer and fall seasons were different based on their observed C/N ratios (Figure 8). Ratios of 6-8 measured during the summer months corresponded to organic carbon that originates from in-situ plankton production, whereas ratios in the fall which approached or exceeded 10 were more typical of terrestrial carbon inputs from vascular plant debris. The additions of suspended particulate matter with distance downstream were mainly mineral in nature as characterized by their inorganic content of 95%. This produced a non-linear increase in POC flux relative to the flux of SPM (Figures 2 and 5). This lack of linearity was caused by the increased flow, and the size and origin of particles. Typical current velocities of 0.5-1.5 m/s

**Table 11. Organic carbon partitioning coefficients ( $\log K_{oc}$ ) for selected chlorinated hydrocarbons in the St. Lawrence River.**

Compound	Mean $\log K_{oc}$	Range	sd $\pm$
T-PCB	6.33	4.85-6.51	0.40
MIREX	6.42	5.98-7.49	0.38
pp-DDE	6.31	4.77-7.60	0.58
HCB	5.88	4.85-6.51	0.41
DIELDRIN	5.34	4.99-6.02	0.24
$\alpha$ -BHC	3.82	3.08-5.74	0.61
$\alpha$ -CHLORDANE	5.75	4.82-6.48	0.46
$\gamma$ -CHLORDANE	5.75	4.82-6.48	0.46

(SD, 1985) in the St. Lawrence would have sufficient hydraulic energy to mobilize and suspend particle sizes of up to 500  $\mu\text{m}$  (van Rijn, 1984), introducing greater amounts of larger mineral aggregates as the current increased with distance downstream. Since particulate organic carbon is usually associated with smaller particles such as silt and clay  $\leq 0.65 \mu\text{m}$ , and to a lesser extent with the silicates, i.e. sand grains  $\geq 0.65-1.0 \mu\text{m}$ , then the low variability in POC concentration throughout the river (Table 4), imply that the new additions of SPM must be erosion products of the predominant granitic geomorphology.

Although the components of DOC are poorly understood its sources are generally thought to be similar, particularly in large lakes, to those of detrital material and POC. However in the St. Lawrence River there may be an exception to this commonality. Many of the major tributaries that drain into the St. Lawrence River carry pulp and paper effluents which are identified as significant sources of fibril and humic substances (Leppard, 1986), and therefore important contributors to DOC (Burnison and Leppard, 1983). Since the carbohydrate concentration in the dissolved fraction constituted less than 16 % of the observed DOC, it was thought that a sizeable humic component would be necessary to complete the organic carbon balance. In addition to pulping wastes, inputs from major urban sewage outfalls noticeably increased localized DOC levels but did not substantially increase the carbohydrate content. Based on this information we felt that the primary sources of DOC did not originate from plankton and terrestrial forest litter, as thought to be the case for POC, but rather mostly from humic materials.

The calculated carbon corrected partitioning coefficients (Table 11) for the individual contaminants ranged from  $\log 3.82$  for  $\alpha$ -BHC to  $\log 6.42$  for mirex, and incorporated a range of SPM from 0.5 to 10 ppm with organic carbon

fractions between 3-70 %. The carbon corrected partitioning coefficients gave excellent agreement to those reported for other areas of the Great Lakes Basin (Oliver, 1987; Lau et al., 1989; Capel and Eisenreich, 1990). The low variability within coefficients implied that compound partitioning between water and particulate behaved in a similar manner throughout the river and was not significantly altered as a result of different organic carbon sources.

The compartmental distribution (partitioning) of the contaminants ( $\Sigma$ ) was statistically tested for (i) a linear relationship between the relative amount (concentration) of the contaminant in the transporting compartment versus the concentration of organic carbon in that phase and, (ii) a linear relationship as to which organic carbon concentration (POC or DOC) influenced the absolute amounts of the contaminant partitioned, expressed as its ratio (ng/m<sup>3</sup> dissolved/ng/m<sup>3</sup> adsorbed). Although the linear associations were weak, the relationships found for the concentration of POC and the amounts of adsorbed contaminant were statistically significant and positively correlated for mirex ( $r=0.40, p=.01$ );  $\Sigma$ HCB ( $r=0.40, p=.01$ );  $\Sigma$ chlordanes ( $r=0.55, p=.003$ );  $\Sigma$ DDT ( $r=0.33, p=.04$ ); and  $\Sigma$ BHC ( $r=0.40, p=.01$ ). No correlation for the sorbed amount of  $\Sigma$ PCB and  $\Sigma$ aldrin was found with regards to POC concentration. Dissolved amounts of  $\Sigma$ HCB ( $r=0.58, p=.003$ ),  $\Sigma$ chlordanes ( $r=0.48, p=.04$ ); and  $\Sigma$ BHC ( $r=0.48, p=.04$ ) were found positively correlated with DOC concentration while  $\Sigma$ DDT ( $r=-0.35, p=.04$ ) was negatively correlated. No relationships were observed between DOC concentration and the dissolved concentrations of  $\Sigma$ PCB, mirex and  $\Sigma$ aldrin.

The partitioning ratio of  $\Sigma$ PCB,  $\Sigma$ DDT and mirex was negatively correlated with concentration of POC. No other relationships between DOC concentration and partitioning ratio were found.

As previously noted, the correlation between sorption of hydrophobic compounds and particulate organic carbon in lakes and sediments has been widely documented. In general, chemicals monitored in the river preferred sorption with POC rather than being dissolved in DOC, although it may not be as apparent as in lakes. The weaker correlations between contaminant and POC concentration were in part due to the grouping of contaminant components ( $\Sigma$ ). For instance the contaminants  $\Sigma$ HCB,  $\Sigma$ chlordanes and  $\Sigma$ BHC correlated with organic carbon concentration in both phases. The relationship with DOC corresponded to the greater solubilities of their group components, pentachlorobenzene (QCB),  $\alpha$ -BHC and heptachlor epoxide. The compound groups exhibiting the greatest hydrophobicity, (Table 11)  $\Sigma$ PCB,  $\Sigma$ DDT and mirex, did not yield strong linear correlations with POC concentration, even though their partitioning ratios were negatively correlated with POC content (i.e. for increasing amounts of POC, less material

was in the solute). The observation of weaker linear correlations in rivers was not unexpected and can be attributed to two main factors. In large river systems steady state equilibrium is rarely achieved as a result of high flows, intermittent inputs and the overall dynamic nature. As already reported, the sudden occurrence of elevated levels of contaminants, especially in the dissolved fraction had been attributed to nearby point source loadings which had not as yet attained a thermodynamic balance with the receiving stream (Kaiser, et al., 1990b). The second reason that contaminants were observed not to "immediately" sorb to SPM even though sufficient adsorptive capacity exists (Platford et al., 1985) is that a critical concentration of SPM or POC appears to be required to affect adsorption. This phenomenon was observed in other major Great Lake's rivers. In the St. Clair, Detroit and Niagara (Oliver, 1987; Platford et al., 1985; Kaiser et al, 1986; and McCrae et al, 1985) chemicals with log Koc < 7 remained "dissolved" when SPM concentrations were below 1-2 ppm until at some critical point beyond these concentrations partitioning occurred. This process was evident in flux diagrams (Figures 10-23) of contaminants in the St. Lawrence River, where burdens in the upper reaches had a larger proportion of material in the dissolved fraction which became bound to particulates by the time they arrived at the river's mouth (Kaiser, et al, 1990b).

#### *Contaminant transport*

Intuitively, pollutant transport in a river should be related to the amounts of water and suspended particulate discharged. However to our knowledge no evidence has ever been reported which actually qualifies the effect these two vectors have on transport.

As previously stated, compartmental distributions were related to both the relative and absolute amounts of organic carbon present in either the dissolved or particulate fraction. Likewise, the flux of dissolved and particulate organic carbon was found to be positively correlated with the rate of water discharge, DOC ( $r=0.53, p=0.003$ ) and POC ( $r=0.79, p=0.000$ ). Correspondingly, the rate of water discharge was correlated to the total amount of contaminant discharged;  $\Sigma$ PCB ( $r=0.80, p<0.001$ ); mirex ( $r=0.57, p<0.001$ );  $\Sigma$ HCB ( $r=0.40, p=0.008$ );  $\Sigma$ DDT ( $r=0.38, p=.01$ );  $\Sigma$ BHC ( $r=0.31, p=.05$ ) and  $\Sigma$ chlordanes ( $r=0.29, p=.06$ ).

Given the association of hydrophobic contaminants with organic carbon, it was not surprising to find stronger linear correlations between the flux of DOC and the dissolved flux of contaminants,  $\Sigma$ chlordanes ( $r=0.74, p<0.001$ );  $\Sigma$ BHC ( $r=0.71, p<0.001$ );  $\Sigma$ HCB ( $r=0.70, p<0.001$ );  $\Sigma$ aldrin ( $r=0.62, p=0.001$ ); mirex ( $r=0.57, p=0.003$ );  $\Sigma$ PCB ( $r=0.48, p=0.02$ ) and conversely the reverse order of correlation between the flux of bound contaminant and POC flux,  $\Sigma$ PCB ( $r=0.71, p<0.001$ ); mirex ( $r=0.63, p<0.001$ );  $\Sigma$ HCB ( $r=0.61, p<0.001$ );  $\Sigma$ BHC ( $r=0.56, p<0.001$ );  $\Sigma$ aldrin ( $r=0.56, p<0.001$ );  $\Sigma$ chlordanes ( $r=0.055, p=0.003$ ).

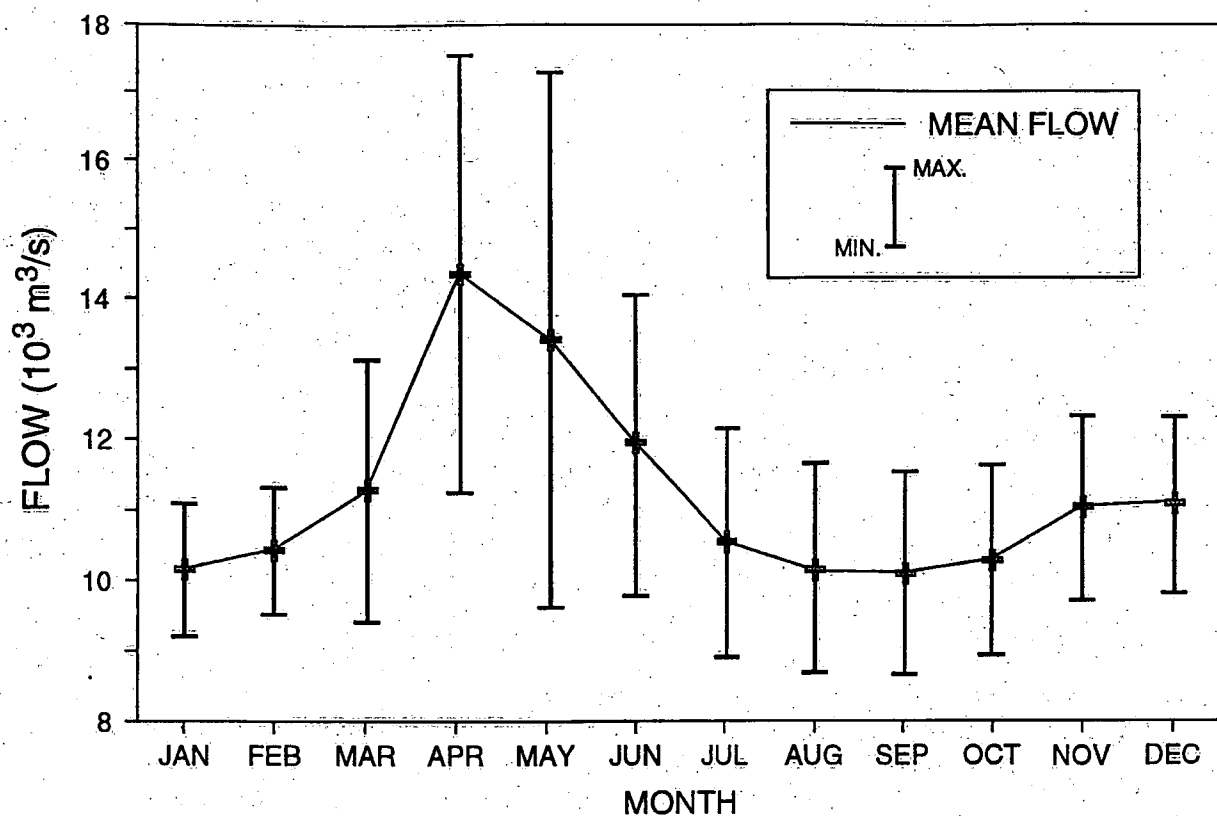


Figure 24. Mean monthly discharge of the St. Lawrence River at Quebec City, 1983-1990.

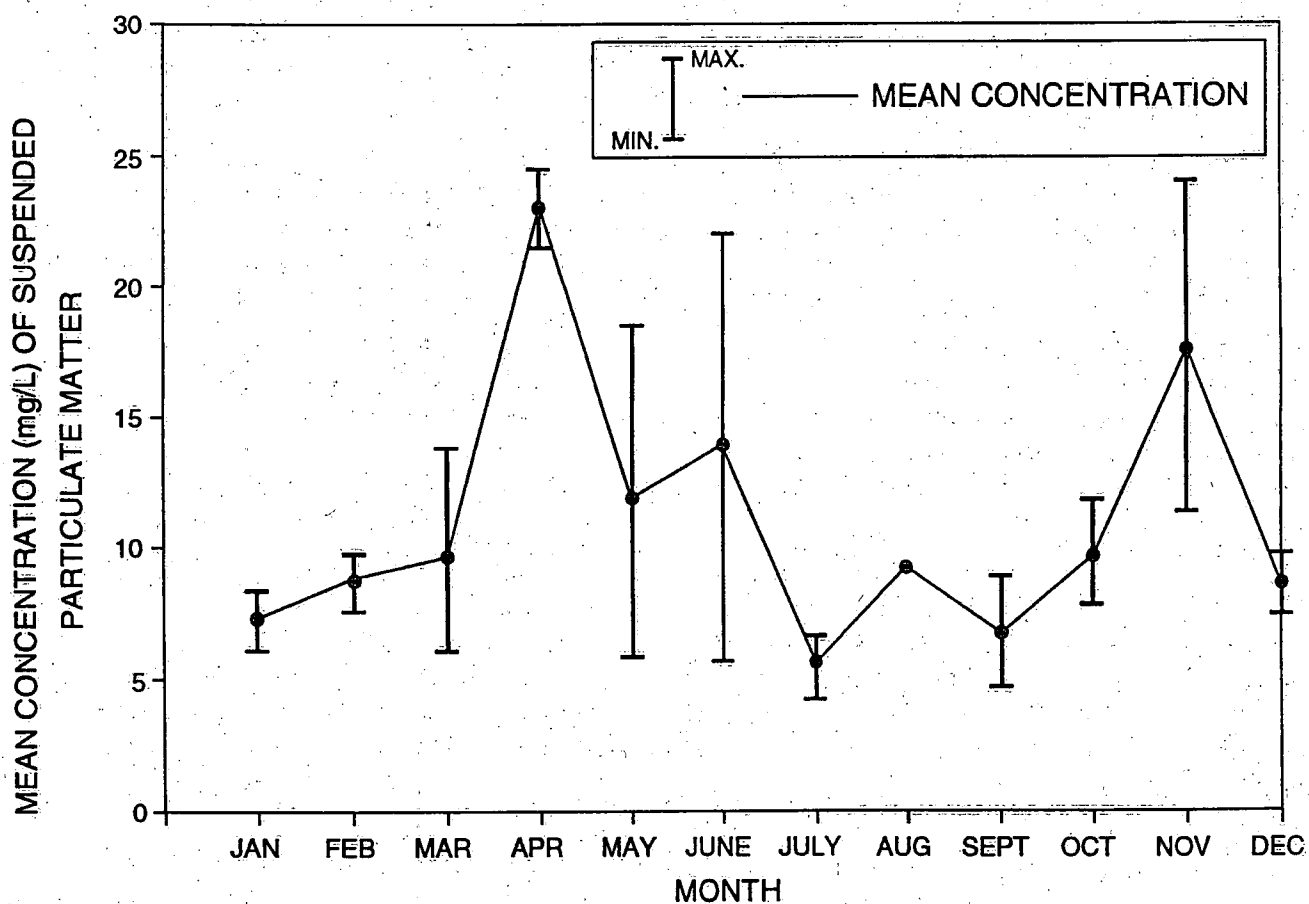
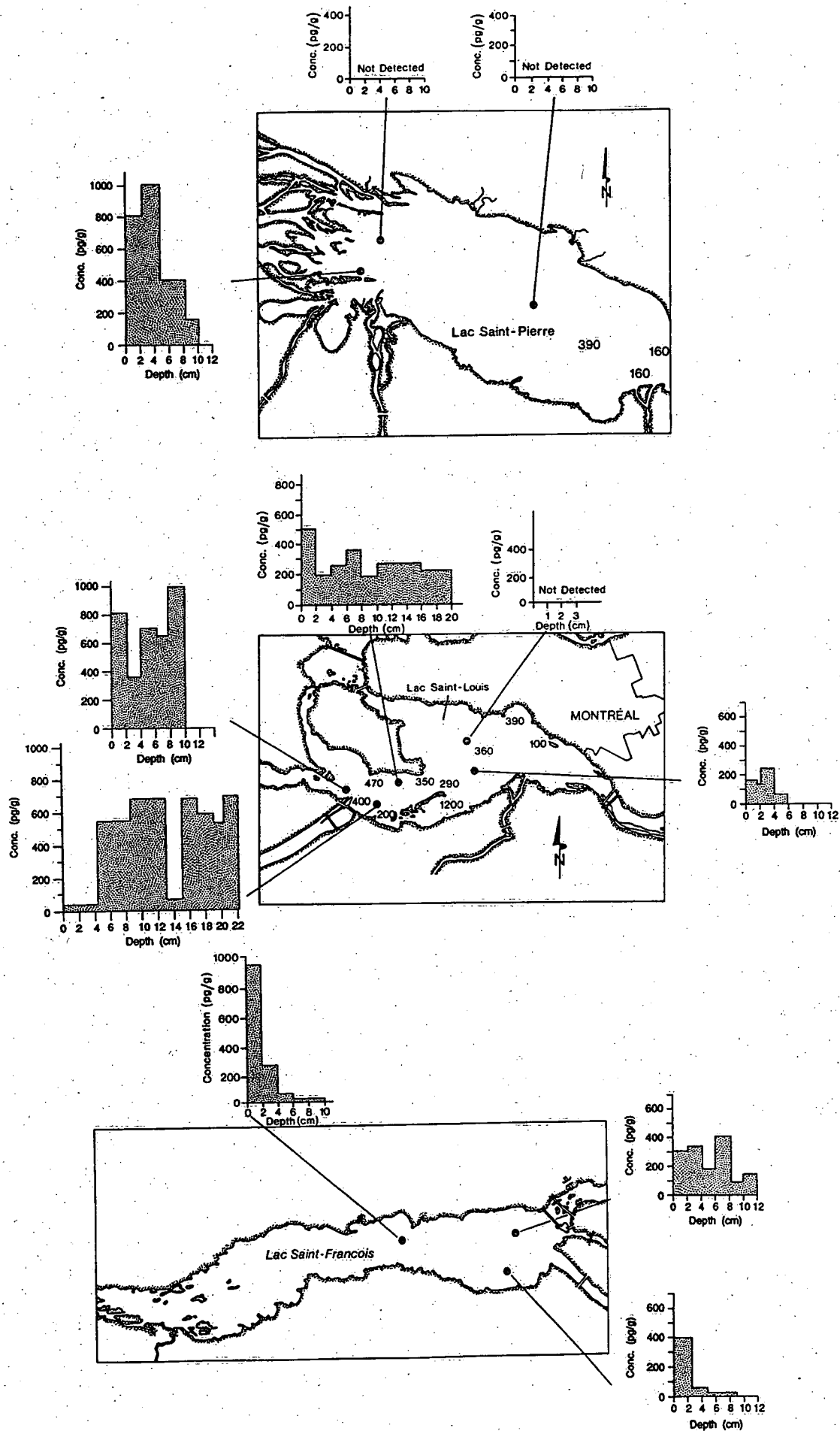


Figure 25. Mean monthly concentration of suspended particulate matter at Quebec City, 1980-1985 (data from Poklington and Tan, 1987).



**Figure 26.** Concentrations of mirex in surficial and core sediments of the St. Lawrence riverine lakes.



**Table 12.** *Estimated flux ( $10^6$  t/a) of suspended particulate matter from lakes in the St. Lawrence River system, 1985-1990.*

Lake Ontario	Lac St. Francois	Lac St. Louis	Lac St. Pierre	Quebec City
$0.29 \pm 0.15$	$0.53 \pm 0.10$	$1.0 \pm 0.23$	$2.9 \pm 1.4$	$3.9 \pm 1.5$

During the last decade the discharge of the two main transport vectors has remained more or less constant. Since 1983 the St. Lawrence River has averaged annual water discharges of  $11,240 \pm 1580$  m<sup>3</sup>/s. The largest discharges were observed in April with smaller amounts during winter and the later summer months (Figure 24). The average rate of water discharged during the course of the periodic sampling between 1985 to 1990 was 10,900 m<sup>3</sup>/s. The reported biweekly measurements (Pocklington and Tan, 1987) of SPM concentration at Quebec City between 1981 and 1985 (Figure 25) had a mean concentration of 11.2 ppm, a value similar to the 10.8 ppm average observed in the 1985 to 1990 surveys. In conjunction with these mean water discharge rates and measured suspended particulate concentrations an average annual discharge of suspended particulate matter was determined to be 3,900 kt. The 1985 to 1990 annual river loading of 3900 kt was slightly greater than the 1981 to 1985 value of 3,600 kt reported by Pocklington and Tan (1987) who observed an average flow rate of  $12,900 \pm 2500$  m<sup>3</sup>/s. The only other measured post 1945 loadings were the 6,800 kt/a between 1974 to 1975 (Yeats and Bewers, 1982 and 6,500 kt/a for 1988 (Fenette et al., 1989). Their higher loading estimates resulted from observations of greater flow discharge  $\sim 14000$  m<sup>3</sup>/s (Yeats and Brewer) and SPM concentration  $\sim 17$  mg/l (Fenette). The relative proportion of sediment loading for each lake-river corridor contribution is given in Table 12. Of the 3900 kt, 8 % originated from Lake Ontario, while the remainder came from sources within the river's drainage area. Over 74 % of the internal flux was contributed by drainage regions inside Quebec. In addition to the above amounts, the Ottawa River (Lac des deux Montagnes) can contribute additional significant short term SPM loads of up to 1.5 kt/d during spring run-off conditions.

Not surprisingly the amounts of organic carbon discharged from the St. Lawrence River in the past ten years has also remained stable, with a measured mean annual POC discharge of  $296 \pm 100 \cdot 10^3$  t/a (Pocklington and Tan, 1987) for 1981 to 1985 and  $199 \pm 66 \cdot 10^3$  t/a, between 1986 and 1990 from the work here. Similarly, the coincidental mean loadings of DOC were  $1.5 \pm 0.50 \cdot 10^6$  t/a (Pocklington and Tan, 1987) and  $1.8 \pm 0.36 \cdot 10^6$  t/a. Consequently the low variability in long term observations of water and suspended particulate matter discharge, and more precisely, the quantities of DOC and

POC discharged should not significantly influence rates of chemical flux, such that any observed differences in the quantities of contaminants being discharged must be in direct response to changes of inputs.

#### *Contaminant trends and fate*

In aquatic systems, many hydrophobic pollutants become bound to particles and are deposited to sediments of the more conservative energy zones. In the St. Lawrence River deposition of riverborne particulate was not found to be a permanent process (Rukavina et al., 1990) and subsequently not a major contaminant sink. Sedimentary deposits in the riverine lakes were reported to contain less than two times the annual flux rate of PCB and experienced less than 7% deposition of annual contaminant flux (Kaiser et. al., 1990b). This short-term retention of hydrophobic compounds in sediment deposits of the riverine lakes was also evident from sediment and sediment core profile data of mirex. Mirex had gone undetected in 1975 and 1981 upper river sediments (Kuntz, 1988; Merriman, 1981), while mirex concentrations in surficial sediments at 10 sites in Lac St. Francois ranged from non detectable to 3.3 ng/g with a mean of  $< 1.0$  ng/g (Sloterdijk 1985). Subsequent measurements of mirex concentration in the top 10 cm of benthos cores from the three riverine lakes averaged 251 pg/g, Lac St. Francois, 728 pg/g, Lac St. Louis and 156 pg/g Lac St. Pierre (Kaiser et. al., 1990b) and in conjunction with later measurements of mirex in riverine lake sediments (Figure 26) were used to compute a 1990 mass budget for mirex. The estimated amount of river remnant mirex was reported to be 22 kg of which 14 kg was accumulated in sediments (Comba et al., 1993). This content of sediment mirex represented 4.8% of the net exported amount (by particulate and water) and corresponded with the predicted net sedimentation rate, reported to average 6 % of the total suspended flux (Carignan et al., 1993). The lack of significant contaminant deposition, however did not appear to lessen the importance of contaminated sediment as a point source. The mobile characteristic of sediments and subsequent resuspension into the water column still appears to play an important role in the amounts of contaminants discharged. This interpretation was made through consistent observations of increased intermittent mirex flux (approximately 20-30%) for stations downstream of Lake Ontario (Comba et al., 1989a, 1989b, 1990).

Often the extent of a contaminant's environmental impact is gauged by the chemical's concentration. However

Table 13. Yearly mean concentrations and trends of some selected pesticide groups in overall St. Lawrence River suspended particulate matter (ng/g) and water (ng/l), 1985-1990.

Year	May 1985	October 1985	July 1986	July 1987	June 1989	June 1990	July 1986	July 1987	June 1989	June 1990
	Suspended particulate matter					Dissolved fraction				
ΣPCB	260 ± 280	1000 ± 1200	2800 ± 1600	540 ± 440	170 ± 62	250 ± 100	1.1 ± 0.52	0.74 ± 0.12	0.97 ± 0.48	0.48 ± 0.07
Mirex	3.3 ± 2.9	8.3 ± 4.8	3.5 ± 3.1	2.0 ± 1.9	0.98 ± 0.61	1.3 ± 1.1	0.005 ± 0.004	0.004 ± 0.002	0.003 ± 0.003	0.001 ± 0.000
ΣBHC	190 ± 200	18 ± 19	13 ± 7	11 ± 8	2.1 ± 0.63	1.4 ± 1.1	5.2 ± 1.5	2.4 ± 0.45	0.65 ± 0.43	0.84 ± 0.40
ΣDDT	33 ± 63	29 ± 32	4.4 ± 3.5	29 ± 32	10 ± 7.7	8.0 ± 3.1	0.19 ± 0.21	0.031 ± 0.032	0.082 ± 0.16	0.076 ± 0.060
ΣChlordane	28 ± 44	no result	BDL	13 ± 9.1	10 ± 5.8	4.3 ± 2.0	0.29 ± 0.19	0.21 ± 0.55	0.041* ± 0.063	0.029 ± 0.046
ΣAldrin	no result	no result	13 ± 15	11 ± 11	13 ± 6.4	8.1 ± 8.0	0.38 ± 0.16	0.31 ± 0.16	0.12* ± 0.20	0.12 ± 0.56
ΣHCB	170 ± 85	18 ± 24	3.7 ± 2.7	49 ± 54	1.5 ± 0.9	2.8 ± 1.9	0.046 ± 0.016	0.047 ± 0.055	0.010 ± 0.008	0.073 ± 0.14

\* data set incomplete, interfering peaks

BDL = Below quantitation limit.

**Table 14. Estimated flux (kg/a) for selected contaminants between Lake Ontario and Quebec City in the St. Lawrence River.**

LAKE ONTARIO	$\Sigma$ PCB	$\Sigma$ HCB	$\Sigma$ DDT	$\Sigma$ CHLORDANE	$\Sigma$ ALDRIN	$\Sigma$ BHC	MIREX
1986	360	14	64	120	170	1600	2.9
1987	327	31	27	70	31	490	2.3
1989	220	1.5	30	21	37	230	0.79
1990	250	7.4	4.8	8.1	18	120	1.1
QUEBEC CITY							
1986	860	18	43	39	110	1900	3.1
1987	830	16	30	73	100	790	3.2
1989	630	4.7	25	29	58	140	3.7
1990	600	5.9	71	43	64	510	0.93

**Table 15. Percent reduction in contaminant fluxes between 1986 to 1990 to and from the St. Lawrence River.**

Contaminant	Lake Ontario	In-stream	St. Lawrence River Exports
$\Sigma$ PCB	31	30	30
$\Sigma$ HCB	47	100	67
$\Sigma$ DDT	93	increase	(+ 39)
$\Sigma$ CHLORDANE	93	0	0
$\Sigma$ ALDRIN	89	increase	42
$\Sigma$ BHC	93	increase	73
MIREX	62	0	70

this approach may be inadequate in large rivers such as the St. Lawrence, where contaminant concentrations are usually in the low parts per trillion and consequently difficult to measure with any great certainty. In conjunction with this, the use of different analytical approaches can give rise to a non-similarity between measurements as a result of sampling artifacts. For example, sampling techniques (Comba et al., 1990, Maguire and Tkacz, 1989), such as centrifugation, filtration, pH and solvent extraction yielded different contaminant concentrations when the organic content varied sufficiently between samples. In light of the normal spatial and temporal variations in contaminant distributions, any combination of above can make fate and trend assessment risky. In order to diminish the importance of singular or localized events we utilized averaged in-stream flux rates obtained from numerous measurements that covered a range of sampling conditions and depths.

The averaged in-stream data for pesticide concentration (Table 13) and flux (Table 14) between 1985 to 1990 signified a definite decrease in all levels of measured chemicals in both transporting compartments. Decreased contaminant concentrations in Lake Ontario have resulted in contaminant flux reductions since 1986 of 31 to 93 percent (Table 15). This trend was not as evident at Quebec City, where contaminant fluxes had decreased only 30-70%. In-stream loadings related to ( $\Sigma$ ) chlordane, DDT, BHC and aldrin exhibited no distinct tendency toward lowered inputs. Instead, concentrations varied and in the case of DDT an increased discharge amount was observed. A reduction in the in-stream loadings of PCB and HCB was observed. The combined reduction in PCB lake and in-stream inputs was reflected in a 1989 sediment survey of Lake St. Francois, which reported PCB levels to be an order of magnitude lower compared to those in the previous decade (Lorrain et al., 1993).

Within a relatively short period of time after introduction into the river (approximately, 5-10 years), the in-stream contaminant flux from water, suspended particulate and migrating biota enters the upper St. Lawrence estuary (Comba et al., 1993). Upon reaching the upper estuary, contaminants are systematically removed to the lower estuary through annual cyclic processes. As a substantial portion of transported organic matter (approximately 75%) undergoes deposition to the bottom sediments of the Laurentian Trough (Lucotte, et al., 1991), the hydrophobic compounds, such as the ones studied, eventually sediment to the ocean floor.

During transit through the estuary, contaminant impact on the marine environment was significant. Bioaccumulation factors of  $10^5$  were observed for PCB (Gagnon et al., 1990) and mirex (Comba, et al., 1993) uptake in fish of the upper estuary and a bioaccumulation

factor of  $10^8$  for mirex in beluga whales (Comba, et al., 1993).

#### ACKNOWLEDGEMENTS

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## REFERENCES:

- Allan, R.J., 1986. The role of particulate matter in the fate of contaminants in aquatic ecosystems. Environment Canada, Scientific Series No. 142. Inland Waters Directorate, National Water Research Institute, Burlington, Ontario. 128 p.
- Baker, J.E., Capel, P.D. and Eisenreich, S.J. 1986. Influence of colloids on the sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters. *Environ. Sci. Technol.* 20: 1136-1143.
- Burnison, B.K., 1980. Modified dimethyl sulfoxide (DMSO) extraction for chlorophyll analysis of plankton. *Can. J. Fish Aquat. Sci.*, 37: 729-733.
- Burnison, B.K. and Leppard, G.G., 1983. Isolation of colloidal fibrils from lake water by physical separation techniques. *Can. J. Fish Aquat. Sci.*, 40: 373-381.
- Capel, P.D. and Eisenreich, S.J. 1990. Relationship between chlorinated hydrocarbons and organic carbon in sediment and porewater. *J. Great Lakes Res.* 16(2): 245-257.
- Carignan, R., Lorrain, S. and Lum, K. 1993. Sediment dynamics in the fluvial lakes of the St. Lawrence River: Accumulation rates, and residence time of mobile sediments. Environment Canada, Centre Saint-Laurent, Montreal, Quebec.
- Comba, M.E., Palabrica, V.S. and Kaiser, K.L.E., 1989a. St. Lawrence River organic trace contaminants study (Part I), 1985. National Water Research Institute, Report 89-50, 71 p.
- Comba, M.E., Palabrica, V.S., Wasslen J., Bengert, G.A. and Kaiser, K.L.E., 1989b. St. Lawrence River organic trace contaminants study (Part II), 1986. National Water Research Institute, Report 89-51, 97 p.
- Comba, M.E., Palabrica, V.S., Wasslen J. and Kaiser, K.L.E., 1990. St. Lawrence River organic trace contaminants study (Part III), 1987. National Water Research Institute, Report 90-01, 39 p.
- Comba, M.E. and Kaiser, K.L.E., 1990a. Suspended particulate concentrations in the St. Lawrence River (1985-1987) determined by centrifugation and filtration. *Sci. Total Environ.* 97/98: 191-206.
- Comba, M.E. and Kaiser, K.L.E., 1990b. Processes influencing the transport of organic contaminants in the St. Lawrence River. Collection Environnement et Geologie, D. Messier, P. Legendre and C.E. Delisle, Editors. 11: 75-84.
- Comba, M.E., R.J. Norstrom, C.R. Macdonald and K.L.E. Kaiser, 1993. A Lake Ontario-Gulf of St. Lawrence dynamic mass budget for mirex. submitted to *Environ. Sci. and Technol.*, 27: 2198-2206.
- DiToro, D.M., 1985. A particle interaction model of reversible organic chemical sorption. *Chemosphere*, 14: 1503-1538.
- Gagnon, M.M., Dodson, J.J., Comba, M.E. and Kaiser, K.L.E., 1990. Congener specific analysis of the accumulation of polychlorinated biphenyls (PCBs) by aquatic organisms in the maximum turbidity zone of the St. Lawrence estuary, Quebec, Canada. *Sci. Total Environ.* 97/98: 739-759.
- EDAMS, 1991, Environmental Data Assessment and Management System. Gorrie, F.I., Backus, S.M., Biberhoffer, H., Comba, M.E. and Kaiser, K.L.E. National Water Research Institute, Lakes Research Branch, Nearshore-Offshore Interactions Project, Burlington, Ontario.
- Fenette, M. Barbeau, C. and Verrette, J.-Ls. 1989. Aspects quantitatifs, dynamiques et qualitatifs des sediments du Saint-Laurent. Environment Canada and Gouvernement du Quebec Report. September 1989.
- Kaiser, K.L.E., Oliver, B.G., Charlton, M.N., Nicol, K.D. and Comba, M.E., 1990a. Polychlorinated biphenyls in St. Lawrence River Sediments. *Sci. Total Environ.* 97/98: 495-506.
- Kaiser, K.L.E., Lum, K.R., Comba, M.E. and Palabrica, V.S., 1990b. Organic trace contaminants in St. Lawrence River water and suspended sediments, 1985 - 1987. *Sci. Total Environ.* 97/98: 23-40.
- Kaiser, K.L.E., Lum, K.R. and Palabrica, V.S., 1988. Review of field applications of the Microtox test in Great Lakes and St. Lawrence River waters. *Water Poll Res. J. Canada*, 23: 270-278 (1988).
- Koprivnjak, J.F., Bourbonniere, R.A., Clair, T.A., Heyes, A., Lum, K., McCrea, R. and Moore, T.R. 1993. The underestimation of concentrations of dissolved organic carbon in freshwaters. unpublished
- Knezovich, J.P., Harrison, F.L. and Wilhelm, R.G. 1987. The bioavailability of sediment-sorbed organic chemicals: A review. 1987. *Water, Air and Soil Pollution*, 32: 233-245.
- Karickhoff, S.W., Brown, D.S. and Scott, T. A., 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Research*, 13: 241-248.
- Kuntz, K.W. 1988. Contaminants in bottom sediments of the St. Lawrence River in June 1975. Inland Waters Directorate, Ontario Region, Burlington, Ontario. Technical Bulletin No. 147, 1-18.

Leppard, G.G. 1986. The fibrillar matrix component of lacustrine biofilms. *Wat. Res.* 20: 697-702.

Lau, Y.L., Oliver, B.G. and Krishnappan, B.G. 1989. Transport of some chlorinated contaminants in the water, suspended sediments, and sediments in the St. Clair and Detroit Rivers. *Environmental Toxicology and Chemistry*, 8: 293-301.

Lorrain, S., Jarry, V. and Guertin, K. 1993. Spatial distribution and temporal changes in polychlorinated biphenyls and mercury in sediments of Lake St. Francois; 1979-1989. Environment Canada, Centre St-Laurent, Montreal, Quebec.

Lucotte, M., Hillaire-Marcel, C. and Louchren, P. 1991. First-order carbon budget in the lower St. Lawrence Estuary from  $^{13}\text{C}$  data. *estuarine, Coastal Shelf Sci.* 32: 297-329.

Lum, K.R. and Kaiser, K.L.E., 1986. Organic and inorganic contaminants in the St. Lawrence River: some preliminary results on their distributions. *Water Poll. Res. J. Canada* 21(4): 592-602.

Lum, K.R., Kaiser, K.L.E. and Comba, M.E., 1987. Export of mirex from Lake Ontario to the St. Lawrence estuary. *Sci. Total Environ.* 67: 41-51.

Lum, K.R., Kaiser, K.L.E. and Jaskot, C. 1989. Distribution and fluxes of metals in the St. Lawrence River from the outflow of Lake Ontario to Quebec City. Presented at Intl. Symposium on the Fate and Effects of Toxic Chemicals in Large Rivers and their Estuaries, October 10-14, 1988, Quebec, Quebec.

Maguire, R.J. and Tkacz, R.J. 1989. Potential underestimation of chlorinated hydrocarbon concentrations in fresh water. *Chemosphere*, 19: 1277-1287.

McCarthy, J.F. and Black, M.C. 1988. Partitioning between dissolved organic macromolecules and suspended particulates: Effects on bioavailability and transport of hydrophobic compounds in aquatic systems. *Aquatic Toxicology and Hazard Assessment: 10th Volume*. W.J. Adams, G.A. Chapman and W.G. Landis, Editors. ASTM, Philadelphia, 223-246.

McCrea, R.C. and Fisher, J.D. 1984. Design and testing of an aqueous phase liquid-liquid extractor (APLE) for the determination of organochlorine contaminants. Environment Canada, Inland Waters Directorate, Burlington, Ontario, 18 p.

McCrea, R.C., Fisher, J.D. and Kuntz, K.W. 1985. Distribution of organochlorine pesticides and PCB's between aqueous and suspended sediment phases in the lower Great Lakes Region. *Water Poll. Res. J. Canada* 20/1: 67-78.

Merriman, J.C. 1987. Trace organic contaminants in sediments of the International section of the St. Lawrence River, 1981. Inland Waters Directorate, Ontario Region, Burlington, Ontario. Technical Bulletin No. 148, 1-10.

Metcalfe, J.L. and Charlton, M.N. 1990. Freshwater mussels as biomonitors for organic industrial contaminants and pesticides in the St. Lawrence River. *Sci. Total Environ.* 97/98: 596-615.

Mudambi, A.R. and Hassett, J.P. 1988. Photochemical activity of mirex associated with dissolved organic matter. *Chemosphere*, 17 (6): 1133-1146.

Mullin, M.D. 1985. PCB Workshop. U.S. EPA Large Lakes Research Station, Grosse Ile, M.I. June.

Munawar, M. and Munawar, I.F. 1986. The seasonality of phytoplankton in the North American Great Lakes, a comparative synthesis. *Hydrobiologia*, 138: 85-115.

Muir, D.C.G., Servos, M.R. and Muir, D.C.G. 1989. Effect of dissolved organic matter from Canadian shield lakes on the bioavailability of 1,3,6,8-tetrachlorodibenzo-p-dioxin to the amphipod *crangonyx laurentianus*. *Environmental Toxicology and Chemistry*, 9: 141-150.

Muir, D.C.G., Ford, C.A., Stewart, R.E.A., Smith, T.G., Addison, R.F., Zinck, M.E. and Beland, P. 1990. Organochlorine contaminants in Belugas, *Delphinapterus leucas*, from Canadian waters. *Can. Bull. of Fisheries and Aquatic Sciences*, T.G. Smith, D.J. St. Aubin and J.R. Geraci, Editors. *Advances in Research on the Beluga Whale*. 165-190.

Oliver, B.G. 1987. Partitioning relationships for chlorinated organics between water and particulates in the St. Clair, Detroit and Niagara Rivers. *QSAR in Environmental Toxicology-II*. K.L.E. Kaiser, Editor. Reidel Publishing. 251-260.

Pham, T., Lum, K.R. and Lemieux, C. 1993. The occurrence, distribution and sources of DDT in the St. Lawrence River, Quebec (Canada). *Chemosphere*, 26 (9): 1595-1606.

Platford, R.F., Maquire, R.J., Tkacz, R.J., Comba, M.E. and Kaiser, K.L.E. 1985. Distribution of hydrocarbons and chlorinated hydrocarbons in various phases of the Detroit River. *J. Great Lakes Res.* 1(3): 379-385.

SD. 1985. Sailing Directions. Gulf and River St. Lawrence. Department of Fisheries and Oceans, Ottawa, Canada, 6th

edition. 1-493.

Sloterdijk, H.H. 1985. Toxic substances in lake St. Francis sediments. Can. Tech. Rep. Fish. Aquatic. Sci., 1368: 249-264.

Poklington, R. and Tan, F.C. 1987. Seasonal and annual variations in the organic matter contributed by the St. Lawrence River to the Gulf of St. Lawrence. *Geochimica et Cosmochimica Acta*. 51: 2579-2586.

Rukavina, N.A., Mudroch, A. and Joshi, S.R. 1990. The geochemistry and sedimentology of the surficial sediments of Lac St. Louis, St. Lawrence River. *The Science of the Total Environment*, 97/98: 481-494.

Swackhamer, D.L. 1988. Quality Assurance Plan , Green Bay Mass Balance Study. I.PCBs and Dieldrin, University of Minnesota, March 11.

TOD, 1987a. Cruise Report of the CSS *Limnos*. Technical Operations Division, National Water Research Institute, Cruise #87-07-001.

TOD, 1987b. Cruise Report of the CSS *Advent*. Technical Operations Division, National Water Research Institute, Cruise #87-22-701.

van Rijn, L.C. 1984. Sediment transport, Part I. Suspended load transport. *Journal of Hydraulic Engineering*. 110 (11): 1613-1618.

Yeats, P.A. and Bowers, J.M. 1982. Discharge of metals from the St. Lawrence River. *Can. J. Earth Sci.* 19: 982-992.

## Appendix

### Detection Limits

NOI reports tabulated data (non-data base) detection limits using the terminology "nominal detection limits". This practice rationalizes the variables of sample amount, sample type, units of mass, amount injected, matrix effect and instrument sensitivity in situations where instrument performance and sample treatment remain within specified procedural boundaries. Operationally defined nominal detection values in NOI procedures can be used to determine the individual Quantitation Limit (QL) of each sample. Generally, sample sets are analyzed in the same manner with the sample variables kept constant, such that the one set of nominal detection limit values can be applied to all the sample sets. This simplified approach allows laboratories to report tabulated compound concentrations for which individual QL's are not reported but can be calculated using the analyzed sample weight. A major difference in NOI philosophy and definition for the reported detection limit, is the weight given to STATISTICAL QUALIFIERS, BLANK and MATRIX correction values. Many laboratories report their statistically qualified limit as their Level of Detection "LOD" or Detection Limit, and in most instances incorporate a blank correction factor or specify a set of method detection limits (MDL's), which refer to a level of detection related to sample size or matrix. NOI considers values of this type to be laboratory variables or data qualifiers, rather than detection limiting criteria. The NOI DL definition is not altered by any of these factors. Instead the QL of the determination changes. In cases where method or sample effects qualify the result, the data are flagged with an abbreviated letter code.

NOI data is classified in one of three formats: "Quantified", "Qualified" and "Not Detected". The term "Detection Limit" represents the unqualified minimum detectable amount of analyte expressed in terms of sample concentration. The term nominal detection limit is the abbreviated detection limit format. Nominal detection limits incorporate the instrument sensitivity (IDL), reconciled to the method extract amount.

### Definitions

#### **Instrument Sensitivity**

The instrument sensitivity is the minimum amount of analyte that generates any measurable response above the optimum electronic baseline.

#### **Detection Limit (DL)**

The detection limit is the quotient of any analytical response for a given analyzed amount measured at optimum instrument and method conditions, at time of use. For linear relationships  $DL = X_{min} = (Y - b/m)/\text{analyzed amount}$ ; where X is the amount of analyte, Y=instrument response, b= instrument electronic baseline and m= instrument sensitivity or slope of the calibration curve.

#### **Quantitation Limit (QL)**

This is the calculated level of detection for an individual sample, qualified by a selected statistical confidence interval (k), and quantitatively converted to mass concentration. The Quantitation Limit is determined for the actual analyzed sample amount, where  $QL = (Y - kb/m)/\text{analyzed sample amount}$ . The minimum acceptable value of k = 2 is used in NOI procedures.

#### **Nominal Detection Limits (NDL)**

NDL's are quantitative factors given in tabulated data reports that can be used to calculate individual sample DL's, when divided with the analyzed sample amount. Tabulated levels of NDL are expressed as  $(Y - kb/m)/\text{for a given unit of sample mass}$ .

#### **Other Levels of QL**

For numerous reasons, other than statistical, many laboratories set user defined thresholds different than those stated for QL. These reasons may include such factors as, blank response, matrix effects, sample size, artificial limits, non-linear applications, etc. Literature examples include such terms as, LOQ, PDL and MDL. In the context here, other user defined levels of QL must have values greater than QL and must include a definition. Data reported in this manner cannot use the term QL, but must instead report quantitation levels using the redefined terminology (ie. PDL).



**Data Qualifiers**

All measured data points not given in numerical format and subject to the conditions and definition of QL and DL must be qualified. The qualifier may represent defined limits (BDL, BQL, BML, BPL), methodology non-compliance (Nr, Ur), matrix effects (Tr, I), censored data (C) or (Is), insufficient sample, etc. A dictionary of terminology should be provided with each report. Data points may also be "flagged" with a qualifier to indicate that the method or field blank values exceeded pre-determined limits.

**Below Quantitation Limit (BQL)**

This data qualifier designates a level of analyte less than the specified QL. The use of BQL implies that the DL definition was not used and that the laboratory censors data values below this limit. The term BQL or BDL cannot be reported for the same data set.

**Below Detection Limit (BDL)**

This designation indicates a null value of analyte less than the specified DL. The use of BDL implies that the reported values met the documented method and detection limit requirements.

**Below Method (BML) and Practical (BPL) Limits**

These designations are used to indicate user defined detection limits and the censoring of data values. User defined limits imply that the achievable QL and DL were not attained.

**Use of the terms BQL, BDL and Trace**

Within the boundary region of detection limit and the statistically defined quantitative limit, analytical amounts (censored data) can be measured. The term BQL is specified in tabulated reports when the value of analyte is less than QL and therefore not reported. The term BDL is used to report a null value of analyte below the DL. The use of the BDL term indicates that all observed data points are reported, even those below QL. Data points of this nature may be of value although by definition they are not statistically reliable.

# Nominal Detection Limits\* for PCB Congeners

CONGENER	DETECTION LIMIT pg/g or pg/l sample*
PCB-1	950
PCB-3	1500
PCB-4-10	90
PCB-7	55
PCB-6	120
PCB-8-5	340
PCB-19	80
PCB-12-13	80
PCB-18 **	140
PCB-17 **	110
PCB-15 ***	U
PCB-24-27	70
PCB-16 **	110
PCB-32 **	110
PCB-26	90
PCB-25	90
PCB-31-28	95
PCB-33-53	110
PCB-22-51	130
PCB-45	65
PCB-46	75
PCB-52	65
PCB-49	60
PCB-47 **	140
PCB-48 **	140
PCB-44	70
PCB-42-37	110
PCB-64-41-71	85
PCB-40	80
PCB-100	85

CONGENER	DETECTION LIMIT pg/g or pg/l sample*
PCB-63	80
PCB-74	75
PCB-70-76	110
PCB-66 **	100
PCB-95 **	110
PCB-91-121	70
PCB-60-56	130
PCB-92-84	160
PCB-89	20
PCB-101	80
PCB-99	55
PCB-119 ***	220
PCB-83	60
PCB-97	50
PCB-87-81	70
PCB-85	80
PCB-136-77 **	33
PCB-110 **	110
PCB-82	70
PCB-151	70
PCB-135-144	55
PCB-107-123 ***	170
PCB-149-118	70
PCB-134-114	110
PCB-146 **	130
PCB-153 **	110
PCB-132-105 **	110
PCB-141	40
PCB-137-176	50
PCB-138-163	90

CONGENER	DETECTION LIMIT pg/g or pg/l sample*
PCB-178-126	100
PCB-158 ***	130
PCB-129 ***	290
PCB-175	90
PCB-187-182	75
PCB-183	110
PCB-128 **	190
PCB-167**	280
PCB-185 **	95
PCB-174	80
PCB-177	90
PCB-202-171-156 **	110
PCB-200-157 ***	150
PCB-172 **	140
PCB-197 **	160
PCB-180	95
PCB-193	100
PCB-191	120
PCB-199	60
PCB-170 **	160
PCB-190 **	95
PCB-198	110
PCB-201	140
PCB-203-196	230
PCB-189 ***	120
PCB-195-208	250
PCB-207	65
PCB-194	90
PCB-205	95
PCB-206	130
PCB-209	170

\* See enclosure: NOI detection limits; terms and definitions, based on one millilitre of extract.

\*\* Single column result plus subtracted value.

\*\*\* Determined by subtraction.

U = unknown

**Nominal Detection Limits\* for Organochlorine Compounds**

Organochlorine	pg/g or pg/l
Pentachlorobenzene	330
Hexachlorobenzene	330
Heptachlor	170
Aldrin	67
o,p-DDE	200
p,p-DDE	200
o,p-DDD	330
p,p-DDD	330
o,p-DDT	330
o,p-DDT	330
Mirex	130
a-BHC	170
b-BHC	170
g-BHC	170
Heptachlor epoxide	330
a-Chlordane	170
g-Chlordane	170
Dieldrin	330
a-Endosulfan	330
b-Endosulfan	330
Endrin	330

\* See enclosure: NOI detection limits; terms and definitions, based on one millilitre of extract

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