

ENVIRONMENTAL LEVELS AND TRENDS

MIREX IN DATED SEDIMENTS OF THE LOWER ST LAWRENCE ESTUARY

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Introduction

Downstream of Lake Ontario, the St. Lawrence River drains an industrialised and populated area, which includes Montreal and ends at Quebec city. The river opens into the upper St. Lawrence Estuary, a zone of high turbidity, and then to the Lower St. Lawrence Estuary (LSLE). The LSLE extends some 200 Km to the east and comprises the starting point of the Laurentian Trough, a 350 m deep channel which opens into the Gulf of St. Lawrence.

Mirex is a highly chlorinated, hydrophobic and persistent organic contaminant (Hexachloropentadiene dimer, C₁₀Cl₁₂, Figure 1), used in the past as a pesticide and flame retardant. Produced in large-scale from 1959 to late 60s by the Hooker Chemical Co. in Niagara Falls¹, Mirex was directly discharged to Lake Ontario by the Niagara and Oswego rivers for more than 15 years. Concentrations, temporal trends and inventories in dated sediment cores as well as the burden of Mirex in Lake Ontario have been documented^{2,3}.

Lake Ontario has been recognized as Mirex only source to the St. Lawrence River and Estuary. Therefore it may be used as a tracer for the transport in the St. Lawrence aquatic system. Recent work confirmed little net particle deposition in the St. Lawrence River lakes, as well as no significant net deposition in other parts of the river⁵. The river lakes retain less than 10 % of the approximately 5-7 million tons per year of suspended solids flux at the river exit⁵. Comba et al. estimated that over a period of 40 years (1950-1990), approximately 184 Kg of Mirex were stored in the LSLE sediments¹. These results suggest that the LSLE sediments represent the first significant zone of permanent accumulation of Mirex downstream of Lake Ontario.

The present work aims to determine the historical records, inventories and the burden of Mirex in the sediments of the LSLE. Mirex sales data and historical records of Mirex in sediments from both Lake Ontario and the LSLE are used to assess the time-scale of Mirex transport between Lake Ontario and the LSLE.

Methods and Materials

Sampling

In early 1990s, three sediment cores were collected along the longitudinal axis of the Laurentian Trough at water depths greater than 300 m. Stations 24A, E3 and C2, were located in the LSLE at 55, 100 and 190 Km downstream from

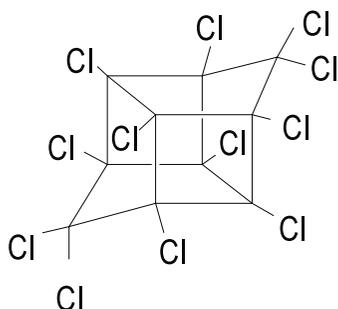


Figure 1. Mirex molecular structure

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Tadoussac, respectively. The sediment cores were immediately sliced in 0.5 cm increments at the top, gradually increasing to 3 cm increments at the bottom. Aliquots of each sediment slice were transferred into solvent-cleaned glass jars for Mirex analysis, and into polypropylene vials for water content and ^{210}Pb analysis.

Sediment analyses

Approximately 10 g of semi-dried sediment were spiked with a surrogate of $^{13}\text{C}_{12}$ labelled Mirex, mixed with 50-100 g of sodium sulfate and then soxhlet extracted overnight with 250 mL of acetone/hexane (1:1). The extract was cleaned up using a 10% deactivated neutral silica gel column, followed by treatment with copper powder to remove sulfur. The cleaned-up extract was evaporated, solvent exchange with nonane and a mixture of two $^{13}\text{C}_{12}$ labelled injection standards (1234-TCDD, 123789-HxCDD) was added. The analyses were performed on a high resolution gas chromatograph operated in splitless mode, on a DB-5 type capillary column with helium as the carrier gas. The GC was coupled to a VG 70SE mass spectrometer operated at a resolution of 10000 using selected ion monitoring. Two ions were monitored. Results were corrected on the basis of the $^{13}\text{C}_{12}$ surrogate recoveries. Radionuclide ^{210}Pb analysis was conducted on a freeze-dried sample of each sediment slice by the measurement of the activity of its granddaughter ^{210}Po .

Results and Discussion

Mirex profiles and levels

Sedimentation rates were calculated from the depth distribution profile of unsupported ^{210}Pb for each core, using the single-layer model⁷. They were used to calculate the age corresponding to the midpoint of each sediment section of the cores. Among the three stations, the core 24A showed the highest sedimentation rate ($0.490 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$) and a limited impact of bioturbation. This is in agreement with previous work⁸ showing that cores located at the head the Estuary best represent the historical record of contaminant accumulation in the LSLE sediments.

U.S. sales data³, Mirex accumulation in a sediment core (station LO90-E30)² from Lake Ontario and Mirex concentration profile in a sediment core (station 24A) from the LSLE are reported in Figure 2. The peak dates of Mirex accumulation in Lake Ontario sediments (1960-1970) compared to those of sales agree well with a direct discharge to the lake, and the decrease period with a decline in Mirex

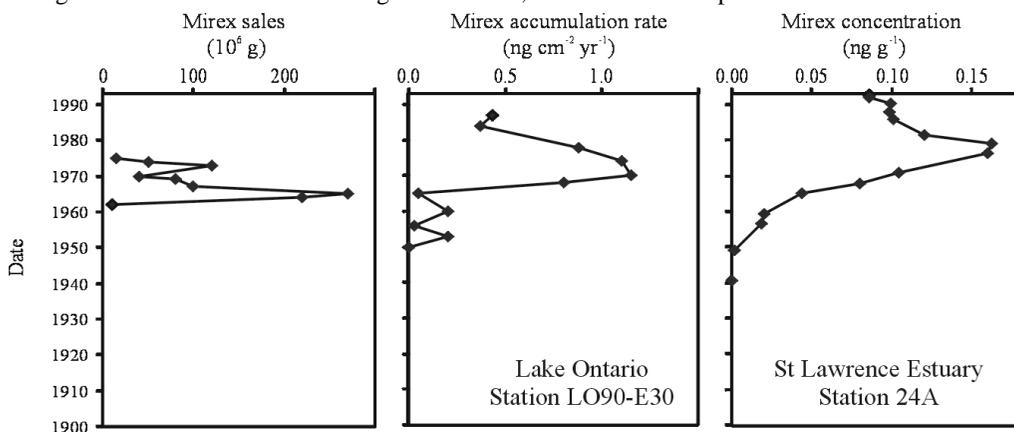


Figure 2. Mirex sales data³, accumulation rate in Lake Ontario² and LSLE sediment cores

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loading, due to its discontinued production and use in 1976³. In the LSLE, Mirex starts to accumulate in sediments by 1960, and shows a sharp peak with maximum of 0.162 ng.g⁻¹ corresponding to late 1970's, followed by a clear decreasing trend till surface (0.086 ng.g⁻¹, 1992). Comparison of Mirex accumulation profile in the 24A with Lake Ontario profile² indicate that Mirex started to accumulate in the LSLE sediments about 2-5 years later than in Lake Ontario sediments and Mirex decrease occurred within a similar time difference. The observed time difference of the well-buried peak in LSLE and Lake Ontario sediments is less than 5 years.

Mirex inventories and burdens

The Mirex inventories (I , in pg.cm⁻²) were calculated in each core according to the equation:

$$I = \sum_{n=1}^n (1 - \phi_i) \bar{\rho} [C] Z_i$$

where ϕ_i represents the measured porosity, $\bar{\rho}$ the density value of 2.65 g.cm⁻³ used for all the sediment samples, $[C]_i$ the Mirex concentration in the layer i , and Z_i the thickness of the layer i in the core. The calculated inventories in g.Km⁻² for the cores 24A, E3 and C2 are given in Table 1.

A decreasing inventory gradient is observed along the LSLE from 24A to C2 (Table 1). The highest Mirex inventory in sediments is found at station 24A (Table 1) suggesting that the head of the LSLE is the major sediment depositional site for accumulation of Mirex.

The inventories were used to estimate the Mirex burden in the LSLE sediments below the 200 m isobath. The Estuary was divided in three zones covering a surface area of approximately 4800 Km², each one of the three zones represented by a sampling station. A Mirex burden estimate of 27.8 Kg in the LSLE sediments was obtained by extrapolating the inventories at each station to its zone (Table 1). Our estimate of the total Mirex burden in the LSLE sediments differs largely from the 184 Kg reported by Comba et al.¹ It should be pointed out that Comba et al.¹ used an average Mirex concentration for each sediment core which they applied to a period of 40 years whereas our inventories were based on Mirex sedimentary profiles.

Table 1. Mirex inventories and burdens in the LSLE sediments

	Surface > 200 m depth (Km ²)	Mirex Inventory (g.Km ⁻²)	Burden (Kg)
24A	721	14.5	10.4
E3	1804	6.64	12.0
C2	2255	2.40	5.41
Total	4800		27.8

One of the main ways of Mirex transport from Lake Ontario to the LSLE is dissolved in water and associated to SPM. Kaiser et al.⁴ reported for 1986-87 an annual flux of Mirex to the St Lawrence Estuary of 2.5 Kg.yr⁻¹ which is in agreement with the value of 3 Kg.yr⁻¹ reported by Comba et al.¹ for 1986-89. An estimate of Mirex load into the LSLE between 1960 to 1990 was made based on the average annual flux of Mirex (2.75 Kg.yr⁻¹ for 1986-89) adjusted for the changes in flux during that period of time. Periods of 2 to 4 years were considered from 1960 to 1990, and the average annual flux

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of Mirex was calculated for each period assuming that the changes in Mirex flux followed the changes in Mirex average accumulation rate during the same periods, as reflected by the Lake Ontario sediment profile (Figure 2). As a result, the Mirex load into LSLE between 1960 to 1990 is estimated at 115 Kg. According to this value, our estimate of 27.8 Kg Mirex burden in the LSLE sediments represents only about 24% of the load from water and SPM whereas Comba's estimate of the Mirex deposited in the LSLE is 1.6 times higher than the estimated load.

The record of Mirex in the sediment core from the head of the LSLE suggests a very fast transport of this compound (within 2 to 5 years) between Lake Ontario and the LSLE. This indicates that the LSLE is rapidly affected by relatively distant (i.e. 800 Km) upstream pollution. The discrepancy between our estimate of total Mirex burden in the LSLE and the one from Comba et al.¹ could possibly be explained by the use of a different analytical technique for Mirex quantification and a different approach to calculate Mirex burden. Very likely, the transport of Mirex from Lake Ontario to the LSLE by highly contaminated migrating eels should also be taken into account in the calculation of the Mirex load to the LSLE. However, little is known on the uptake of Mirex by living organisms within the LSLE, and the export of Mirex by SPM, water and fish (including eels) downstream to the Gulf of St Lawrence.

Acknowledgments

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