SPATIAL AND TEMPORAL EVOLUTION OF THE GEOCHEMISTRY AND SEDIMENTARY PROCESSES OF LAKE SAINT-FRANÇOIS IN THE 20TH CENTURY

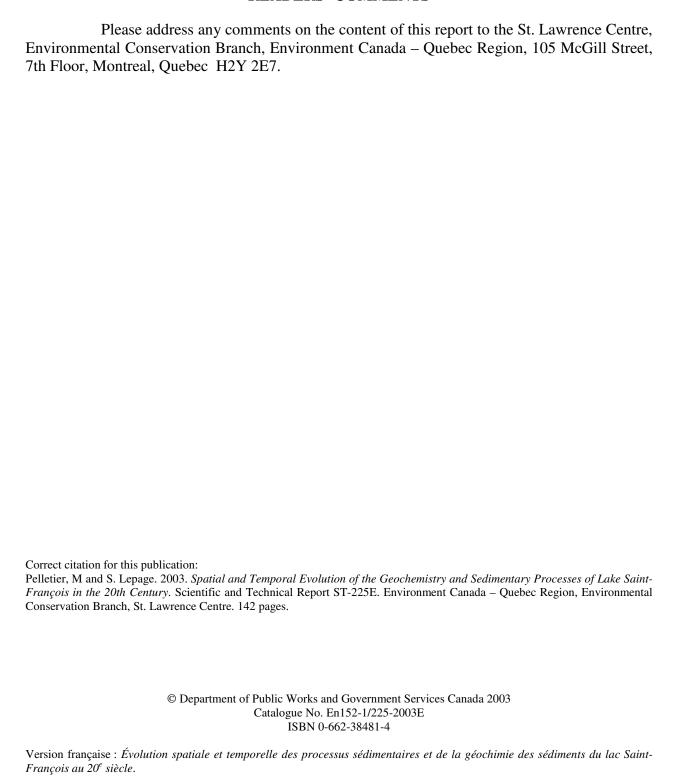
Report ST-225E

Spatial and Temporal Evolution of the Geochemistry and Sedimentary Processes of Lake Saint-François in the 20th Century

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St. Lawrence Centre Environmental Conservation Branch Environment Canada

READERS' COMMENTS



Management Perspective

This study was conducted within the framework of the Nature Table with the aim of understanding and reducing the incidence of human activities on the health of ecosystems and assessing their impacts on the state of the St. Lawrence River. It is also an element of the State of the St. Lawrence Monitoring Program, whose results are a priority for the Environmental Conservation Branch in the Quebec Region in 2002–2003.

Perspective de gestion

Cette étude a été réalisée dans le cadre de la Table Nature « Nature » dans le but de comprendre et de réduire les incidences des activités humaines sur la santé des écosystèmes, et d'évaluer leurs impacts sur l'état du Saint-Laurent. Elle constitue également un élément du Programme de suivi de l'état du Saint-Laurent, dont les résultats sont prioritaires pour la Direction de la conservation de l'environnement, Région du Québec, en 2002–2003.

Acknowledgments

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Abstract

A snapshot of trends in sediment geochemistry in Lake Saint-François during the past 20 years was produced by compiling and interpreting physical and geochemical data drawn from 27 sediment cores and three surface-sediment sampling campaigns. Certain anthropogenic events in Lake Saint-François during early industrial development of the Cornwall-Massena area greatly contributed to altering the lake's hydrodynamics and changed the dynamics governing sediment deposition. The resulting major temporal and spatial modifications have caused annual sediment accumulation rates to vary from 0.2 to 1.9 cm and have led to variations in the particle-size distribution of particles deposited in the basin. Five sedimentary units were defined for recent sediments based on these quantitative variations and different areas of sediment accumulation in Lake Saint-François were correlated. In interpreting the geochemical data, we have been able to assess, both in time and space, variations in the geochemical components of contaminants deposited in lake sediments following industrial development in the Cornwall–Massena area. The study of the geochemical trend led to a determination that, beginning in the 1970s, contaminant concentrations declined considerably, with average mercury and total PCB levels falling from 0.47 to 0.23 µg/g and 0.397 to 0.028 µg/g, respectively. We also identified four different cycles of variations in contaminant concentrations in the lake since the turn of the 20th century.

Résumé

La compilation et l'interprétation des données physiques et géochimiques provenant de 27 carottes de sédiments et de trois campagnes d'échantillonnage de la couche superficielle de sédiments du bassin sédimentaire du lac Saint-François depuis 20 ans permettent de dresser un portrait de l'évolution des sédiments et de leur géochimie durant le dernier siècle. Certaines activités anthropiques qui se sont déroulées au lac Saint-François depuis le début de l'industrialisation ont largement contribué à modifier non seulement les composantes hydrodynamiques, mais également la dynamique sédimentaire. Il en résulte des modifications temporelles et spatiales importantes qui font varier les taux de sédimentation de 0,2 à 1,9 cm par année ainsi que la répartition granulométrique des particules déposées dans le bassin. Ces variations des proportions quantitatives permettent la définition de cinq unités sédimentaires reliées aux sédiments récents et la corrélation des différentes zones de sédimentation du lac Saint-François. L'interprétation des données géochimiques permet d'évaluer, tant dans l'espace que dans le temps, les variations des composantes géochimiques des contaminants qui s'étaient logés dans les sédiments à la suite du développement industriel du secteur de Cornwall-Massena. L'étude de cette évolution géochimique permet notamment d'estimer qu'à partir des années 1970, il s'est produit une diminution considérable des concentrations, faisant passer respectivement les teneurs moyennes en mercure et en BPC_{totaux} de 0,47 à 0,23 mg/g et de 0,397 à 0,028 mg/g, et de définir quatre cycles de variation des concentrations depuis le début du 20^e siècle.

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1 Introduction

Lake Saint-François forms both a provincial and an international boundary, and every year its waters accommodate many ships transporting goods, oil and tourists. Its surface is used for pleasure boating, but primarily also as a refuge by many birds, several species of aquatic animals and a host of emergent and submerged plants. Considered one of the most beautiful lakes in the St. Lawrence River, its sedimentary and geochemical history — including that part that dates back as recently as the end of the 19th century — are still poorly understood.

Since the end of the 1800s, many anthropogenic activities have considerably disrupted and altered the tranquility of Lake Saint-François. Construction of dams both upstream and down, an increase in water levels in the lake, dredging of the St. Lawrence Seaway and industrial development in the boundary areas of Cornwall and Massena have all affected sediment dynamics and geochemical characteristics to a greater or lesser extent. This human activity took place against a backdrop of natural variations in the flow of the St. Lawrence River over the years, with periods of erosion of the lake's islands and shores combined with periods of sediment deposition.

Over the past century, sediments in Lake Saint-François were contaminated by anthropogenic inputs containing mercury (Hg) and polychlorinated biphenyls (PCBs) (Sloterdijk 1985, 1991; Lorrain et al. 1993; Vanier et al. 1996; Richard et al. 1997). These pollutants remain in the sediments and may be resuspended as a result of human activities or water-level changes (Lepage 1999). Although present-day surface sediments now pose less of a risk of contamination to the aquatic environment (Lorrain et al. 1993), sediments that are buried beneath this thin layer of cleaner deposits pose a serious threat in the event of a natural or anthropogenic disruption or change in sedimentary conditions.

This document describes the main events that have affected the evolution of sediments in Lake Saint-François and their geochemistry since the waters of the Champlain Sea receded over 8000 years ago. Although few details are available concerning the formation of the current shoreline and basin, the past century is relatively well documented and it is becoming possible to focus on many aspects that characterize the lake and its sediments. Since the late 1970s, Environment Canada has been working to characterize the sediments that have been deposited on

the bed of Lake Saint-François since its formation. Three campaigns were conducted to collect sediment samples and samples for geochemical analysis, the first in 1979 (Sloterdijk 1985), the second in 1989 (Lorrain et al. 1993) and the third in 1999 (Lepage et al. 2001). In addition to these samples of surficial sediments, almost thirty sediment cores were collected over the entire lake, from Cornwall to Valleyfield. The resulting data can be used to produce sedimentary and geochemical profiles of the sediments throughout the 20th century and to assess the degree of sediment contamination and the impact of environmental action taken since the beginning of the 1970s.

2 Study Area and Sedimentary Setting

Lake Saint-François is the first natural fluvial lake in the St. Lawrence River downstream of the Great Lakes. It marks the provincial boundary between Quebec and Ontario and, in its upstream reaches, the international border between the United States and Canada. The upstream cities of Cornwall, Ontario, and Massena, New York (U.S.A.), and the downstream city of Sallaberry-de-Valleyfield, Quebec, are the three main urban centres situated on the lake (Figure 1). The remainder of the land along the river is shared by the residents of a dozen small municipalities and the Aboriginal people of the Akwesasne reserve (Figure 1).

At 50 km in length and up to 8 km in width in places, Lake Saint-François covers an area of 233 km² in the heart of a relatively flat section of the St. Lawrence River hydrographic basin. The lake is 5.1 m deep and has a complex bathymetry, with several channels that are up to 26 m in depth. Most of these channels converge into a single channel, creating several shoals less than 1.5 m below the surface as well as numerous islands. There are five deeper basins where sedimentation tends to occur: the Pointe des Cèdres, Thompson, Lancaster, Grenadier and Saint-Zotique basins (Figure 2).

Lake Saint-François is fed primarily by the waters of the St. Lawrence River, but has several other tributaries. From the south, the largest of these are the Grasse, Raquette, St. Regis, Salmon and La Guerre rivers. From the north, the Raisin and Beaudette rivers are the lake's largest tributaries (Figure 1). Since the construction of the Iroquois Dam some fifty kilometres upstream of Lake Saint-François, the average regulated flow at Cornwall has been 7800 m³/s, 95% of which comes directly from Lake Ontario, with 5% originating from the tributaries upstream of Cornwall (SLC 1997). The average combined flow from the tributaries of Lake Saint-François (150 m³/s) accounts for only 2% of the total inflow. Various authors consider that tributary inputs have only a minimal impact on the main water mass of Lake Saint-François and that this water mass remains homogeneous both in summer and in winter (Désilets and Langlois 1989; Verrette 1990). A recent study shows, however, that the tributaries on the south shore of the lake are capable of affecting the water mass that flows along the south of the navigation channel in winter (Lepage et al. 2000).

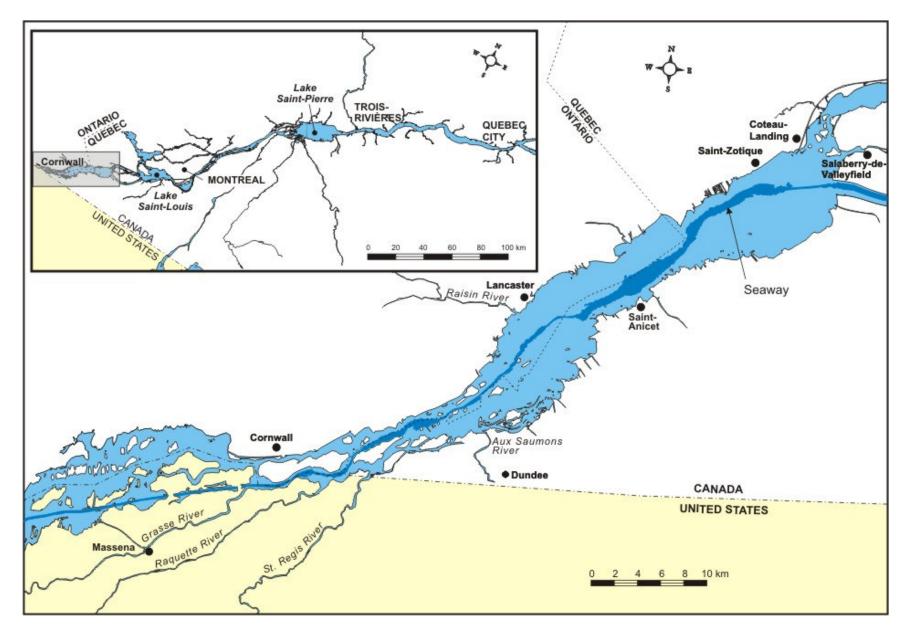
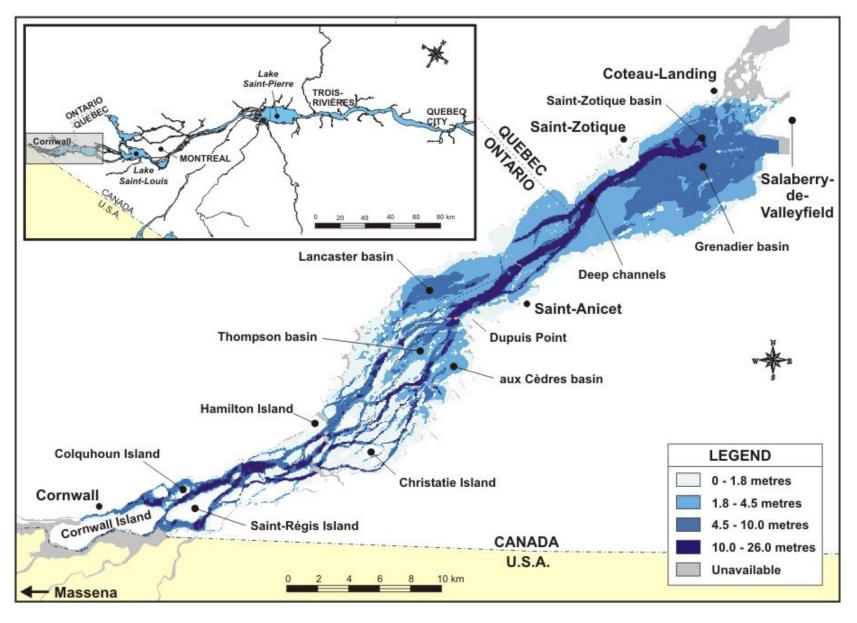


Figure 1 Communities in the vicinity of Lake Saint-François



Source: Adapted from Fortin et al. 1994.

Figure 2 Bathymetry of Lake Saint-François

Most of the recent sediments in Lake Saint-François were produced by the erosion of the Quaternary deposits that make up the shorelines and the bottom of the lake and by the resuspension of upstream sediments (Coakley et al. 1989). The Quaternary deposits are comprised almost solely of Champlain Sea clays (8000 to 12 000 years before present [BP]) and Wisconsinian glacial tills (12 000 to 80 000 years BP). The randomly distributed till deposits combine with the clays to form a cover that ranges from a few metres to several dozen metres in thickness, overlying the basement rocks (Landry and Mercier 1992).

Because the physiography of the Great Lakes promotes sedimentation of suspended solids in the deep basins located upstream of Kingston, the waters that flow through the international stretch of the St. Lawrence toward Lake Saint-François are transporting only a small amount of suspended solids. Based on studies conducted from 1989 to 1993, the average suspended solids concentration is estimated at 1.0 ± 0.6 mg/L (Rondeau et al. 2000). At such a concentration, the annual load originating in the Great Lakes can be estimated at 200 000 metric tons (mt).

The load delivered by the tributaries is more difficult to assess because of the lack of information on suspended solids concentrations in these rivers. According to the work of Frenette et al. (1989), the tributaries contribute an annual load of over 250 000 mt, most of which originates from the rivers on the south shore. Of this total load of 450 000 mt/yr (200 000 mt + 250 000 mt), approximately 90 000 mt is deposited annually in the deepest parts (≥ 4.5 m) of Lake Saint-François, which account for approximately 28 km² of its area (Carignan et al. 1993). This deposition of materials corresponds to a sedimentation rate of between 0.13 and 1.91 cm/yr (Carignan 1990; Carignan et al. 1993), contradicting previous hypotheses, which concluded that sedimentation in Lake Saint-François was temporary (Allan 1986; Sloterdijk 1985).

With regard to suspended solids contamination, the study by Lepage (1999) shows that the northern part of Lake Saint-François received suspended solids with mercury (Hg) levels exceeding background values until the end of 1996, while the southern part was still being affected by polychlorinated biphenyl (PCB) sources.

3 Methodology

3.1 SAMPLING

During the 1979 campaign (Figure 3), surface sediments were sampled in two stages. The first involved gathering sediment from locations near the shores using an Ekman dredge and positioning them by means of visual reference points. In the second stage, samples were collected at stations located at some distance from shore using a Shipek grab sampler and a tellurometer system to position them (Sloterdijk 1985). Because the Shipek sampler is an effective means of collecting undisturbed samples, it was also used during the 1989 and 1999 campaigns (figures 3 and 4). In 1999, technological progress made it possible to position samples by means of a global positioning system (GPS) in differential mode, a more precise method than the tellurometer that was still being used in 1989 (Table 1).

The sampling grid used in 1979 was random and ungrouped, whereas the 1989 grid was systematically configured to make it possible to identify the spatial distribution of the sources of variation in sediment quality. This grid was also stratified as a function of factors governing the spatial distribution of sediments, including bathymetry, relief, currents and the distribution of macrophyte beds (Lorrain et al. 1993). Most of the samples collected in 1999 were sampled using the same sampling grid as the one used in 1989 in order to facilitate comparison of the results of the two campaigns.

The 1990, 1992, 1994 and 1996 sediment cores were all collected by the same method, regardless of the water level at the sampling stations (Figure 4). Divers inserted 12-cm butyrate tubes into the sediment without disturbing the surface layer. Measurements in 1990 (Lorrain and Carignan 1992) indicate that, among other advantages, this sampling technique is associated with a low compaction rate (approximately 3%). In 2000, sediment cores were also collected using a percussion corer in order to reach and penetrate the layer of marine clay underlying the recent sediments (Saulnier and Gagnon in preparation).

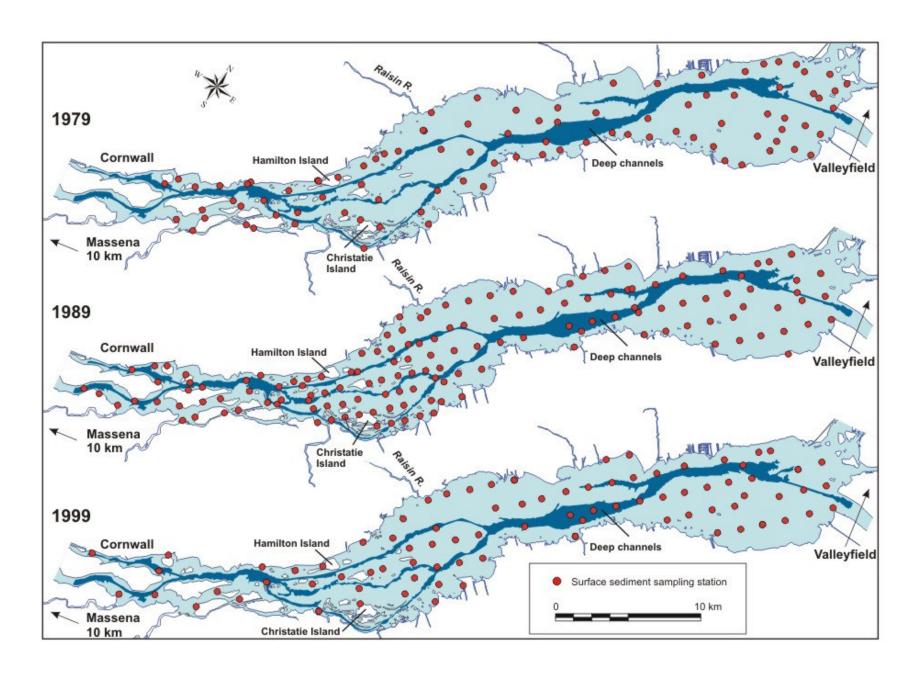


Figure 3 Location of sampling stations during the 1979, 1989 and 1999 campaigns

Table 1 Summary of field and laboratory methodologies used for the various sediment cores and sampling campaigns

	Sediment Cores			Sampling Campaigns				
	1990	1992	1994	1996	2000	1979	1989	1999
Positioning of stations	Not specified	Not specified	Not specified	Not specified	GPS Differential mode	Tellurometer MRB 201 and visual means near banks	Microwave tellurometer MRD-1	GPS Differential mode
Sampling tools	12-cm butyrate tube inserted by divers	12-cm butyrate tube inserted by divers	Not specified	12-cm butyrate tube inserted by divers	8-cm polycarbonate tube - percussion drilling	Akman dredge Shipek sampler	Shipek sampler	Shipek sampler
Sampling	Various	Various	Various	Various	Various	0 to 4 cm	0 to 3 cm	0 to 3 cm
Particle size	Sieving and SediGraph X-ray	Sieving and SediGraph X-ray	Sieving and SediGraph X-ray	Sieving and SediGraph X-ray	Sieving and laser SediGraph	Sieving, pipette and sedimentation tube	Sieving and SediGraph X-ray	Sieving and laser SediGraph
Carbon Nitrogen	Carlo Erba NA-1500 CNS analyser	Carlo Erba NA-1500 CNS analyser		LECO12 carbon analyser	LECO12 carbon analyser	Hewlett Packard 185 CHN analyser	Hewlett Packard 185 CHN analyser	LECO12 carbon analyser
Metals	ICP - HNO ₃ , HClO ₄ , HF and HCl extraction	ICP and AA (Pb) - HNO ₃ , HClO ₄ , HF and HCl extraction		AA - total HNO ₃ , HClO ₄ , HF and HCl - extractable 1N HCl	AA - total HNO ₃ , HClO ₄ , HF and HCl - extractable 1N HCl		AA - total HNO ₃ , HClO ₄ , HF and HCl - extractable 1N HCl	
Mercury				Spectrophotometer with UV detector - HNO ₃ , HCl extraction and K permanganate and persulphate oxidation	Cold vapour atomic absorption - HNO ₃ , HCl extraction and K permanganate and persulphate oxidation	Spectrophotometer with UV detector - HNO ₃ , HCl extraction and K permanganate and persulphate oxidation	Cold vapour atomic absorption - HNO ₃ , HCl extraction and K permanganate and persulphate oxidation	Cold vapour atomic absorption - HNO ₃ , HCl extraction and K permanganate and persulphate oxidation
Organic compounds		Gas chromatography— acetone/hexane and dichloromethane extraction, Florisil column purification		Gas chromatography— acetone/hexane and dichloromethane extraction, Florisil column purification		Gas chromatography— acetone/hexane and dichloromethane extraction, Florisil column purification	Gas chromatography— acetone/hexane and Florisil column purification	Gas chromatography— acetone/hexane and Florisil column purification
References	Carignan and Lorrain 2000	Carignan et al. 1994	Barua 1995 and this study	Rukavina 2000; Barua 1996 and this study	Saulnier and Gagnon in preparation	Sloterdijk 1985; Sloterdijk 1993	Lorrain et al. 1993; Lorrain and Jarry 1993	This study

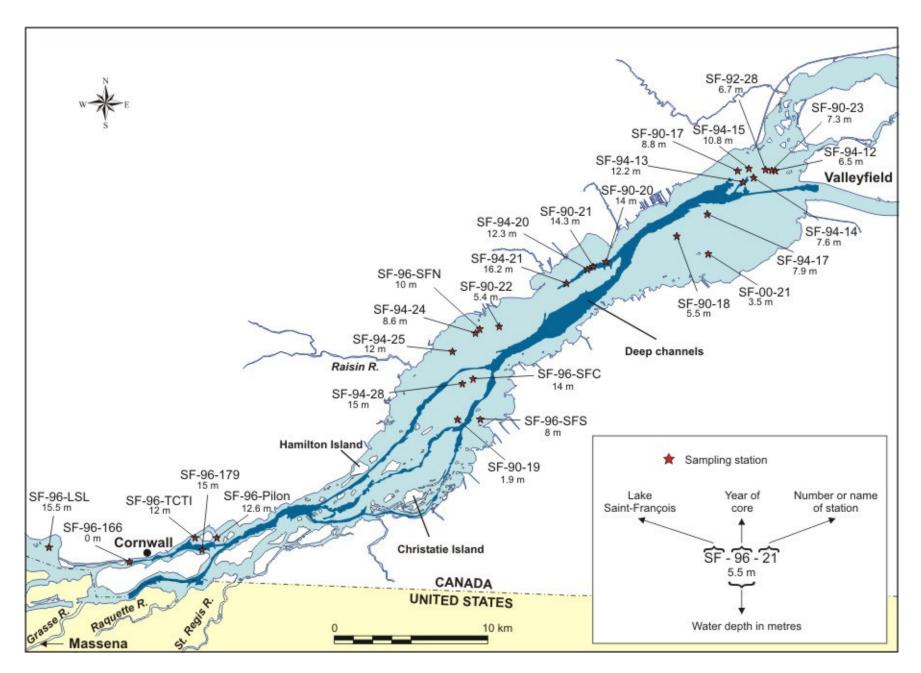


Figure 4 Location of sediment core sampling stations

In the case of the grab samples, only the first three centimetres were collected and they were deposited in containers that were already prepared to receive metals or organic compounds (Environment Canada 1979). However, subsampling of cores varied depending on the objectives of the various projects for which the samples had been collected. Consequently, subsamples of the 1990 cores were collected every centimetre, while the 1992 and 1996 cores were subsampled every 2 cm and the 1994 cores every 5 cm.

3.2 ANALYSES

All sediment samples and subsamples were analysed to identify the various particle-size fractions (appendices 1 and 2 and Table 1). Samples were lyophilized and then sieved to remove the coarsest fractions; a SediGraph was then used for the fine fractions. This method can be used to obtain particle-size distribution curves for every half-phi (ϕ) diameter interval (Duncan and Lahaie 1979). In 1979, the fine-particle distribution was measured using a sedimentation tube.

Organic carbon was analysed in all samples except the 1994 cores (appendices 1 and 2 and Table 1). Organic carbon was quantified by using a CNS or CHN analyser to measure total carbon in the samples and then subtracting the inorganic carbon content determined by treatment with sulphuric acid (H₂SO₄) (Environment Canada 1979). The CNS and CHN analysers were also used to determine the total nitrogen concentration in the samples.

The sediments obtained in the 1979, 1989 and 1999 sampling campaigns were analysed for total mercury content by cold vapour atomic absorption spectroscopy (AAS) following nitric acid (HNO₃) and hydrochloric acid (HCl) extraction and potassium permanganate and persulphate oxidation (Appendix 1 and Table 1) (Environment Canada 1979).

The total metal content of parts of sediment cores collected in 1990, 1992 and 1996 and surface sediment collected during the 1989 campaign was determined by open digestion following lyophilization, sieving and crushing of the samples to fine powder (appendices 1 and 2 and Table 1). Total digestion was carried out with nitric acid (HNO₃), perchloric acid (HClO₄), hydrofluoric acid (HF) and hydrochloric acid (HCl) until the sample was completely destroyed. The digestates were then analysed by AAS in 1989, 1992 and 1996 and by inductively coupled plasma atomic emission spectrometry (ICP/AES) in 1990 and 1992 (Environment Canada 1979).

A partial digestion of sediments from the 1989 campaign was also carried out, with a view to quantifying the extractable fraction containing metals bound to organic matter, to carbonates, and to iron and manganese oxyhydroxides, and adsorbed on fine particles (Appendix 1). This quantification was carried out by atomic absorption spectrometer (AAS) utilizing the products of a 1N hydrochloric acid extraction (Environment Canada 1979).

Organic solvents (acetone/hexane and dichloromethane) were used to extract all the organic compounds contained in the sediments, which then underwent the recommended treatments (cleaning, purification, concentration, etc.). Gas chromatography was used for the quantitative analysis of PCBs, hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT), Mirex and other substances, while polyaromatic hydrocarbons (PAHs) were measured using liquid chromatography (appendices 1 and 2 and Table 1) (Environment Canada 1979). It is important to note that the combination of organic compounds was different for each sampling campaign and for the cores. Finally, PCB results for the 1979 and 1989 campaigns are expressed as total Aroclor concentrations (A 1242 + A 1254 + A 1260). The results for PCBs from the 1999 campaign and the 1996 cores cover 41 congeners, while those for core SF-92-28 represent a total for 11 congeners.

3.3 DEFINITIONS OF TYPE PROFILES

Sediment cores were selected for purposes of developing type profiles for the particlesize distributions of the sediments and for the geochemistry of the metals. The cores were chosen on the basis of the following criteria:

- the cores had to have been analysed for radiometric isotopes (Pb-210 and Cs-137);
- the cores had to have come from a known sedimentation area (Lancaster basin, Saint-Zotique basin);
- the cores had to have been subsampled at intervals of 2 cm or less;
- the cores had to have been analysed for various physico-chemical components (particle size, organic carbon, metals).

Cores SF-90-17, SF-90-22, SF-90-23, SF-92-28 and SF-96-SFN (Figure 4) were selected for developing the sediment type profile, while cores SF-90-17, SF-90-22, SF-92-28 and SF-96-SFN (Figure 4) were used to produce type profiles for the geochemistry of the metals. It

should be noted that the profiles for mercury and the organic compounds were obtained using cores SF-92-28, SF-96-SFN and SF-96-SFS (Figure 4).

The type profiles were developed as follows:

- Radiometric ages were used to chronologically order the various sediment intervals in the cores selected.
- Data on radiometric age, grain sizes and geochemistry were smoothed with a moving average on the order of 7 data points; this smoothing was chosen on the basis of the dating precision, which is approximately 2 to 5 years, and an average sedimentation rate of about 1–1.5 cm/yr (Carignan et al. 1994); it was therefore necessary to combine the values in the three upper and lower intervals for calculation purposes.
- The smoothed data were then plotted on X-Y diagrams, with the age data and sedimentation rates on the ordinate, and the particle-size and geochemistry results, obtained by smoothing, on the abscissa.

3.4 CONVERSION OF PCB CONGENERS TO AROCLORS

Total PCB results for the 1979 and 1989 sampling campaigns combine concentrations of Aroclors 1242, 1254 and 1260, while the results for 1999 cover the concentrations of 41 congeners. Total PCBs for 1999 are not directly comparable with historical results. In order to be able to draw a comparison, the approximate values of these Aroclors must be calculated from the congeners and their distributions as Aroclor compounds. Each Aroclor actually contains a different quantity of congeners. Schulz et al. (1989), Manchester-Neesvig and Andren (1989) and Frame et al. (1996) provide tables comparing certain Aroclors and the 209 PCB congeners analysed with reference to various reference materials. Based on these tables, two calculation methods were developed: one that uses the relative percentages of the congeners associated with the Aroclors, and the other the relative percentages of the various chlorinated groups (n Cl) also associated with the Aroclors. The average of the two was then used to interpret the results.

Method 1

Aroclor =
$$\sum \frac{[\text{congener } i] \times (\% \text{ of congener } i \text{ in the Aroclor})}{100}$$

Method 2

Aroclor =
$$\sum \frac{[\text{chlorine group } i] \times (\% \text{ of chlorine group } i \text{ in the Aroclor})}{100}$$

where

Aroclor refers to the calculated concentration of Aroclor;

congener *i* refers to the concentration of the congener (41 congeners);

chlorine group i refers to the concentration of the chlorinated group (sum of the congeners with the same number of chlorine atoms – total of 10 groups);

% of congener i in the Aroclor is the percentage taken from Manchester-Neesvig and Andren, 1989, Table: I;

% of chlorinated group i in the Aroclor is the percentage taken from Manchester-Neesvig and Andren, 1989, Table: III.

The total value of PCBs for the 1999 sampling campaign was determined by adding the three calculated Aroclors (A 1242, A 1254 and A 1260).

In order to verify these calculations, 26 samples collected in 1989 and containing known amounts of Aroclors were reanalysed for PCB congeners. Although this conversion of PCB congeners to Aroclors remains an approximation, the calculations show a significant correlation coefficient of 0.72 between the measured and calculated values for all 26 samples (Appendix 3).

3.5 PLOTTING THE RESULTS

According to Lorrain et al. (1993), the main contaminants identified in Lake Saint-François originate from the Cornwall area on the north side of the river and from the Massena area on the opposite shore. Since water flow and deposition of the main contaminants occur along the shore of the lake with an almost complete absence of lateral mixing, it is reasonable to plot results in a way that makes it possible to group the stations on each side of the channel and treat them separately. Accordingly, the results were plotted in two phases. In the first phase, results from sampling stations located on different sides of the navigation channel were separated; in the second, an interpolation was produced by kriging the data on each of the two sides.

MapInfo, Version 6.5, and Vertical Mappers, Version 3.0 were used for the interpolation; the kriging grid node spacing was 50 m and the search radius was 50 m. For most maps, colour definition was adjusted on the basis of 1989 data. Data on PCB congeners are the sole exception to this rule since they were only analysed in 1999.

For sediment particle size, results were first classified according to Shepard's diagram (Shepard 1954) as a function of sand, silt and clay content. A weighting of 1 to 10 was then

assigned to each sample, according to its sediment class, with a view to producing a monochrom plot to highlight and enhance areas of fine sediment.

3.6 CALCULATION OF CONTAMINATION INDEX (CI)

The sediment contamination index (CI) is calculated according to the following formula:

$$CI = \frac{\sum \frac{(\text{content}) i}{(\text{standard}) i}}{K}$$

where

K represents the number of parameters for which interim criteria have been established for assessment of sediment quality (SLC and MENVIQ 1992).

In the case of metals, these standards are based on partial analyses. For organic compounds, a value of zero was assigned where analytical results were below the detection limit, while for nonpolar organic contaminants, standards were normalized on the basis of the percentage of total organic carbon (TOC) (Fortin et al. 1994).

4 Sedimentary Evolution

This chapter is divided into two sections: the first describes the temporal evolution of sedimentation in Lake Saint-François, and the second gives an overview of the spatial evolution of sediments in this fluvial lake over the past 20 years.

The study of the temporal evolution of sedimentation in Lake Saint-François was based primarily on interpretation of granulometric data from sediment cores collected between 1990 and 2000. These results were used to draw up a type profile for recent lake sediments, within which five sedimentary sequences were identified and related to various anthropogenic activities that have had an impact on sediment dynamics and hydrodynamics in this lake basin. This type profile was developed on the basis of Pb-210 and Cs-137 radiometric ages obtained for sediment cores SF-90-17, SF-90-22, SF-90-23, SF-92-28 and SF-96-SFN (Figure 4), which reflect the sedimentary history of the lake through 70 cm of deposition back to the end of the 1800s.

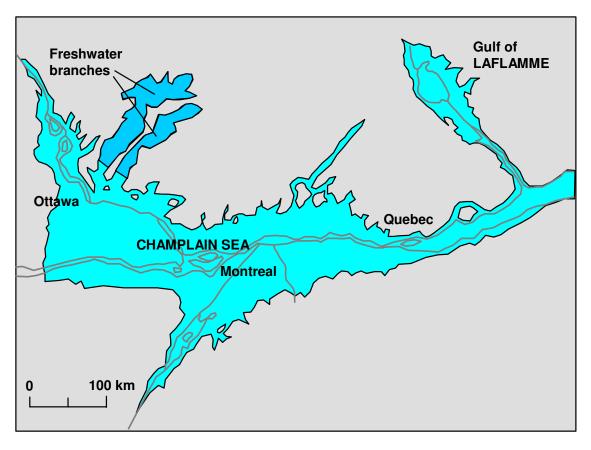
The study of the spatial evolution of sediments in Lake Saint-François was based on granulometric results from sampling campaigns conducted at decadal intervals (1979, 1989 and 1999) (Figure 3). A sedimentological classification can be used to provide an overview of sediment dynamics and hydrodynamic flow by showing spatial variations in the various types of sediments in this fluvial lake.

4.1 TEMPORAL EVOLUTION OF SEDIMENTATION

4.1.1 Champlain Sea clays

The gradual retreat of the Wisconsinian ice cap began approximately 14 000 years ago in the Great Lakes–St. Lawrence Lowlands region. The melting ice would result in the formation of several large post-glacial lakes and an inland sea, referred to today as the Champlain Sea. By 12 000 years ago, the front of the ice sheet had receded north of the St. Lawrence Valley, leaving the surface of the land depressed to a point below sea level and allowing the salt waters of the Atlantic Ocean to invade (Prest 1972; Bariteau 1988). At that time, at an elevation of over 200 m, the Champlain Sea covered the St. Lawrence Valley, extending to the foot of the Laurentian Mountains in the north and the Appalachians in the south. The height of land was situated at the

present-day location of Kingston, Ontario (Prichonnet 1977; Parent and Occhietti 1988; Occhietti 1989; Bérubé 1997) (Figure 5).



Source: Occhietti 1989.

Figure 5 Maximum extent of the Champlain Sea

During this period, a significant quantity of very fine particles produced by the erosion of the glacial deposits and the rocks of the Precambrian Shield were transported toward the Champlain Sea by the fresh water generated by the melting of the ice that still covered the Canadian Shield. The particles accumulated to form major clay deposits reaching thicknesses of almost 80 m in certain places. These deposits consist primarily of silty clays or clay loams that are homogeneous or stratified according to provenance, compact, grey-blue in colour and contain little water or organic material (< 1%) (Bérubé 1997; Crémer 1979).

During the 2000 years (from 12 000 to 10 000 years BP) that followed the formation of the Champlain Sea, the continent rebounded isostatically at a rate of 8 cm/yr, with periods of slow rise alternating with periods of faster uplift (Corbeil 1984). As the continent rose, the brackish waters were gradually expelled toward the Atlantic Ocean, making way for the fledgling drainage network of the St. Lawrence River. For the next 2000 years, from 9750 BP to 8000 BP, the Lake Saint-François area was occupied by Lake Lampsilis (Bariteau 1988). During the Lake Lampsilis episode, a ridge of bedrock emerged near Valleyfield (MacPherson 1967) and probably blocked the drainage of the water downstream, causing this portion of the river to expand (Bariteau 1988). Finally, by around 8000 BP, Lake Saint-François had almost reached its present-day configuration (MacPherson 1967; Crémer 1979).

The clay deposits of the Champlain Sea are therefore not part of the sedimentary deposits of Lake Saint-François. They formed much earlier in a marine setting that is completely different from the current fluvial context of the St. Lawrence River. However, because of the erosion of banks and streambeds and the input of tributaries that wend their way across these clay deposits, they are a significant source of fine particles in recent sediments. As a result, marine clays must be included in an analyis of the physical and chemical constituents of the overall St. Lawrence environment.

During the coring of sediments in Lake Saint-François, the topmost portion of Champlain Sea clay deposits was collected at sampling stations SF-94-17, SF-96-SFC and SF-00-21 (Figure 4). Particle-size analyses of these clay samples indicate that the clay fraction generally exceeds 80%, with sands usually comprising less than 3% (Table 2).

Table 2
Average particle-size composition of Champlain Sea clays

Sand	Silt	Clay
$1.9 \pm 1.3\%$	$7.0 \pm 5.5\%$	$91.0 \pm 6.2\%$

4.1.2 Between the Champlain Sea clays and recent sediments

After the salt waters of the Champlain Sea receded (8000 years BP), the new pattern of the St. Lawrence River developed over the years as the river carved a bed in the underlying clays and glacial deposits in response to the isostatic rebound of the continent and the spring floods. During this period, a significant volume of sand was transported from the upstream reaches toward the estuary, adding to the present-day cover overlying part of the marine sediments (Bérubé 1997; Crémer 1979).

In the Lake Saint-François area, few traces remain of this period of erosion, which seems to have ended around 1850 with the start of the main work involved in the St. Lawrence Seaway project. The lack of sediments predating the end of the 19th century suggests that the Lake Saint-François basin served only as a transition zone for sediments during periods of high water flow (Carignan and Lorrain 2000; Carignan et al. 1994; Allan 1986).

Recent observations (Saulnier and Gagnon in preparation) indicate that the interface between the marine clays and modern sediments is commonly characterized by the presence of gravel mixed with pieces of clay. This mixed zone could reflect the period of erosion that is responsible for the lack of conformity between recent and postglacial sediments.

4.1.3 Recent sediments

Present-day sediments in Lake Saint-François probably date back a little over one hundred years to the late 19th century. Radiometric dating of sediment in cores collected in the main accumulation zones in the lake indicates approximate ages of 100 (SF-90-22) and 115 years (SF-90-17) for the oldest recent sediments. The appearance of fine particles in the sediment is likely related to work carried out on the St. Lawrence Seaway Project between 1850 and 1960 (Lorrain and Carignan 1992; Carignan and Lorrain 2000). Moreover, certain hydrological studies suggest that the oldest recent sediments that are still present in Lake Saint-François would have been deposited around 1870. In fact, extreme flows of 11 600 m³/s and 11 200 m³/s were recorded in 1862 and 1888, respectively. Energy conditions in 1862 appear to have been high enough to resuspend the sediment in Lake Saint-François, whereas the duration of the 1888 event seems to have been too short. The high hydrodynamic energy that affected the basin in 1862

offers a plausible explanation for the absence of sediments predating 1870 (Morin and Leclerc 1998).

The type profile of recent sediments in Lake Saint-François, which is based on the results of age dating, particle-size analysis and measurements of organic carbon in cores SF-90-17, SF-90-22, SF-90-23, SF-92-28 and SF-96-SFN (Figure 4), suggests that sediments accumulated in the Lake Saint-François basin cover five major temporal phases (Figure 6).

These sedimentary sequences are primarily defined on the basis of quantitative variations in sands, silts and clays over time. The time frames for the various sequences are as follows:

from 1985 to the present	Upper Saint-Zotique
from 1960 to 1985	Middle Saint-Zotique
from 1950 to 1960	Lower Saint-Zotique
from 1920 to 1950	Upper Lancaster
from 1870 to 1920	Lower Lancaster

The names of the units are based on their prevalence in the sedimentary basins of Lake Saint-François. The Saint-Zotique unit is well defined in the Saint-Zotique basin, as is the Lancaster unit in the Lancaster basin.

4.1.3.1 Lancaster unit¹ (1870 to 1950)

The Lancaster unit comprises sediments deposited between 1870 and 1950. Observations indicate that this unit is present throughout the Lake Saint-François sedimentary basin and is particularly well defined in the Lancaster basin. The Lancaster unit is divided into two sequences: the Lower Lancaster, from 1870 to 1920, and the Upper Lancaster, from 1920 to 1950.

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¹ Unit: Any group of lands that can be individualized for tectonic and/or stratigraphic reasons.

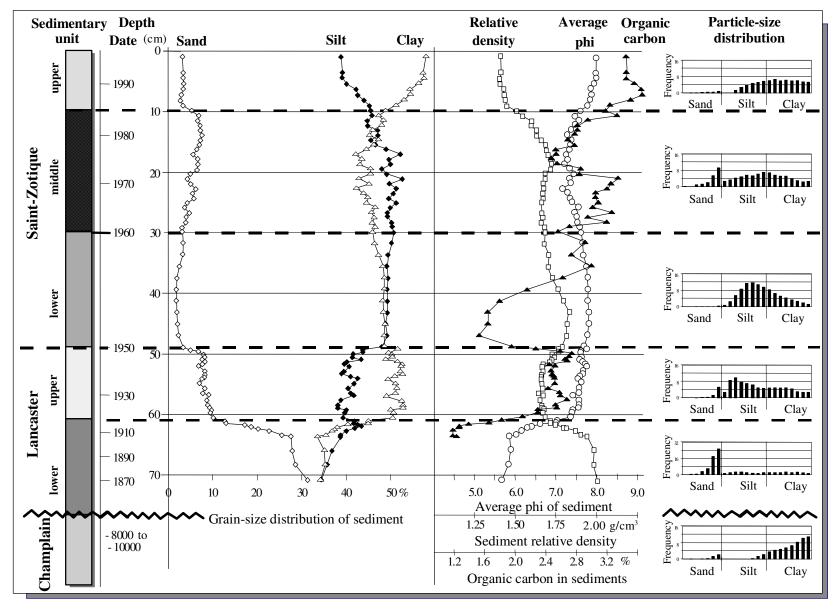


Figure 6 Type profile of recent sediments in Lake Saint-François

4.1.3.1.1 Lower Lancaster (1870 to 1920)

Table 3 Physical characteristics of the Lower Lancaster

- The time interval spans 50 years between 1870 and 1920;
- The quantity of sand decreases gradually from over 30% to less than 10%;
- The quantities of silt and clay rise from 35% to over 40%;
- The sediment density drops from 2.01 to 1.72 g/cm³;
- The particle-size distribution is asymmetric and centred on fine sands;
- The average thickness of the unit is 9 cm (calculated on the basis of cores SF-90-22, SF-90-17, SF-94-28, SF-94-24, SF-94-20, SF-94-17, SF-94-13, SF-96-SFN);
- The sedimentation rate during this period is only 0.18 cm/yr;
- The concentration of organic carbon increases significantly from 1.19% in 1910 to 2.53% in 1925, where it remained unchanged;
- The average values for the physical parameters of the sediments are:

Sand: $22.4 \pm 6.4\%$ Silt: $39.6 \pm 3.0\%$ Clay: $38.0 \pm 4.0\%$

Average phi: $6.2 \pm 0.5\%$ Moisture: $45.2 \pm 7.1\%$ Density: $1.86 \pm 0.11 \text{ g/cm}^3$

The type profile developed on the basis of the main sediment cores collected in Lake Saint-François indicates that the particle-size composition of sediments in the Lower Lancaster varies greatly with time. This particle-size variation reflects the loss of close to 60% of the sand content over a period of approximately 50 years (Figure 6).

The gradual decrease in sand content combined with the increase in the amount of fine particles suggests a constant and significant decline in hydrodynamic energy throughout the basin over time. Such a decrease in energy would have contributed to changes in the input of particles into the sedimentary basin, favouring the deposition of finer particles in the deeper basins with coarser sediments being left further upstream. However, the truncation of the distribution profile below sands, the asymmetric nature of the profile and the low sedimentation rate suggest that the basin as a whole had not yet reached maturity and that it remained relatively unstable. It is therefore likely that fine sediments (silt and clay) were deposited in the basin temporarily, when water levels were low, and subsequently resuspended during fall and spring flooding and

ultimately removed from the lake via the many downstream channels (Bérubé 1997; Crémer 1979).

The study by Morin and Leclerc (1998) shows that during this period, the average flow of the river at Cornwall gradually dropped from 8000 m³/s to approximately 6500 m³/s. This decrease could have significantly affected the hydrodynamic energy in the basin between 1860 and 1920, favouring deposition of increasingly fine sediments. In addition to this change in flow rates, industrial projects in the Valleyfield area, which could have had an impact on sedimentary dynamics in Lake Saint-François, must be taken into account. For example, the Beauharnois Canal was constructed between 1842 and 1845 and replaced in 1899 by the Soulanges Canal to allow the passage of ships. In addition, the small-scale Saint-Timothée hydro plant (1911–1949) and the provincial power plant (1901–1930) were developed and brought into service. In 1914, the main channel of the St. Lawrence River was also developed at Des Cèdres Rapids to allow the opening of the Les Cèdres power plant, which is still in operation (Morin et al. 1994; Morin and Leclerc 1998).

Finally, the rapid increase in organic carbon concentrations between 1910 and 1925 could reflect a rapid increase in biomass throughout the basin. According to a number of simulation studies, the stabilization of water levels would have established ideal conditions for the development and growth of submerged macrophytes in the basins of Lake Saint-François. This increase in macrophyte abundance would also coincide with an increase in nutrients in the basin, which would have doubled the amount of biomass over the course of a few decades (Morin and Leclerc 1998; Reavie et al. 1998; Morin et al. 2001).

4.1.3.1.2 Upper Lancaster (1920 to 1950)

In the early 1920s, the sedimentary dynamics in Lake Saint-François changed significantly. Quantities of sand, silt and clay stabilized and remained constant for a period of almost 30 years. This consistency in particle-size composition suggests a hydrodynamic stability throughout the sedimentary basin. Moreover, the hydrodynamic stability in Lake Saint-François seems to have coincided with a period of stability in the flow rates of the river, which varied between 6000 m³/s and 7000 m³/s, and the construction of dams at Coteau-Landing between 1932 and 1942 (Morin and Leclerc 1998).

Table 4 Physical characteristics of the Upper Lancaster

- The time interval spans 30 years between 1920 and 1950;
- There is little variation in the proportions of sands, silts and clays;
- The fine fraction consisting of silts and clays accounts for almost 90% of particles;
- There is little variation in relative density (1.66 to 1.77 g/cm³);
- The particle-size distribution is centred primarily on coarse- to medium-grained silts, with a strong asymmetry toward the clay fraction;
- The average thickness of the Upper Lancaster unit is approximately 12 cm (based on cores SF-90-23, SF-90-22, SF-90-17, SF-94-24, SF-94-17, SF-94-13, SF-96-SFN);
- The sedimentation rate is 0.4 cm/yr for a 30-year period;
 - The average values for the physical parameters of the sediments are:

Sand: $8.2 \pm 1.2\%$ Silt: $40.7 \pm 1.7\%$ Clay: $51.1 \pm 1.3\%$

Average phi: 7.6 ± 0.1 Moisture: $56.3 \pm 2.3\%$ Density: 1.69 ± 0.04 g/cm³

From a more detailed perspective, Figure 7 draws a parallel between the sand content of core SF-96-SFN, river flow rates at Cornwall, and water levels recorded at Coteau-Landing between 1919 and 1950. These profiles suggest that variations in the sand content of the sediments are closely related to fluctuations in river flow rates and changes in water levels. A significant correlation coefficient (r) of 0.72 is also noted between average river flow and the sand content of this core.

4.1.3.2 Saint-Zotique Unit (1950 to the present)

The Saint-Zotique unit comprises all the sediments that have been deposited in the Lake Saint-François basin since 1950. Based on particle-size variations among the sands, silts and clays and variations in organic carbon content, three sedimentary sequences can be identified. These sequences seem to be related to anthropogenic activities that were important in the development of the basin.

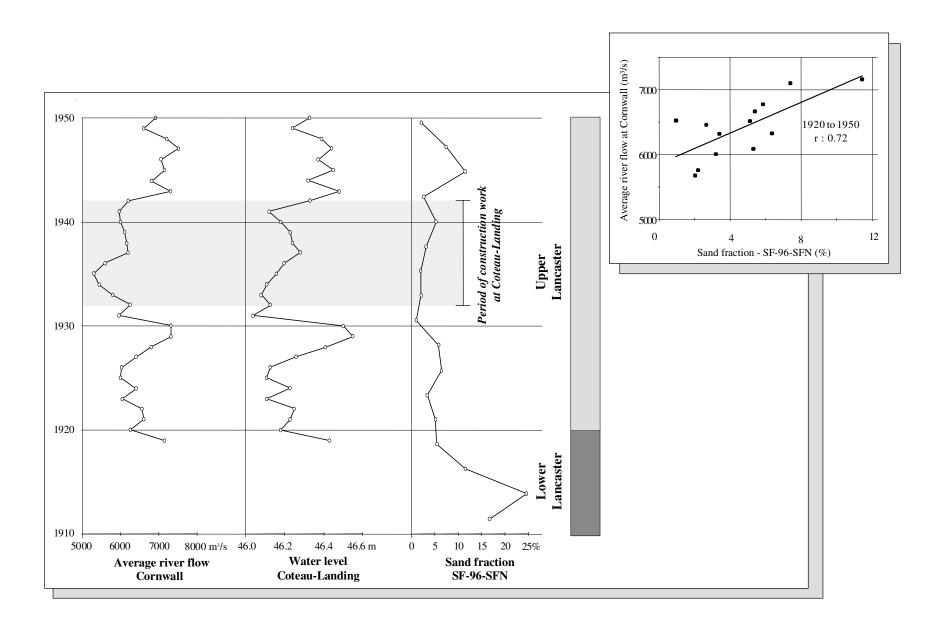


Figure 7 Relationship between river flow, water level and sand fractions of sediments of the Upper Lancaster

4.1.3.2.1 Lower Saint-Zotique (1950 to 1960)

Table 5 Physical characteristics of the Lower Saint-Zotique unit

- The time interval spans 10 years between 1950 and 1960;
- The quantity of sand in the sediment falls 75%, decreasing from 8.2 % to 1.9%;
- The organic carbon content drops from 2.74% to 1.53% between 1947 and 1951;
- The relative density changes over time, initially rising to 1.83 g/cm³ (1953) and later dropping to 1.68 g/cm³ (1960);
- The particle-size distribution is well defined by a histogram that is almost symmetrical and centred on medium- to fine-grained silts;
- The thickness of sediments in this unit ranges from 7 to 38 cm, with an average of 19 cm (based on cores SF-90-23, SF-90-17, SF-92-28, SF-94-28, SF-94-17 and SF-96-SFN);
- The sedimentation rate is high at 1.9 cm/yr;
- The average values for the physical parameters of the sediments are:

Sand: $2.4 \pm 0.7\%$ Silt: $49.3 \pm 0.5\%$ Clay: $48.3 \pm 0.7\%$

Average phi: 7.7 ± 0.1 Moisture: $51.4 \pm 3.4\%$ Density: 1.76 ± 0.05 g/cm³

Following the period of stable sedimentation during the Upper Lancaster, the start of the Lower Saint-Zotique is marked primarily by a 75% decline in the sand content of the sediments, a decrease of approximately 50% in organic carbon concentrations, and a significant increase in sedimentation rate. The sand content remained unchanged throughout the 1950s, while organic carbon concentrations returned to their original levels toward the end of the decade.

Variations in particle-size composition during the period of deposition of the Lower Saint-Zotique suggest that at the beginning of the 1950s, the Lake Saint-François basin was affected by a significant loss of hydrodynamic energy. This energy loss seems to be correlated with two important anthropogenic events. The first occurred around 1941–42, during the Second World War, at a time when the water level in Lake Saint-François was raised by 30 cm in order to increase the power output of the Beauharnois power plant. Afterwards, the water level was not restored to its original level. In fact, the second phase of the plant began operations in 1951–52, increasing the flow through the turbines from 2350 m³/s to 4500 m³/s and leading to a further 10-cm increase in the level of the lake (Figure 8). This second event also helped reduce average annual variations to less than 10 cm (Morin et al. 1994; Morin and Leclerc 1998). The filling of

the upstream dams may have contributed to a decrease in hydrodynamic energy, giving suspended particles enough time to deposit in the basin.

However, this decrease in energy does not seem to be significant enough to account for the major increase in sedimentation rate, which rose from 0.4 to 1.9 cm/yr over the course of a few years, and it does not explain the decrease in organic carbon concentrations. Based on the sedimentation rate of the Middle (1960 to 1985) and Upper (1985 to the present) Saint-Zotique and the fact that water levels remained unchanged after 1950, the sedimentation rate during the Lower Saint-Zotique should be approximately 0.85 cm/yr. It should therefore be concluded that the input of terrigenous particles changed significantly during this period, resulting in a higher sedimentation rate and the dilution of organic matter inputs.

Observations suggest that the artificial elevation of water levels may have imposed new constraints on bank erosion and the dynamic restructuring of beaches and flats (Figure 9). For example, at these water levels, the erosive impact of waves on the shoreline as a result of wind strength and direction may have caused subsidence along certain slopes and the reworking of sediments at shallow depths (< 2 m) (Morin et al. 2001). Recent work by Lepage et al. (2002) shows that a 40-cm rise in water levels can cause a 400% increase in the rate of erosion and shore recession (Figure 9). Since the middle of the last century, some of this erosion has been controlled by protective structures installed by people living along the river (Centreau 1973). However, erosion of islands seems more significant because they receive little protection from the gardens and infrastructures installed by shore dwellers (Bruce et al. 1973). Since 1935, a number of islands have disappeared completely, a phenomenon that is particularly obvious off the north shore, upstream of Mouillée Point, and along the south shore in the vicinity of Grosse Point, near the Beauharnois Canal (Figure 1). In this way, a large quantity of fine-grained terrigenous sediment with limited organic matter and generated by the leaching of newly submerged materials may have contributed to the increased sedimentation rate and the reduction of organic carbon concentrations.

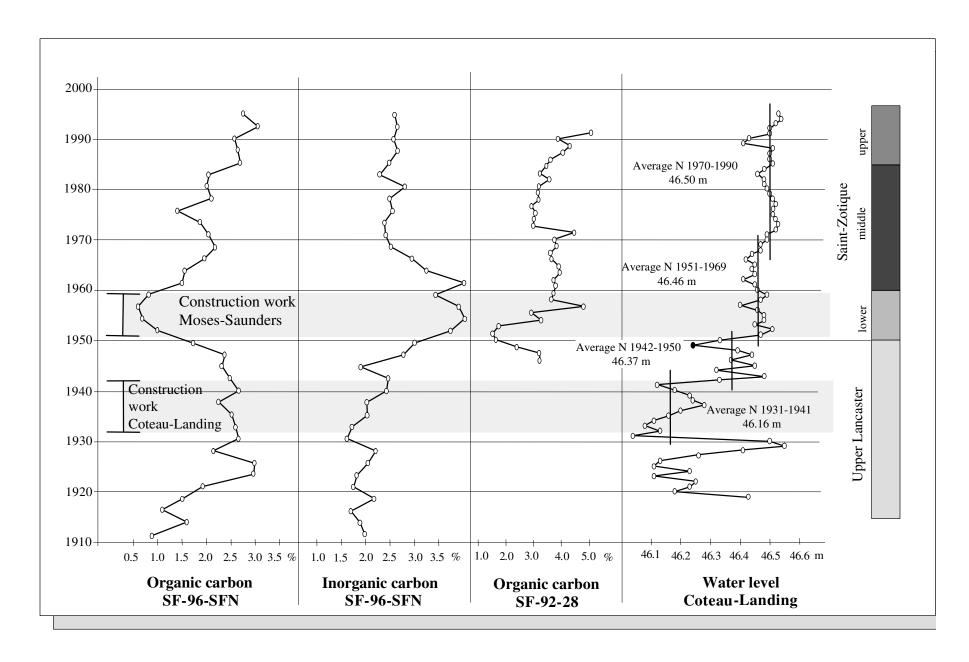
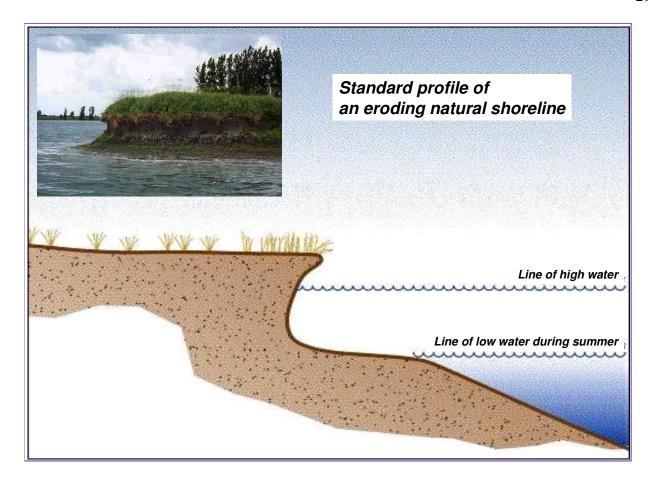


Figure 8 Relationship between water level and organic carbon concentration in the Lower Saint-Zotique



Source: Web site of the Canadian Wildlife Service, Quebec Region.

Figure 9 Profile of a natural shoreline undergoing erosion

In addition to the erosion of islands in Lake Saint-François, the many development projects in the area upstream of Cornwall that have significantly altered the natural flow in the St. Lawrence River must also be taken into consideration. This work includes the construction of two dams, numerous navigable channels and two locks, as well as the dredging of large areas, the construction of several kilometres of dikes and of two bridges, built between 1954 and 1959 to link Cornwall Island and the shores of the river (NYPA 1992). The Moses-Saunders Dam and the Long-Sault spillway were built at the Long-Sault Rapids, now flooded by the reservoir lake known as Lake St. Lawrence, radically changing the flow and the morphology of the river as far away as the Iroquois Dam, 50 km upstream (Morin et al. 1994). Such major construction projects inevitably required the use of large quantities of gravel, crushed rock and cement for the

construction of the dikes, jetties and other infrastructure involved. These fill and construction materials would have contained little organic matter or contaminants, but could have contained relatively significant amounts of fine particles, including calcium carbonate (cement). When they were being used, some of these fine, terrigenous particles came into contact with the water mass of the river and could have been carried off by the current toward the waters of Lake Saint-François. This input of fine particles could have contributed to the increase in the sedimentation rate and the dilution of organic carbon concentrations. This theory is also supported by an increase in the concentration of inorganic carbon in core SF-96-SFN, most likely the result of the use of calcium carbonate (Figure 8).

4.1.3.2.2 Middle Saint-Zotique (1960–1985)

Table 6 Physical characteristics of the Middle Saint-Zotique

- The time interval spans 25 years between 1960 and 1985;
- The quantity of sand rises gradually from 2% to over 7%;
- The organic carbon content varies greatly and drops considerably after 1970;
- The relative density remains stable until 1975 and then drops from 1.73 g/cm³ to 1.50 g/cm³ (1985);
- The particle-size distribution is bimodal, with one peak centred on fine sands, and one centred on clayey silt;
- The thickness of sediments ranges from 10 to 35 cm, with an average of 20 cm (based on cores SF-90-23, SF-90-17, SF-92-28, SF-94-25, SF-94-28 and SF-96-SFN);
- The sedimentation rate is 0.8 cm/yr;
- The average values for the physical parameters of the sediments are:

Sand: $5.7 \pm 1.3\%$ Silt: $48.9 \pm 2.3\%$ Clay: $45.5 \pm 1.9\%$

Average phi: 7.4 ± 0.1 Moisture: $58.1 \pm 3.2\%$ Density: $1.66 \pm 0.05 \text{ g/cm}^3$

The appearance of coarser particles in the sediments of the Saint-Zotique and Lancaster basins suggests a change in the hydrodynamic regime and sediment dynamics in Lake Saint-François. This change seems to have been produced during the period of overlap between the Lower Saint-Zotique and the Middle Saint-Zotique around 1960. Studies conducted on core SF-92-28 indicate the existence of a relationship between the flow in the river and the quantity of sand in the sediments for this period of sedimentation (Carignan et al. 1994). An in-depth study

of the particle-size distribution in core SF-96-SFN as a function of the average flow of the river also confirms a strong correlation (r = 0.91) between an increased flow and an increase in the quantity of sand particles, but only for the period from 1964 to 1973 (Figure 10). During this period, the average flow in the river rose from almost 5500 m³/s to over 8500 m³/s, initially prompting an increase of approximately 5% in the quantity of sand. However, for the other periods (1950–1962 and 1976–1995), the relationship between flow and particle-size distribution is less significant, suggesting that at the time, other hydrodynamic mechanisms were probably playing a role in the input of sandy particles.

As previously discussed, during the 1950s, Lake Saint-François reached the highest water levels ever recorded, resulting in the erosion of banks and flats. Because of the weak sediment dynamics that characterized the environment during this period, only fine particles seem to have been leached from submerged materials along the shores.

However, the opening of the St. Lawrence Seaway in 1959 brought a significant increase in the transportation of goods between Montreal and Lake Ontario, with annual tonnages rising from 15 metric tons (mt) to close to 60 mt between1955 and 1980 (Transport Canada 1996). This increase suggests an increase in ship-generated waves, which may also have had a strong impact in terms of the resuspension of coarser particles and the deposition of recent sediments (Lepage et al. 2002; Dauphin and Lehoux 2000).

Although there is no direct cause-and-effect relationship, it is interesting to note that a significant correlation (r = 0.86) exists between tonnages transported and the quantity of sand contained in the sediments in core SF-96-SFN, collected in Lancaster basin (Figure 11). Given that several islands located upstream of Lake Saint-François could have been partially submerged as a result of the rising water levels, the energy of ship-generated waves would have been particularly concentrated in areas that were flooded to shallow depths. This assumption of shoreline erosion rather than fluvial input is supported by the bimodal particle-size distribution, which could indicate the accumulation of sediments from different sources or the action of different reworking processes (Lorrain et al. 1993; Reineck and Singh 1986).

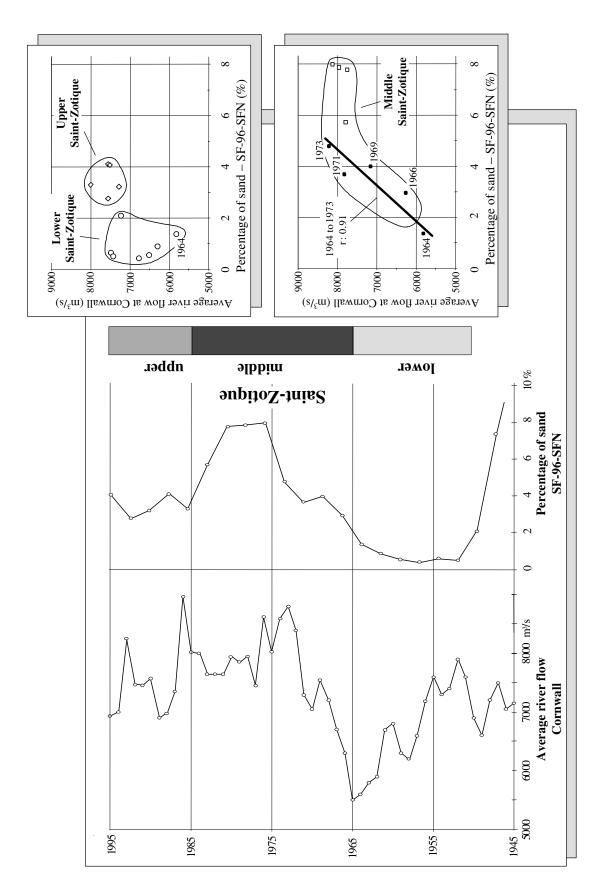


Figure 10 Relationship between average river flow and particle-size distribution in the Middle Saint-Zotique

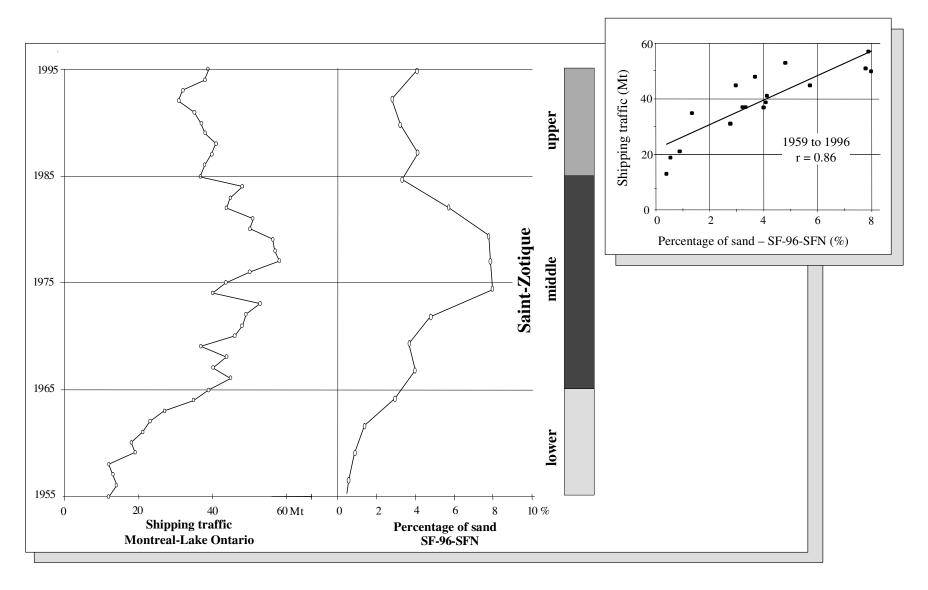


Figure 11 Relationship between shipping traffic and particle-size distribution in the Middle Saint-Zotique

4.1.3.2.3 Upper Saint-Zotique (1985 to the present)

Table 7

Physical characteristics of the Upper Saint-Zotique

- The time interval spans 11 years, from 1985 to 1996 (most recently age-dated core);
- The amount of sand in the sediment drops to 3.2% and remains fairly stable;
- The amount of clay increases gradually after the end of the 1970s, rising from 45.2% to 58.1%;
- The organic carbon content increases gradually after the end of the 1970s, reaching over 3.5% by the end of the 1980s:
- The relative density gradually drops from 1.73 g/cm³ to 1.50 g/cm³;
- The average moisture content rises from 58% to 73%;
- The unimodal particle-size distribution is centred on silty clays;
- The thickness of sediments in this unit ranges from 5 to 15 cm, with an average of 10 cm (based on cores SF-90-23, SF-90-17, SF-92-28, SF-94-25, SF-94-28 and SF-96-SFN);
- The sedimentation rate is 0.9 cm/yr;
- The average values for the physical parameters of the sediments are:

Sand: $3.2 \pm 0.3\%$ Silt: $41.4 \pm 2.6\%$ Clay: $55.4 \pm 2.4\%$

Average phi: 7.9 ± 0.1 Moisture: $72.9 \pm 1.1\%$ Density: 1.43 ± 0.02 g/cm³

Variations in certain physical characteristics of the sediments of this last unit, including increasing moisture content and decreasing relative density, seem to be consistent with the type of changes that are ordinarily observed within the water-sediment interface zone and the mixed sediment layer (Carignan and Lorrain 2000; Loiselle et al. 1997). However, it is difficult to use surface sedimentary processes to explain the decrease in the proportion of sand and the increase in the amount of clays after the middle of the 1980s. These phenomena seem to be related to anthropogenic events or to a change in the sedimentary regime related to a change in particle input over time.

The only significant anthropogenic event to occur in the basin at this time took place between 1979 and 1988. After 1979, intensive maintenance dredging of the St. Lawrence Seaway began between Cornwall and Lancaster Bar at the upstream end of Lancaster basin. By the end of the 1980s, almost 200 000 m³ of sediments had been removed from the navigation channel and dumped in the lake near the dredged areas. In addition, in 1989 and 1990, the bottom of the navigation channel was levelled in the area immediately east of Cornwall Island (Morin et al. 1994).

Upstream of Lancaster basin, the navigation channel crosses the delta area of Lake Saint-François. The channel bottom consisted primarily of well-compacted sands and gravels, deposited over the clay sediments of the former Champlain Sea. The presence of sand and gravel can be explained by the high transport and erosion capacity of the river in this upstream part of the lake (Lorrain et al. 1993; Crémer 1979). The quantity of sediment lost during a dredging operation is related to the texture of the sediment, hydrodynamic conditions at the dredging site, and the type of dredge used. It is also estimated that between 2–6% of dredged sediments are lost in the water column. Between 50–70% of the sediments are deposited on the bottom within a radius of approximately 500 m of the work site (Bérubé 1994). The strength of the current at the dredging site, combined with the nature of the dredged materials (sand, gravel, marine clay) and the release of these materials in the open water near the dredged areas suggest that dredging operations could be responsible for the increase in the percentage of clay in the sediments in Lancaster and Saint-Zotique basins.

Around 1990, after the end of these operations, particle inputs into the basin returned to their pre-dredging levels. The percentage of sand shifted toward its Middle Saint-Zotique level. Although this trend is not evident in the type profile of the sediments (Figure 6), it can still be seen in the top sections of certain cores between 1994 and 1996. This process is consistent with comments by Carignan and Lorrain (2000) concerning the mixed layer, indicating that the river has a very short memory of past conditions (2 to 5 years) because of variations in load resulting from the dredging period that ended in 1988.

Despite this return to initial conditions in terms of the quantities of sand deposited in the sediments, the amount of clay remains relatively high in comparison to concentrations observed in the past. This extra clay could be a reflection of increased erosion of marine clays both in the St. Lawrence Seaway, where they were uncovered by dredging, and from islands located upstream that have been heavily altered since the middle of the last century.

4.2 SPATIAL EVOLUTION OF SEDIMENTATION

4.2.1 Basin stratigraphy

Several sediment cores were used to describe the temporal evolution of sedimentation in Lake Saint-François. The various sedimentary units were defined on the basis of inherent variations observed in the sand and in the fine fraction in the profiles of these cores. Although the proportions of the various grain sizes vary from core to core, these sedimentary units can still be identified in most of the other cores.

Figures 12 to 14 present stratigraphic sections in the Saint-Zotique and Lancaster sedimentary basins and in the Beaudette Point sediment transport area (see Figure 4 for the location of the cores for these sections). These various stratigraphic sections make it possible to visualize the development of each of these sedimentary units and to estimate their thicknesses, not only over time, but also spatially.

Comprised almost exclusively of sediments subsequent to 1940, the units deposited in the Saint-Zotique basin are distinguished from those in other sectors by the predominance of fine particles belonging to the Saint-Zotique sedimentary unit (Figure 12). The almost complete lack of coarse sediments is likely related to the distance from the main erosion zones, which are located primarily upstream, around islands, and in the Cornwall area. At the centre of the basin, the thickness of sediments varies from 60 to 70 cm under 10 m of water.

The sediments in the Lancaster basin are much older than those in the Saint-Zotique basin (Figure 13). Fine- to coarse-grained sands from the Lancaster sedimentation period (1870–1950) have accumulated primarily in the downstream part of the basin. This basin receives not only the majority of the coarse particles originating in the Cornwall transport zone, but also suspended particles produced by the erosion of banks and islands. The sediments deposited during the Upper Saint-Zotique are particularly abundant here (over 25 cm in core SF-94-24), possibly because of the proximity to maintenance dredging carried out between Lancaster Bar and Cornwall between 1979 and 1988.

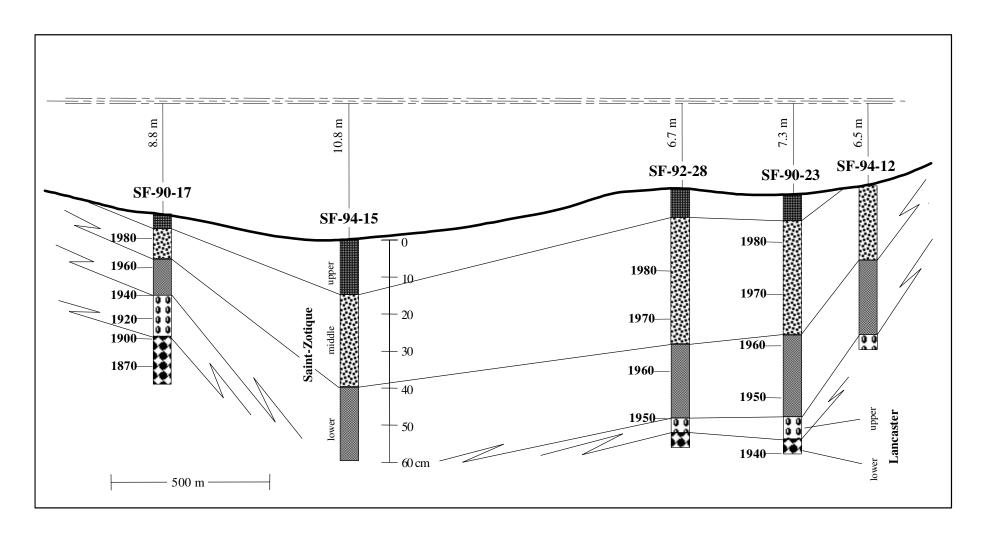


Figure 12 Stratigraphic section of recent sediments in the Saint-Zotique basin

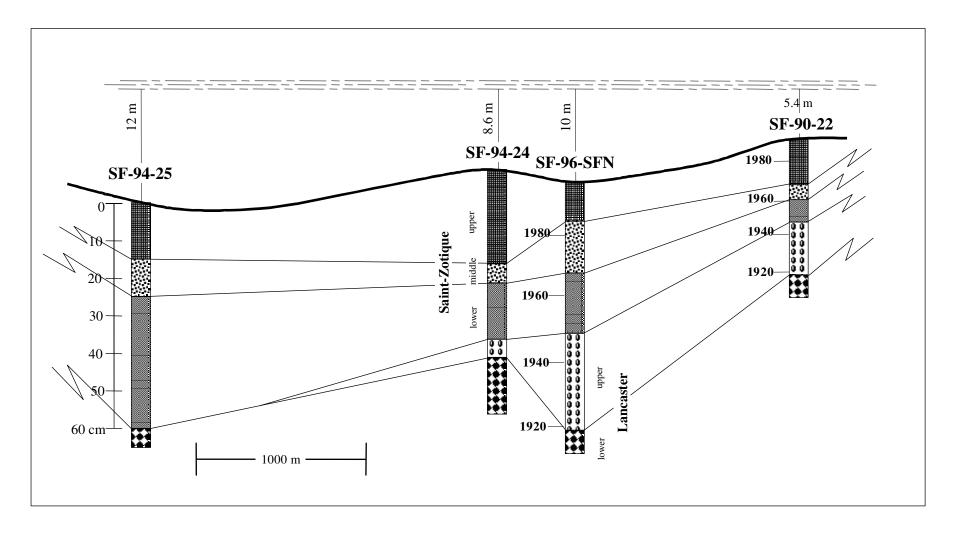


Figure 13 Stratigraphic section of recent sediments in the Lancaster basin

Relative to the adjacent Lancaster and Saint-Zotique basins, the Beaudette Pointe area is regarded as a sediment-transport zone (Lorrain et al. 1993). However, a deep channel, in which some 15 m of water overlies 50 to 60 cm of sediments, is also located in this area. These sediments are much coarser than those in neighbouring basins (Figure 14). The two main sedimentary units in Lake Saint-François can be identified in the particle-size distribution profiles of sand, and the sedimentological link between the Lancaster and Saint-Zotique basins can be established. Moreover, as seen in the stratigraphic section, the Lancaster unit tends to decrease in thickness from upstream to downstream, whereas the Saint-Zotique unit increases, suggesting a relative loss of energy between the two main basins.

The Cornwall area is also considered to be a sediment transport zone. Analyses of sediment in cores SF-96-Pilon, SF-96-179 and SF-96-TCTI reveal very large amounts of sands and gravels. However, the Lancaster and Saint-Zotique units can be identified in these three cores on the basis of the particle-size distribution profiles. While these interpretive results are at the limit of the technical application of the method used to identify the units, when combined with radiometric age dates they indicate that a relatively significant amount of sediment would have been deposited in this area after the water level in Lake Saint-François was raised at the end of the 1940s.

In the case of all the other sediment cores collected in Lake Saint-François, it has been possible to identify the various sedimentary units wherever the depth of the water exceeds 5 m. This depth of water was identified as the physical limit for permanent sedimentation in the main basins of Lake Saint-François (Lorrain et al. 1993; Carignan et al. 1994). In general, shallower areas contain sandier sediments that are not as deep as those in the basins and are considered areas of temporary sedimentation.

The stratigraphic data as a whole indicate that the sedimentary basins, i.e. the Saint-Zotique and Lancaster basins, contain most of the sediments that have been deposited in Lake Saint-François over the past century. These sediments consist primarily of silt- and clay-sized particles and a small percentage of fine sand. Outside the boundaries of these sedimentary basins, where water depth is less than 4 or 5 m, sediments become sandier and overlie ancient Champlain Sea clay deposits.

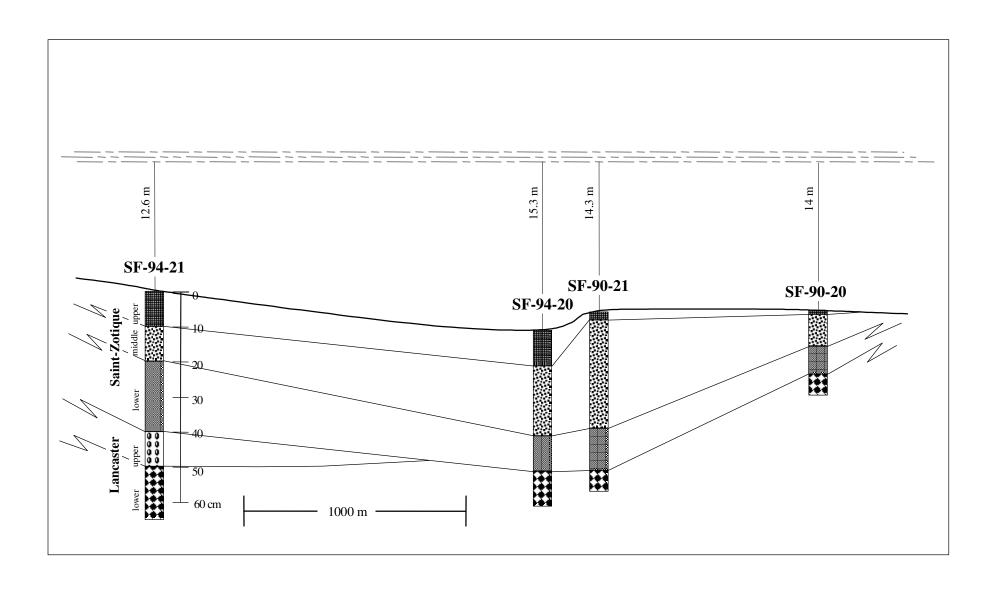


Figure 14 Stratigraphic section of recent sediments in the Beaudette Point area

4.2.2 Particle-size classification of sediments

In 1979, 1989 and 1999, Environment Canada conducted sediment sampling campaigns throughout Lake Saint-François from Cornwall to Beauharnois (Sloterdijk 1985; Lorrain et al. 1993; Lepage et al. 2001). Samples were analysed on the basis of several elements and chemical compounds as well as most physical parameters related to particle size. These three sampling campaigns led to the development of a spatial model of the decade-by-decade composition of bottom sediments. The 1979 campaign covered the period of the Middle Saint-Zotique while the 1989 and 1999 campaigns focused on the Upper Saint-Zotique. Unfortunately, the sediments that were sampled in the 1999 campaign cannot be compared with those of the cores because no complete cores have been collected since 1996.

Bearing in mind that most of the samples were collected from outside the main sedimentation zones, surficial sediment samples contain a much larger proportion of coarse-grained particles than the sediments in previously described cores. However, variations in the proportions of the various particle-size fractions in surficial samples seem to match variations observed for the various periods of sedimentation. In fact, a proportional decrease in sand and silt content and a significant increase in clay content is observed in both surficial samples and cores between 1979 and 1989.

Various groups of stations corresponding to distinct sedimentary environments become apparent when percentages of particle-size fractions are plotted on a Shepard-type ternary diagram (Shepard 1954; Lorrain et al. 1993). Figure 15 presents ternary diagrams for each of the sediment sampling campaigns. These diagrams show that the proportions of the various sediment particle sizes have changed over time.

The sediments collected in 1979 consisted primarily of sands and silty sands, whereas in 1989, two types of sediments were found: sands and clayey silts. The type of sediment in each of the two groups seems to be directly related to the location of the 1989 sampling stations. Stations located at the edge of the lake and in the channels belonged to the sandy group of sediments and reflected high-energy settings; the other group was found in low-energy environments, located in areas of accumulation (Lorrain et al. 1993).

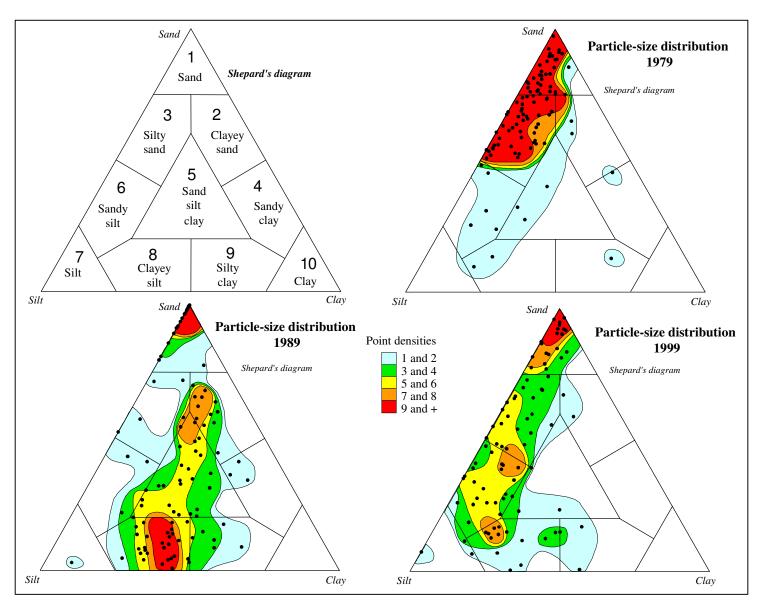


Figure 15 Ternary diagrams depicting particle sizes of surficial sediments collected in 1979, 1989 and 1999

Once again, particle-size data for 1999 reflected a single group of stations ranging from sands, to silty sands, to sandy silts. The results indicated that the majority of sediments contained less clay in 1999 than in 1989. This decrease in the proportion of clay could suggest an increase in hydrodynamic energy. However, it should be recalled that the sedimentary environment in Lake Saint-François was affected by dredging work in the St. Lawrence Seaway between 1979 and 1988. These dredging projects would have caused a temporary increase in the silt and clay content of sediments, resulting in an overestimation of silt and clay content in particle-size findings for 1989.

4.2.3 Sediment mapping

Surficial sediments in Lake Saint-François were mapped by classifying sediments collected in the 1989 campaign according to the nomenclature of Shepard (1954) (Figure 16). This map identifies several low-energy zones, such as the Saint-Zotique, Grenadier, Des Cèdres, Thompson and Lancaster basins, as well as high-energy zones in the upstream reaches of the lake, the Saint-Anicet area and the edges of the river, particularly adjacent to the mouths of tributaries (Fortin and Desrochers 1990; Lorrain et al. 1993; Morin et al. 2001).

The overall sedimentological characteristics identified in Lake Saint-François in 1989 were not significantly changed by the particle-size distribution results from the 1999 campaign. In fact, since construction of the Moses-Saunders Dam was completed in the late 1950s, the sedimentary dynamics in the lake have been governed primarily by the flow of water in the river and the gradual erosion of the islands and shores of the lake through continuous wave action generated by winds and ships.

Mapping sediments from the three campaigns (1979, 1989 and 1999) using a weighted particle-size distribution based on the nomenclature of Shepard (1954) provides a better idea of the evolution of the Lake Saint-François sedimentary basin (figures 15 and 17). These maps make it possible to quickly visualize the changes that have occurred in sediments throughout Lake Saint-François over the past two decades.

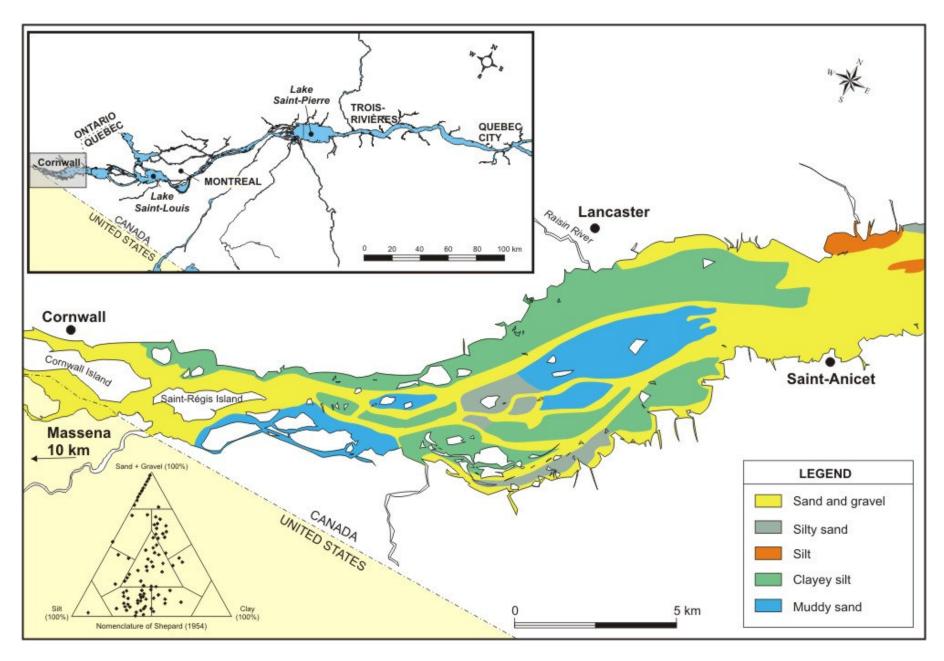


Figure 16 Map of surficial sediments of Lake Saint-François

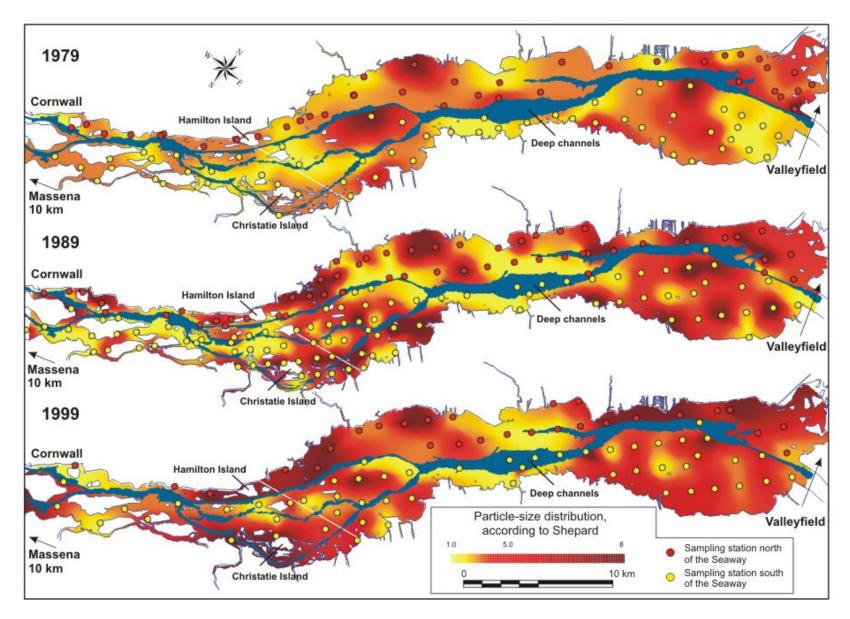


Figure 17 Particle-size distribution maps for Lake Saint-François sediments in 1979, 1989 and 1999

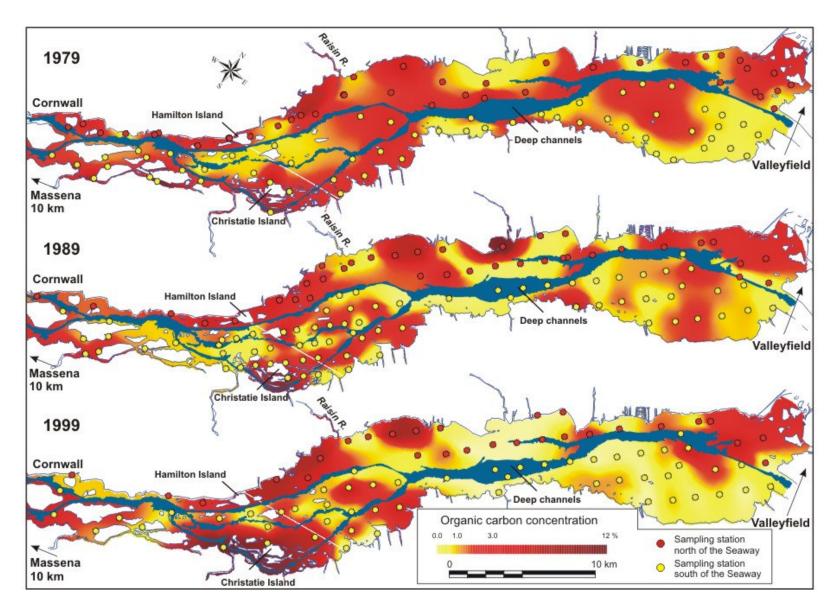


Figure 18 Maps of organic carbon concentrations in Lake Saint-François sediments in 1979, 1989 and 1999

In the five previously identified sedimentary basins and further upstream in the area of Hamilton and Christatie islands, a significant increase is seen in the extent of fine sediments consisting primarily of clayey silts and sandy silts. The surficial sediments of 1979 appear to be much sandier than those of 1989 and 1999. Conversely, from 1989 to 1999, the trend toward siltier sediments seems to persist throughout all areas likely to receive fine sediments. When these observations are compared against the type profile of sediments developed on the basis of the sediment cores (Figure 6), the Middle Saint-Zotique sediments, which include the surficial sediments sampled in 1979, are sandier than those of the Upper Saint-Zotique, which comprise the sediments sampled in 1989 and 1999. Finally, the 1989 and 1999 particle-size-distribution map indicates a greater surface area for fine clayey sediments.

This spreading out of sedimentation zones suggests a drop in hydrodynamic energy and a weakening in sedimentary dynamics that could be explained by the gradual decrease in river flow from 8500 m³/s to close to 7500 m³/s between 1975 and 1995. However, part of the spreading out of sedimentation zones could also be related to an input of clay resulting from the more direct erosion of upstream clay areas exposed by the dredging of the St. Lawrence Seaway between 1979 and 1988, and by erosion of the tills that form the internal structures of most upstream islands (Bariteau 1988).

Maps of organic carbon (Figure 18) provide additional information on the evolution of sedimentation zones in Lake Saint-François. These maps show a decreasing trend in the amount of organic carbon in the Grenadier, Saint-Zotique and Lancaster basins between 1979 and 1999. This trend is much less pronounced in the Thompson and Des Cèdres basins. However, in the Hamilton and Christatie islands areas, organic carbon content tends to rise, reaching its highest levels in the 1999 sampling campaign (11.1% at the mouth of the Salmon River).

5 Geochemical Evolution

Since the beginning of the 20th century, the upstream sector of the Lake Saint-François basin has undergone relatively significant economic development because of its geographic location at the intersection of a provincial and an international boundary, but also because of its accessibility, thanks to the St. Lawrence Seaway. However, this industrial and manufacturing expansion, which was also associated with hydroelectric development, placed an anthropogenic pressure on the water, the sediments and the organisms living in the St. Lawrence. By analysing and interpreting the geochemical components of the sediments, it is possible to develop an understanding of the temporal and spatial evolution of this contamination.

Of the 27 sediment cores collected in Lake Saint-François between 1990 and 2000, only eight were fully analysed for inorganic elements and two for organic compounds. Pb-210 and Cs-137 dating of four of these cores (SF-90-17, SF-90-22, SF-92-28 and SF-96-SFN) have provided a time frame for the geochemical data (Figure 4). Based on analytical results for these cores, geochemical profiles were constructed on the basis of average levels of the main inorganic elements — mercury (Hg), copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), lead (Pb), cadmium (Cd), lithium (Li) and aluminum (Al) — and certain organic compounds (PCB, HCB, Mirex, DDE and DDD) (figures 19 to 22).

5.1 TEMPORAL EVOLUTION OF CONTAMINANTS

5.1.1 Marine sediments

As discussed in the section on sedimentological evolution, the marine deposits underlying the recent sediments were laid down more than 8000 years ago by the Champlain Sea. The particles comprising these sediments came primarily from glacial deposits and the metamorphic rocks of the Laurentian Mountains to the north of the St. Lawrence Valley, and of the Adirondacks to the south of the study area (Tremblay 1997).

The chemical and mineralogical composition of the Champlain Sea clays remains poorly understood and has received little attention. Core SF-90-19 (Figure 4), collected in Lake Saint-François, and more recently the work of Saulnier and Gagnon (in preparation), have made it possible to detail the geochemical composition of several tens of samples collected along the

fluvial section and in the fluvial lakes (Table 8). These chemical analyses of the clays indicate relatively high average levels of Cr, Ni, Zn, Cu and Li, that are more than two to four times greater than the average levels observed in pre-industrial sediments, while levels of Hg, Cd, Pb and Al are similar to concentrations seen in more recent sediments.

Table 8
Average metal concentrations in the sediments of Lake Saint-François

	Hg µg/g	Cu µg/g	Zn μg/g	Pb μg/g	Ni μg/g	Cr µg/g	Cd µg/g	Al μg/g	Li µg/g
Pre-industrial sediments									
From Carignan et al. 1994 $(n = 4)$	_	17	78	15	32	62	0.15	_	_
From Saulnier and Gagnon, in prep.	0.022	24	63	15	24	49	0.30	54350	21
(n=4)									
Core SF-90-17 $(n = 3)$	_	12	55	18	22	63	0.18	72309	16
Marine clay									
From Saulnier and Gagnon, in prep.	0.015	47	98	17	61	108	0.22	72652	44
(n = 23)									
Core SF-90-19 $(n = 1)$	_	45	103	14	72	152	0.05	93296	46
Sediment quality criteria									
NET – SLC and MENVIQ 1992	0.05	28	100	23	35	55	0.20		

Legend: (Al) aluminum, (Cd) cadmium, (Cr) chromium, (Cu) copper, (Hg) mercury, (Li) lithium, (Ni) nickel, (Pb) lead, (Zn) zinc.

5.1.2 Recent sediments – Pre-industrial period

By definition, the pre-industrial period corresponds to the sedimentary cycle that was free of anthropogenic input or influence. It is assumed that Lake Saint-François would contain no pre-industrial sediments given that the start of sedimentation coincides with the start of work on the St. Lawrence Seaway infrastructure. As indicated by the organic element profiles (figures 19 and 20), sediments deposited between 1870 and 1910 are already affected by the start of the industrial period.

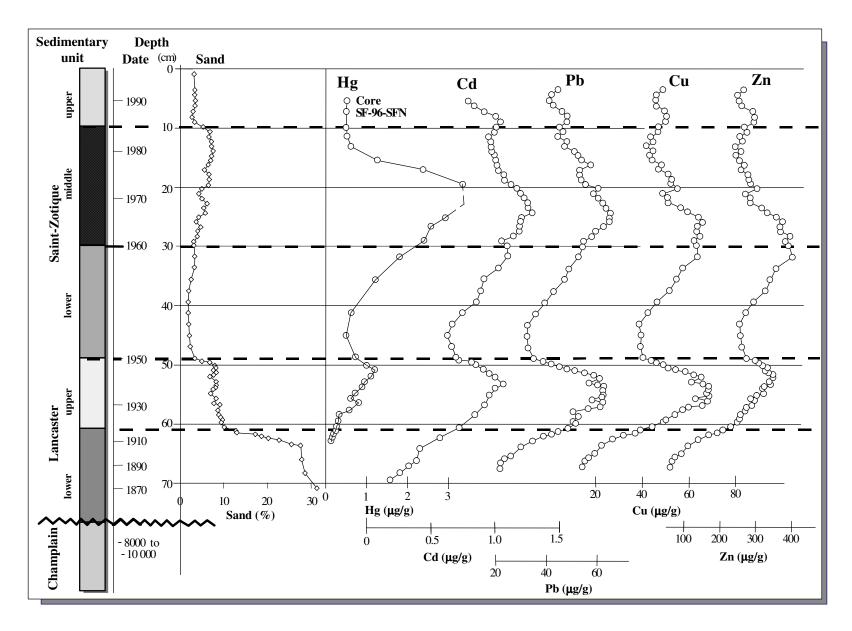


Figure 19 Geochemical profiles showing average levels of Hg, Cd, Pb, Cu and Zn in the sediments of Lake Saint-François

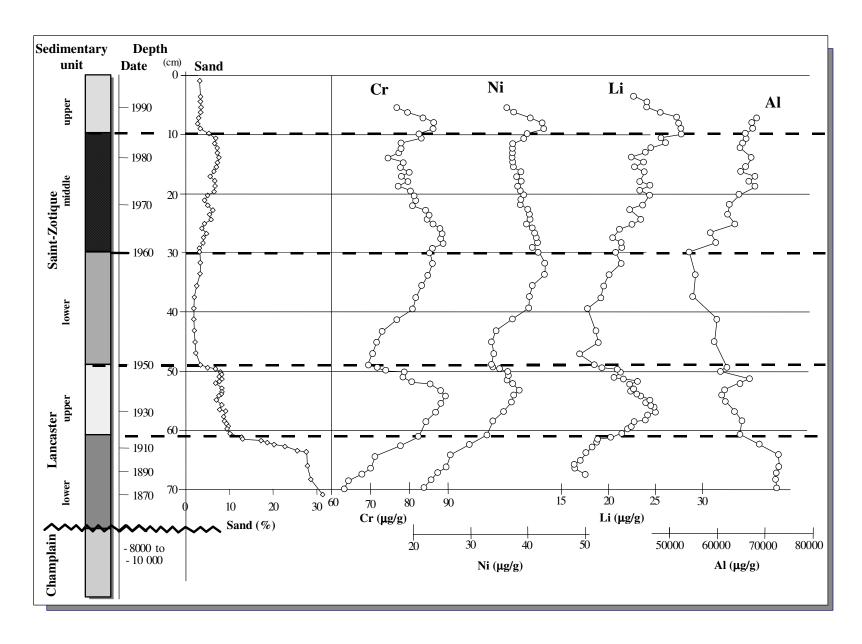


Figure 20 Geochemical profiles showing average levels of Cr, Ni, Li and Al in the sediments of Lake Saint-François

However, sediments from core SF-90-17 (Figure 4 and Table 8) date back to the part of the Lower Lancaster between the end of the 19th century and the beginning of the 20th century. With the exception of a few elements (Cu and Zn), average levels of metals in this portion of the sediments in core SF-90-17 are comparable to pre-industrial levels identified in Lake Saint-Louis by Carignan et al. (1994), to concentrations prescribed as no-effect thresholds (NETs) in the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment,* (SLC and MENVIQ 1992) and to pre-industrial levels determined by Saulnier and Gagnon (in preparation) for Lake Saint-François. As discussed earlier, these levels are also distinctly lower than the concentrations observed in the marine clays. Although the terrestrial origin of the pre-industrial sediments is similar to that of the clays, geochemical behaviour and concentrations in these sediments have been affected by weathering (erosion and chemical alteration) and diagenetic processes.

In addition, increased biomass (simulation) (Morin and Leclerc 1998) in the Lake Saint-François basin during the Lower Lancaster would have been likely to favour an increase of organic matter input to the sediments (Figure 6), which in turn may have had a dilution effect within the sedimentary matrix, causing a corresponding decrease in geochemical levels.

5.1.3 Recent sediments – Industrial period

After the beginning of the Lancaster (1870), levels of metals in the sediments tend to increase gradually (figures 19 and 20). With the exception of Al, all the inorganic elements analysed reach their highest levels around 1940. Levels of Hg, Cd, Pb, Cu and Zn are 2.5 to 4.5 times greater than pre-industrial values. Chromium, Ni and Li levels also increase, but more moderately (1.5 times), while the level of Al drops by almost 20% over the same period.

These changes in the levels of metals in the sediments seem to be directly related to three historical events that occurred in the upstream sector of Lake Saint-François: 1) the establishment of the ALCOA aluminum smelter in Massena in 1902 and the Domtar paper mill in Cornwall in 1881 (Fortin et al. 1994); 2) a 50% increase in the population of the Cornwall region between 1921 and 1931 (Cornwall Economic Development 2001); 3) the establishment in the early 1930s of several industrial plants, including Courtaulds Canada Inc.'s rayon manufacturing mill, and the chlorine and caustic soda plant owned by Canadian Industries Limited (CIL), now

ICI Canada (Fortin et al. 1994). This industrial and demographic expansion resulted in a significant increase in the amount of wastewater discharge reaching Lake Saint-François.

Despite the lack of data on certain organic contaminants, the appearance of HCBs in the mid-1920s, several PCB congeners between 1930 and 1940, DDTs at the beginning of the 1940s, and finally Mirex in 1960 should be noted (Carignan et al. 1994). Sediment cores collected in Lake Ontario reveal a significant increase in the concentrations of these organic compounds between 1940 and 1960 (Oliver et al. 1989).

The decrease in aluminum levels between 1920 and 1940 could indicate that these levels were being diluted by an increase in organic matter or by other anthropogenic compounds. During this period, however, little variation is seen in the content of organic and inorganic carbon in sediments deposited in the Lancaster basin (Figure 8). Therefore, the decrease in Al levels indicates that the input of aluminosilicate minerals may have declined. These minerals originate primarily from the metamorphic rocks of the Canadian Shield and make up the largest part of the terrigenous fraction of suspended materials produced by the erosion of tills and clays (Tremblay 1997). Because the flow in the river decreased gradually during this period, resulting in a corresponding reduction in hydrodynamic energy and in the erosive action of the currents (Morin et al. 2001; Morin and Leclerc 1998), the flux of aluminosilicate-bearing terrigenous material probably decreased proportionally in response to this energy loss.

Moreover, the period from 1940 to 1950 corroborates this assumption regarding aluminum. During these years, Al levels increase rapidly, rising from 60 894 μ g/g to 66 633 μ g/g before dropping back to close to 60 000 μ g/g around the middle of the 1950s. The increase in Al levels is probably not related to an anthropogenic input since the main industries that are potential sources of Al only began operations around the middle of the 1950s. However, in the early 1940s, the water level in Lake Saint-François was raised about 30 cm. This increase in water level directly exposed new, significantly more fragile surfaces to erosion by wave and current action. This period of erosion would have resulted in an increase in the terrigenous fraction and therefore also in Al concentrations in the sediments.

This increase in aluminosilicate-bearing terrigenous material had the opposite effect on other geochemicals. Between 1940 and the early 1950s, concentrations of Hg, Cu, Zn, Pb, Cd, Ni, Cr and Li dropped considerably, returning almost to levels seen in the sediments at the beginning

of the century. Although the basin continued to receive an anthropogenic input of contaminants due to industrial development, the quantity of terrigenous materials it also received during this period of erosion resulted in a significant dilution in levels of inorganic elements. Although the Cr, Ni and Li content of marine clays is high, it should be noted that levels of these geochemicals also tended to decline, and it is therefore likely that the terrigenous material eroded contained little clay.

During the Lower Saint-Zotique (1950–1960), the upstream sector of Lake Saint-François underwent significant changes that radically altered the flow of the river. These changes included the construction of several dykes as well as the Moses-Saunders Dam. Given that concentrations of inorganic carbon doubled during this brief period (Figure 8), the materials used for these infrastructures must have contained a significant quantity of calcareous materials (cements, calcium carbonates and limestones). The input of allochthonous materials to the Lake Saint-François basin had the effect of lowering levels of metals, including Al, as well as the concentrations of organic compounds (figures 19 to 22).

These dilution-induced reductions in levels of geochemicals were short-lived. Between the mid-1950s and the mid-1960s, concentrations of all metals (except Al and Li) and of organic compounds rose to levels equal to or greater than those of the early 1940s (figures 19 to 22). Mercury and Zn reached concentrations over five times greater than their pre-industrial levels. Copper and Cd more than quadrupled the values of these reference levels, and Pb concentrations tripled. Nickel and Cr increases were more moderate and returned to 1940 levels, having exceeded pre-industrial levels by one-and-one-half to two times. It should be noted that the highest levels of Hg, Pb and Cd and of most organic compounds were reached in the late 1960s, whereas the other metals reached their maximum values around the beginning of that same decade (Carignan et al. 1994; Fortin et al. 1994). Most of these increased contaminant concentrations can be related to the commissioning of several plants and factories in Cornwall and Massena, in particular General Motors and Reynolds Metals, which took advantage of the increased electrical power made available by the Moses-Saunders Power Dam.

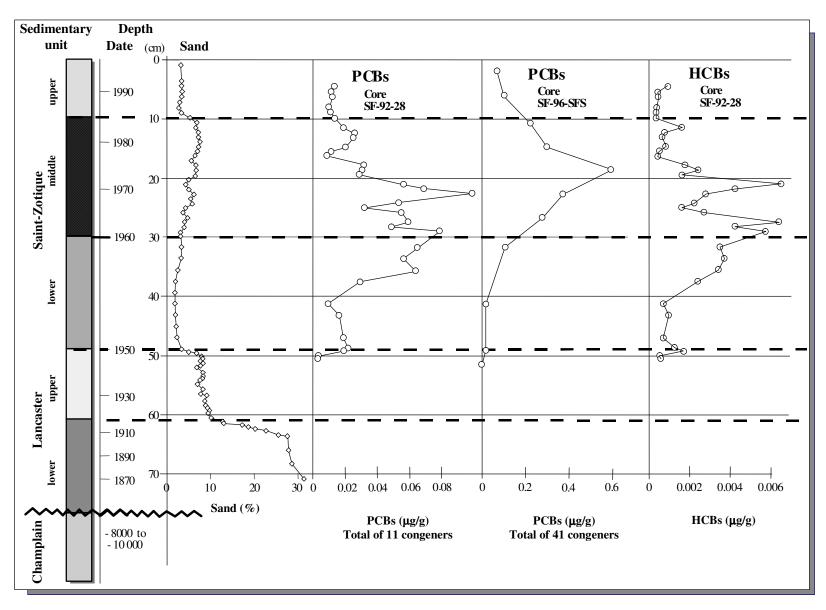


Figure 21 Geochemical profiles showing levels of PCBs and HCBs in selected sediment cores from Lake Saint-François

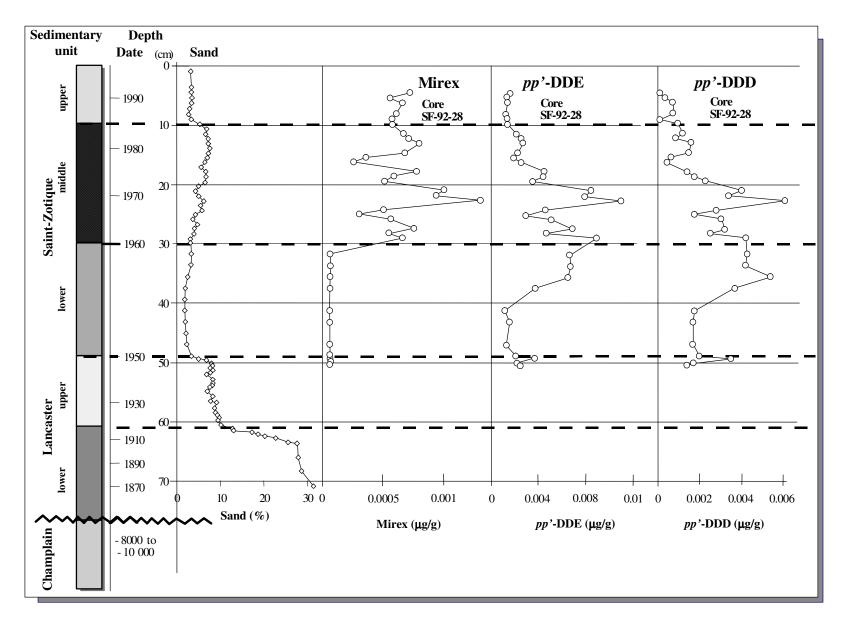


Figure 22 Geochemical profiles showing levels of Mirex, pp'-DDE and pp'-DDD in selected sediment cores

Between 1960 and 1985, during the Middle Saint-Zotique, new hydrodynamic constraints were imposed on the Lake Saint-François basin (see Section 4.1.3.2.2). During this period, whether it was because of increased flow in the river, rising water levels or increased ship-generated waves, the quantities of sand in the sediments gradually increased, rising on average from 2.4 to 5.7%. This increase in terrigenous materials, which is supported by a gradual increase in Al levels, would have had the effect of once again diluting contaminant concentrations in the basin. As suggested by the work of Carignan et al. (1994), for each 1000-m³/s increase in river flow, zinc levels may drop from 20 to 30 μg/g, thereby helping to dilute contaminant levels. The approximately 150-μg/g decrease in zinc levels between 1960 and 1985 would require an increase in flow of over 5000 m³/s and therefore it must be assumed that other dynamic factors, including ship-generated waves and higher water levels, affected sediment deposition and helped dilute contaminant levels.

Whatever the explanation, between 1960 and 1985, Zn, Pb, Cu and Cd levels declined by approximately 25 to 35%, while concentrations of organic compounds (PCB, DDT, Mirex and HCB) fell by about 75 to 85%. These significant reductions in concentrations must be attributed primarily to measures introduced during the 1970s to reduce and restrict the use of many commercial products. Specifically, the use of DDT was prohibited (1971) as was the production of Mirex (1976). In addition, the *Fisheries Act* restricted the discharge of toxic substances (1970), leaded gasoline was replaced by unleaded (between 1969 and 1974), and sewage effluent discharge by municipalities was reduced by the commissioning of sewage treatment plants in the late 1970s (Carignan et al. 1994; Fortin et al. 1994).

Finally, after 1985, the many similar measures introduced to control environmental contamination should have caused contaminant concentrations in the Upper Saint-Zotique to continue to decline to pre-industrial levels, at least in the case of metals. However, a new anthropogenic factor emerged to affect sediment composition during the 1980s. Dredging of the St. Lawrence Seaway seems to have caused the resuspension of a certain quantity of fine materials containing contaminants and clay particles. Moreover, type profiles of the metals show an increase in Cr, Ni and Li levels at the end of the 1980s. The increase was smaller in the cases of Cd, Pb, Cu, Zn and most organic contaminants (1980 to 1990) and, in the case of mercury, it was non-existent, probably because results were too fragmentary. For its part, Al is resistant to

this anthropogenic factor and levels of this element did not increase. Taken together, all these observations suggest that materials released into the water column during dredging operations contained a high percentage of clay particles relative to the number of possibly contaminated particles. By comparison with pre-industrial sediments, marine clay contains high levels of Li, Ni, Cr, Zn and Cu and equivalent levels of Pb, Cd and Al. If particles of marine clay became mixed with contaminated sediments already deposited in the basin, increases in Pb, Cd, Cu and Zn would probably have been relatively smaller than increases in the other metals (Cr, Ni and Li), and Al, which is not one of the contaminants, would likely have been unaffected by the process. These final observations on the geochemical profiles of contaminants indicate that, by resuspending older deposits, dredging projects in the Lake Saint-François sedimentary basin may have had a significant impact on environmental contamination and particularly on the sediments.

5.2 SPATIAL EVOLUTION OF CONTAMINANTS

Toxic substances found in the surficial sediments of Lake Saint-François have three main sources: river water coming from the Great Lakes, tributaries and municipal effluent. No major industry is located directly on the shore of Lake Saint-François. However, the industrial infrastructure of the Cornwall–Massena region has contributed to the pollution of the lake by discharging many toxic substances into tributaries and in effluents (Fortin et al. 1994). Sedimentological and geochemical studies conducted since the 1970s have revealed high levels of contamination by Hg and PCBs in sediments and suspended solids (Sloterdijk 1985; Lorrain et al. 1993; Vanier et al. 1996; Lepage 1999; Lepage et al. 2000).

Work by Lorrain et al. (1993) suggests a reduction of approximately 95% in PCB contamination in the northern parts of the lake and an 87% reduction for eastern areas between 1979 and 1989. In addition, over the same period, mercury concentrations also seem to have dropped by 40% on the north side and 16% on the south side of the lake. Calculated from kriged values, these reductions correspond to decreases of approximately 30% and and 85%, respectively, in Hg and PCB levels observed in fish flesh (Laliberté 1992; Bureau and Sloterdijk 1992). Part of the PCB reductions could be attributed to a reduced PCB load from Lake Ontario (Sylvestre et al. 1987; Sylvestre 1987).

5.2.1 Mercury (Hg)

With the industrial plants in the Cornwall area (Domtar, ICI, Cornwall Chemicals, Stanchem and Courtaulds) and wastewater from Cornwall as its main sources, mercury spread through the environment of Lake Saint-François for over fifty years (Anderson and Biberhofer 1990; Chan 1980; Krauss et al. 1988). Despite a significant reduction in contaminated industrial waste between 1970 and 1980, by the beginning of the 1980s, industrial effluents still significantly exceeded the Ontario standard for mercury (Fortin et al. 1994).

Table 9 presents average values and relative decreases in mercury levels in sediments relative to 1979 values for areas north and south of the navigation channel. These average levels were calculated without any physical restrictions and were not corrected for the quantity of organic matter or on the basis of the particle-size fractions. Figure 23 shows the spatial distribution of mercury in the sediments of Lake Saint-François for each of the sampling campaigns (1979, 1989 and 1999).

Table 9
Average mercury levels in surficial sediments of Lake Saint-François between 1979 and 1999

	North Sector		South Sector	
	Level in μg/g (n)	Decrease in concentration relative to 1979	Level in µg/g (n)	Decrease in concentration relative to 1979
1979 campaign	$0.47 \pm 0.40 (40)$	_	$0.12 \pm 0.11 (57)$	_
1989 campaign	0.33 ± 0.21 (24)	30%	$0.12 \pm 0.07 (38)$	0%
1999 campaign	0.23 ± 0.23 (29)	51%	$0.08 \pm 0.08 (53)$	33%

n: number of samples.

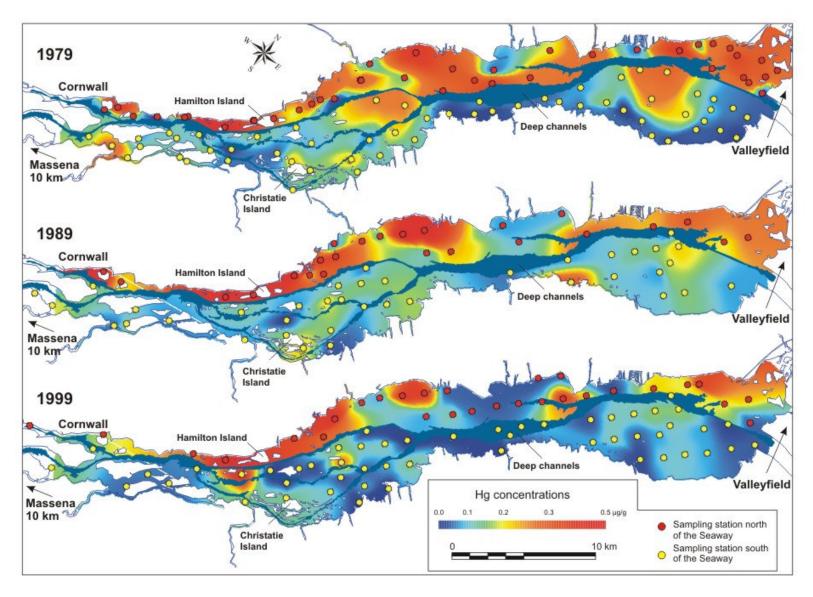


Figure 23 Spatial distribution of mercury in surficial sediments of Lake Saint-François in 1979, 1989 and 1999

The work of Lorrain et al. (1993) shows that average mercury levels for areas north of the navigation channel decreased gradually from 0.47 μ g/g in 1979 to 0.23 μ g/g in 1999, representing a drop of approximately 50% over 20 years. The average levels in the northern areas are now close to the minimal effect threshold of 0.2 μ g/g set by the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment*, (SLC and MENVIQ 1992). In the areas south of the channel, average mercury levels did not begin to decline until 1989 and are now 33% below concentrations seen in 1979. However, average levels in southern areas are close to the no effect threshold of 0.05 μ g/g and to average pre-industrial levels in sediments, which have been established at 0.032 \pm 0.018 μ g/g (Saulnier and Gagnon in preparation).

The 1979 field season offers an initial complete account of mercury levels in the sediments of Lake Saint-François. According to this account, most of the samples collected from areas north of the channel contained mercury concentrations in excess of the minimal effect threshold of 0.2 μg/g set by the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment* (SLC and MENVIQ 1992), with particularly high levels upstream of Hamilton Island (4 samples), close to the shore in Lancaster basin (1 sample) and in the Saint-Zotique basin (1 sample). These six samples contained levels ranging from 1.1 to 1.5 μg/g, which exceeds the toxic effect threshold of 1.0 μg/g set by the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment* (figures 2 and 23). On the south side of the channel, only Grenadier and Thompson basins and the stretch of the river near Massena had sediments with levels that exceeded the minimal effect threshold set by the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment* (0.2 μg/g).

A map of mercury values from the 1989 campaign reveals a significant decrease in concentrations relative to 1979, particularly in the Saint-Zotique basin and between Beaudette Point and Mouillée Point on the north side of the channel, and in all areas south of the channel (figures 3 and 23). Only the samples collected in the Lancaster basin and Hamilton Island areas remained heavily contaminated, with levels above $0.5 \,\mu\text{g/g}$ but below the toxic effect threshold of $1.0 \,\mu\text{g/g}$.

Finally, in the samples collected in 1999, an equally significant drop in Hg levels was seen relative to 1989 samples. This inorganic contamination persisted along the shores of the Lancaster basin and in the Hamilton Island area, where levels varied from 0.4 to $0.5 \,\mu\text{g/g}$. In

addition, one sample collected near Cornwall contained 1.09 μ g/g (figures 3 and 23). This high value near Cornwall could be explained by the proximity of the sampling station to the former source of contamination and by the low sedimentation rate in the area.

The gradual decreases in mercury concentrations in sediments calculated on the basis of average values and sediment maps for the various decades suggest that the American authorities and the Ontario Ministry of the Environment have been successful in their efforts since the 1970s to reduce industrial waste. Areas where mercury concentrations still exceed the minimal effect threshold set by the Interim Criteria for Quality Assessment of St. Lawrence River Sediment, (SLC and MENVIQ 1992) now represent approximately 30% of the total surface area of Lake Saint-François. Contaminated sediments can still be found and are located primarily on the north side of the navigation channel between Cornwall and the Raisin River in an area that includes Hamilton Island (figures 3 and 23). This accumulation zone, which is characterized by fine, clayey silt sediment, is also characterized by high concentrations of organic carbon (figures 17 and 18). It should be noted that this area forms the upstream extension of the Lancaster basin; here, water depths are generally less than 2 to 3 metres. The accumulation of fine sediment in this area may be controlled by the development of extensive aquatic plant beds (Lorrain et al. 1993). However, because of its shallow depths, this portion of Lake Saint-François is very sensitive to violent weather events and could be affected by water-level decreases or by nearby infrastructure projects.

5.2.2 Metals and metalloids

Of the plants and industries located in the Cornwall and Massena regions, the Courtaulds rayon and cellophane plants are the only major local sources of Pb, Zn and Cu emissions (Anderson 1990; Anderson and Biberhofer 1990). However, inputs of metals from the Great Lakes and the international section of the St. Lawrence River must also be taken into consideration. These inputs could be up to twice as large as those generated by local plants (Lorrain et al. 1993; Carignan et al. 1994).

In 1989, surficial sediments were analysed for certain metals and metalloids in order to describe the spatial distribution of these inorganic contaminants throughout the Lake Saint-François basin. Total digestion and extractable digestion analyses included those phases with

which metals from anthropogenic sources associate (Lorrain and Jarry 1993). Table 10 presents the average concentrations obtained by analyses of the total fractions and the extractable fractions for each area of Lake Saint-François.

Table 10 Average levels of metals and metalloids in surficial sediments of Lake Saint-François in 1989

	North Sector $(n = 25)$		South Sector $(n = 41)$	
	Total fraction Level (µg/g)	ExtractablefFraction Level (µg/g)	Total fraction Level (μg/g)	Extractable fraction Level (µg/g)
Metals				
Cu	30.0 ± 15.8	22.9 ± 12.5	22.5 ± 13.6	16.9 ± 10.8
Zn	224.7 ± 122.4	184 ± 122	112.0 ± 64.7	75.7 ± 55.9
Pb	27.5 ± 12.9	23.3 ± 13.3	23.5 ± 12.9	19.8 ± 12.2
Ni	24.0 ± 10.0	10.2 ± 5.2	19.6 ± 8.9	8.4 ± 4.6
Cr	4.4 ± 18.4	8.5 ± 4.1	35.2 ± 11.7	6.5 ± 3.3
Cd	0.52 ± 0.1	0.52 ± 0.3	0.56 ± 0.2	0.56 ± 0.4
Fe	23268 ± 6586	5592 ± 2818	22308 ± 5900	4997 ± 2677
Mn	426 ± 109	186 ±106	459 ± 104	192 ±105
Al	55339 ± 6598	2719 ± 1361	53273 ± 6915	2287 ±1209
Metalloids				
As	4.4 ± 2.1		3.3 ± 1.6	
Se	1.3 ± 0.7		0.8 ± 0.6	

Legend: (Al) aluminum, (As) arsenic, (Cd) cadmium, (Cr) chromium, (Cu) copper, (Fe) iron, (Mn) manganese, (Ni) nickel, (Pb) lead, (Se) selenium, (Zn) zinc.

With the exception of Cd and Mn, in the case of both total fractions and extractable fractions, average metal and metalloid levels were all higher in areas located on the north side of the St. Lawrence Seaway than on the south side. Conversely, manganese (Mn) levels were higher on the south side than on the north side, while Cd levels appeared to be similar on both sides of the lake. The relative differences between the two areas range from five to 25% for all elements except Zn, which differs by 50%, and selenium (Se), which differs by 40%.

Figure 24 presents three maps of contamination indices for the main metals analysed in 1989:

- For the total fraction (Cu_{tot}, Zn_{tot}, Pb_{tot}, Cr_{tot}, Ni_{tot}, Cd_{tot}), relative to pre-industrial levels in Lake Saint-François;
- For the extractable fraction (Cu_{ext}, Zn_{ext}, Pb_{ext}, Cr_{ext}, Ni_{ext}, Cd_{ext}), relative to the NET (no effect threshold) set by the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment*;
- For the total and extractable fractions (As_{tot}, Hg_{tot}, Cu_{ext}, Zn_{ext}, Pb_{ext}, Cr_{ext}, Ni_{ext}, Cd_{ext} and 20 organic contaminants), relative to the MET (minimal effect threshold) set by the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment*.

The contamination indices show, on the one hand, that the main contaminated zones are located on the north side of the St. Lawrence Seaway, with relatively significant exceedances in the Lancaster and Saint-Zotique basins and in the area between Cornwall and the mouth of the Raisin River. South of the channel, the edges of Christatie Island and the mouth of the Raquette River are also contaminated. Zinc, Cu, Cd and As seem to be the most problematic contaminants. However, it should be pointed out that with the exception of mercury, which was discussed in the preceding section, no inorganic element exceeds the toxic effect threshold set by the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment* (Fortin et al. 1994; SLC and MENVIQ 1992). Given that quality criteria are exceeded by only small percentages, it would appear that the sediments of Lake Saint-François are generally not highly contaminated by metals, with the exception of Zn. Finally, most metals are associated with oxides of Fe_{ext} and Mn_{ext} and with organic carbon, and only Ni_{ext}, As, Se and Cu_{ext} are associated with the silty fraction of the sediments (Lorrain and Jarry 1993).

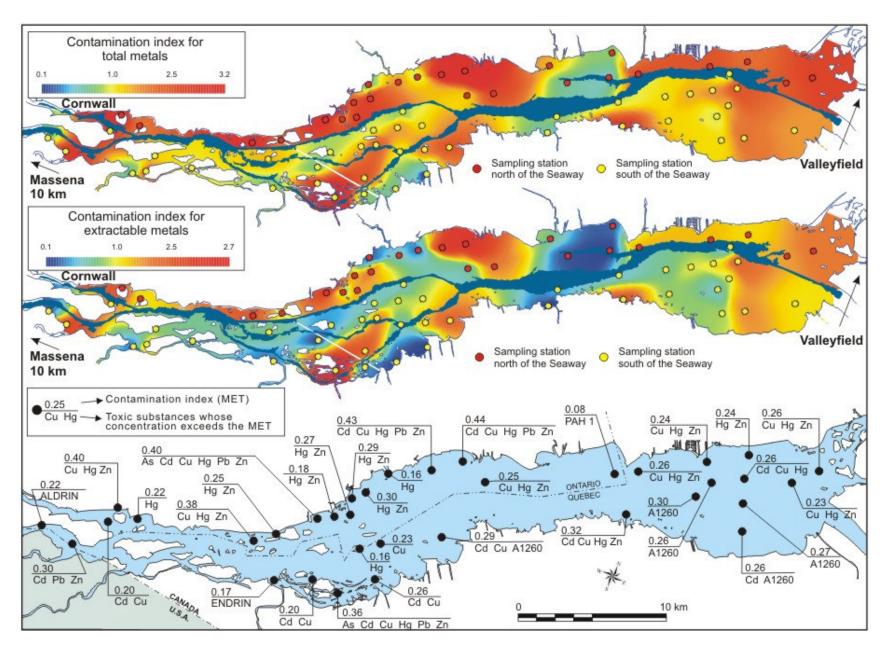


Figure 24 Spatial distribution of contamination indices for metals and organic compounds in surficial sediments of Lake Saint-François in 1989

5.2.3 Polychlorinated biphenyls (PCBs)

The main sources of the PCBs in Lake Saint-François are effluents produced by the aluminum smelters of the Reynolds Metal Company and ALCOA and by the General Motors Corporation–Central Foundry Division facility (Anderson and Biberhofer 1990; Chan 1980; Krauss et al. 1988). The first restrictions on these synthetic products date back to the 1970s, when their use was limited to transformers and electrical condensers. Toward the end of that decade, laws were enacted that definitively restricted the use of these substances. During the 1980s, a number of remediation and monitoring measures were introduced in the areas of wastewater treatment and treatment of contaminated runoff with a view to reducing the amount of PCBs entering the environment. The work of Lorrain et al. (1993) shows a significant decrease (about 90%) in PCB concentrations in sediments throughout Lake Saint-François between 1979 and 1989.

Table 11 presents average levels and relative decreases in total concentrations of Aroclors by comparison with 1979 levels for both the north and south sectors. It should be noted that 1999 values for Aroclors were produced by converting PCB congeners to Aroclors (see Chapter 3).

Table 11
Average PCB levels in surficial sediments of Lake Saint-François between 1979 and 1999

	North Sector		South Sector	
Aroclors	Level of A 1242, A 1254, A 1260, in μg/g (n)	Decrease in concentration relative to 1979	Level of A 1242, A 1254, A 1260, in μg/g (n)	Decrease in concentration relative to 1979
1979 campaign*	$0.202 \pm 0.240 (40)$	-	$0.397 \pm 0.447 (57)$	-
1989 campaign*	0.018 ± 0.013 (12)	91%	$0.063 \pm 0.057 (35)$	84%
1999 campaign*	0.010 ± 0.018 (29)	95%	$0.028 \pm 0.037 $ (54)	93%
PCB congeners	Level of 41 congeners, in μg/g (n)	Difference relative to Aroclors of 1999	Level of 41 congeners, in μg/g (n)	Difference relative to Aroclors of 1999
1999 campaign*	0.028 ± 0.052 (29)	36%	$0.078 \pm 0.101 (54)$	36%

^{*} Measured values. ** Computed values.

The 91% and 84% decreases in Aroclors for the north and south sectors, respectively, between 1979 and 1989, confirm the comments by Lorrain et al. (1993) concerning these same kriged results. This decline in concentrations relative to 1979 levels continued between 1989 and 1999, reaching 95% in the sector to the north of the St. Lawrence Seaway, and 93% in the sector to the south. Overall, average levels of Aroclors dropped from 0.317 μ g/g to 0.022 μ g/g between 1979 and 1999, representing a 93% decrease over 20 years for Lake Saint-François as a whole.

As shown by the average levels of the 41 congeners analysed in the sediments in 1999, total Aroclor values appear to represent only 36% of PCB congeners. This small percentage is primarily attributable to the fact that Aroclor 1248 is not included in the Aroclor total. This Aroclor, which is considered to have been one of the most used in the Massena area (Planas et al. 1992; Vanier et al. 1996), was not included for analysis in any sampling campaign. Based on no effect, minimal effect and toxic effect thresholds for total PCBs of 0.02 µg/g, 0.2 µg/g and 1 µg/g, respectively, as set out in the *Interim Criteria for Quality Assessment of St. Lawrence River Sediment* (SLC and MENVIQ 1992), the average levels of 0.028 µg/g and 0.078 µg/g calculated for PCB congeners in the two sectors of Lake Saint-François are between the no effect and the minimal effect thresholds.

The results for 1979 as a whole show that Aroclor levels in almost 85% of the samples exceeded the no effect threshold of $0.02~\mu g/g$, and in 20% the levels were above the minimal effect threshold of $0.2~\mu g/g$. In 1989, 50% of the samples still exceeded the no effect threshold, but all were below the minimal effect threshold set by the criteria. Finally, in 1999, only 22% of the samples remained above the no effect threshold and one sample had an Aroclor level above the minimal effect threshold. Although it must be borne in mind that the Aroclor values do not include Aroclor 1248 and underestimate the actual amount by which the criteria are exceeded, the decrease in the number of exceedances provides an impression of the degree of improvement in sediment quality throughout Lake Saint-François. If this downward trend is sustained in the coming years, all samples should be below the no effect threshold set by the quality criteria by the end of the current decade.

Figure 25 shows a spatial representation of total Aroclor concentrations for the three sampling campaigns (1979, 1989 and 1999), while Figure 26 presents the distribution of total concentrations of PCB congeners for 1999. These maps make it possible to visualize the changes

that have occurred in the various basins of Lake Saint-François. It should be noted that, in order to make it possible to better identify the locations of accumulation zones that may contain PCBs, the levels shown on these maps have not been corrected for organic carbon percentage.

In every area north of the navigation channel, the distribution of elevated concentrations of Aroclors changed radically between 1979 and 1989. In 1979, levels exceeded 0.06 μ g/g in almost all areas, but in 1989 and 1999, only the sediments in the north part of the Saint-Zotique basin, near Coteau-Landing, still contained levels of Aroclors above 0.04 μ g/g.

In southern areas, the improvement in sediment quality seems to have occurred more slowly. Whereas in 1979 all such areas contained sediments contaminated by PCBs, by 1999, only sediments in the Grenadier basin, in the area upstream of the Des Cèdres basin near the mouth of the Salmon River, and at the mouths of the St. Regis and Raquette rivers contained PCB levels in excess of $0.06~\mu g/g$. Sediments in these areas are also characterized by a sedimentary matrix of clayey or sandy silt and a relatively high organic carbon content. They are also located in a shallow environment and could be resuspended by violent weather events or by events related to anthropogenic activities. In this regard, the work of Lepage (1999) and Lepage et al. (2000) shows that suspended solids with contamination levels that sometimes exceed the minimal effects threshold are circulating on the south side of the upstream sector of Lake Saint-François.

Finally, by mapping the congeners, it is possible to visualize the PCB dispersion plume throughout the southern areas of the lake (Figure 26). From the Raquette and Grasse rivers, which are located upstream of Lake Saint-François, to downstream of the lake, levels of PCB congeners in the various samples tend to remain between 0.4 µg/g and 0.04 µg/g, forming a corridor of contaminated sediments along the south shore of the lake. Although the present document does not provide a map of each congener, this lateral dispersion could have been identified using each congener or each group of congeners (2Cl, 3Cl, etc.). The pattern suggests that the main PCB source is located upstream of Lake Saint-François, in the area of Massena and the Grasse and Raquette rivers.

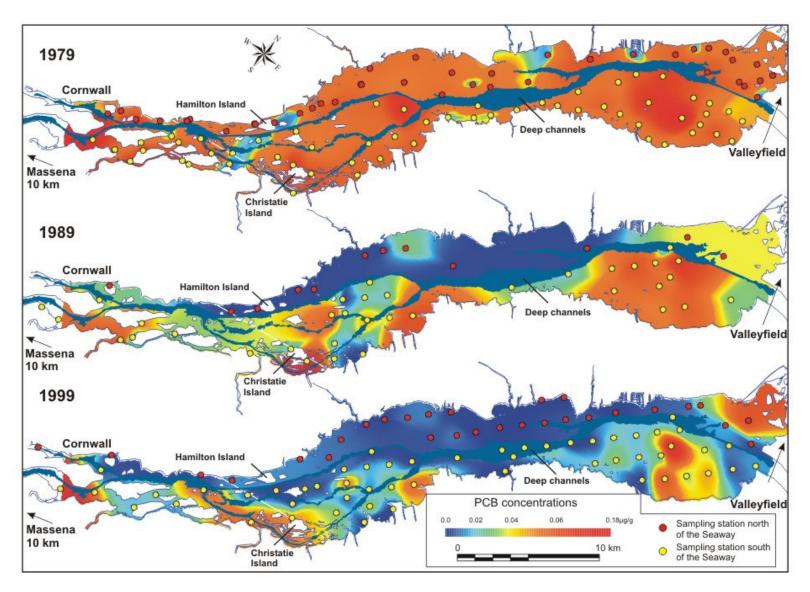


Figure 25 Spatial distribution of Aroclors in surficial sediments of Lake Saint-François in 1979, 1989 and 1999

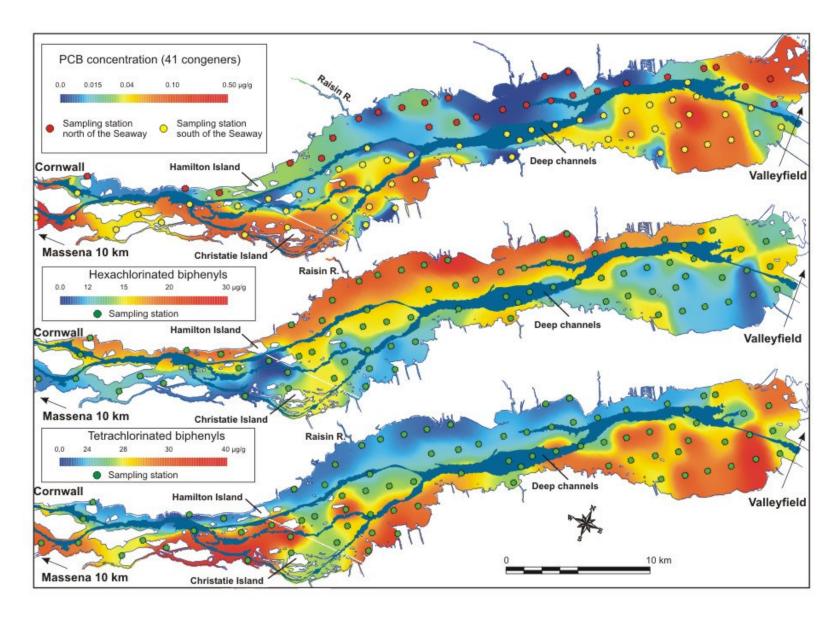


Figure 26 Spatial distribution of PCB congeners and relative ratios of congeners in surficial sediments of Lake Saint-François in 1999

However, the dispersion also suggests that PCB concentrations in the northern areas of Lake Saint-François are not related to PCBs that originate from the Massena industrial sector. This theory is consistent with comments by Lorrain et al. (1993) concerning the existence of two separate sources, one on the south shore (i.e. the Massena area), and the other on the north shore. The latter source is likely related to water moving down the river from the Great Lakes. Work by Lepage (1999) and Lepage et al. (2000) shows that PCBs found in suspended sediments circulating in the southern part of Lake Saint-François correlate with the types of Aroclor found in the Massena area, and that violent weather events can cause increases in concentrations measured in samples collected at a distance of thirty kilometres downstream of this industrial area

Interpretation of the various analytical results for the congeners also suggests that there are two potential sources. In fact, even if levels of the different congeners are still more elevated on the south side of the waterway than on the north, the relative predominance of each congener varies from one area to another and from one congener to another (Figure 26). Congeners that contain six or more chlorines make up a higher relative proportion of the total on the north side of the waterway, while those that contain four chlorines or fewer constitute a greater proportion of the total on the south side. In other words, PCBs measured on the north side contain more chlorine than those on the south. This difference in the geochemical signatures of the PCB congeners suggests that the PCBs in the sediments of Lake Saint-François have two sources. One of these sources appears to be located in the Massena area and to be composed primarily of the less chlorinated congeners, Aroclors 1242 and 1248 (Planas et al. 1992). The other source may be the waters of the St. Lawrence River, composed of more highly chlorinated congeners such as Aroclors 1254 and 1260.

5.2.4 Other organic compounds

In addition to PCBs, 20 to 30 other organic compounds were analysed for all sediment samples from Lake Saint-François in 1979 and 1989 (Sloterdijk 1985; Lorrain and Jarry 1993). Most of the levels measured in these compounds were at the analytical detection limits. Only a few contained levels exceeding the no effect threshold and even fewer exceeded the minimal effect threshold set by the *Interim Criteria for Quality Assessment of St. Lawrence River*

Sediment (Fortin et al. 1994; SLC and MENVIQ 1992). Figure 24 shows the locations of sediment samples collected in 1989 that contain levels of organic compounds exceeding their minimal effect thresholds. This map shows that the main criteria exceedances are located near Christatie Island at the mouth of the Salmon River and further upstream, at the mouth of the Grasse River. Contamination by insecticides and polycyclic aromatic hydrocarbons (PAHs) appears to be minor. Because of the small number of samples with levels exceeding detection limits, it was not possible to produce a spatial representation that could assist in targeting the source or sources of these contaminants (Lorrain and Jarry 1993).

6 Conclusion

Type profiles of sedimentary and geochemical processes in the Lake Saint-François basin have been developed as a function of the temporal evolution of the basin. In addition, the spatial distribution of its various environmental contaminants has been assessed based on analysis and interpretation of various sedimentary materials collected in the lake since the end of the 1970s.

The type profile of the physical constituents of the sediments suggests that deposition of the sedimentary material in the Lake Saint-François basin was significantly affected by several anthropogenic events which, over the years, caused fluctuations not only in particle-size composition, but also in sedimentation rates. These fluctuations have led to the development of five separate sedimentary units since the beginning of the 20th century:

- The Lower Lancaster (1870–1920) consists primarily of sediments from the early industrial period that were deposited at an average rate of 0.2 cm/yr.
- The Upper Lancaster covers 30 years of sedimentation (1920–1950) during which flow rates in the river were relatively low and water levels were raised by the construction of dams downstream of the lake.
- The Lower Saint-Zotique (1950–1960), characterized primarily by a very high sedimentation rate of 1.9 cm/yr, represents a period of relative instability related to a substantial input of terrigenous particles probably associated with the erosion of banks and the construction of the run-of-river Moses-Saunders Dam at Cornwall.
- The Middle Saint-Zotique (1960–1985) was marked by an increase in flow in the river and the opening of the St. Lawrence Seaway, which resulted in an increase in the movement of goods between Montreal and Lake Ontario. These events seem to have promoted more aggressive erosion of shoreline deposits and islands.
- During the Upper Saint-Zotique (1985 to the present), dredging of the navigation channel may have resuspended a significant quantity of fine materials, which would have been deposited in the deeper areas of Lake Saint-François.

The spatial distribution of sediments throughout Lake Saint-François suggests a relatively significant evolution in particle-size distribution since 1979. Between 1979 and 1999, the overall composition of sediments changed from silty sand to clayey and sandy silt. This shift seems related to a significant decrease in hydrodynamic energy, and to the erosion of clay zones upstream. The reduction in energy is related to hydrodynamic changes and to the presence of an

increased number of submerged plants in shallow areas such as Christatie and Hamilton islands (Figure 1). Since 1989, this energy drop also seems to have favoured the deposition of silty fractions and organic matter in the upstream sector of the lake.

The profiles of the main contaminants suggest that the geochemical evolution of contaminants took place in four major phases and that it may correlate with the main sedimentary units.

- Traces of inorganic contaminants initially appear in the sediments around the beginning of the Lancaster unit with the establishment and opening of the first factories and a rapid expansion in the population of the city of Cornwall. With no environmental controls in existence, concentrations of metals gradually rose, reaching a peak around 1940.
- In the late 1940s, and during the Lower Saint-Zotique unit, concentrations of metals dropped considerably, reaching levels close to those of the pre-industrial period. This decrease seems to be related to a significant dilution of concentrations resulting from a major inflow of clean, allochthonous particles into the basin.
- After this period of dilution of concentrations, levels of metals and organic compounds rose again, at a more accelerated rate, reaching values similar to those of 1940. During the Middle Saint-Zotique unit, concentrations began to decrease gradually again as a result of initial measures aimed at mitigating and remediating the effects of the discharge of toxic substances.
- Finally, toward the end of the 1980s, levels of most contaminants rose for a short period of time (≈5 years), temporarily interrupting the previous trend, probably during the period following the dredging of the St. Lawrence Seaway between 1988 and 1995.

Spatial representation of the results obtained for mercury and PCBs shows that these two contaminants have very different sources. Sediments in areas north of the navigable waterway were heavily contaminated by mercury originating primarily from the Cornwall area, while sediments in southern areas of Lake Saint-François were contaminated by PCBs from plants in the Massena area. This distinction can also be observed in the results for other inorganic elements and organic compounds.

In addition, spatial variability of contaminants among sampling campaigns conducted at decadal intervals suggests that contamination by mercury and PCBs has decreased significantly over the past twenty years. In the case of Hg, the decrease seems to be on the order of 50%, while for PCBs, it is much greater and may be close to 95%. These declines seem to be related not only

to the closure of certain plants, but also to application of and compliance with environmental legislation and to an influx of cleaner materials into the Lake Saint-François sedimentary basin.

The sedimentological and geochemical variations identified in this study indicate that the sedimentary environment in Lake Saint-François is highly sensitive to all types of anthropogenic activities that either directly or indirectly affect the sedimentary dynamics or the hydrodynamics of the basin. These activities include the construction of infrastructure, the dredging of sediments and the discharge of clean or contaminated materials into the environment.

References

- Allan, R.J. 1986. The limnological units of the lower Great Lakes–St. Lawrence River corridor and their role in the source and aquatic fate of toxic contaminants. *Water Poll. Res. J. Canada* 21(2): 168–186.
- Anderson, J. 1990. St. Lawrence River Environmental Investigations Vol. 4: Assessment of Water and Sediment Quality in the Cornwall Area of the St. Lawrence River, 1985. Environment Ontario, Water Resources Branch, Great Lakes Section.
- Anderson, J. and H. Biberhofer. 1990. Water and Suspended Sediment Quality in the St. Lawrence River at Cornwall/Massena. St. Lawrence River Remedial Plan Action Plan Data Report. 14 pp.
- Bariteau, L. 1988. La cartographie géomorphologique au 1 : 20000 de modelés polygéniques : Un exemple des basses terres du Saint-Laurent. Master's thesis. Faculty of Arts and Sciences, Geography Department, University of Montreal.
- Barua, M. 1996. *St. Lawrence River, Cornwall (LSL # 2, Pilon 2, LSF N1, TCTI, LSF S2, LSF #2).* Laboratory Report. Direction de la restauration des écosystèmes aquatiques, Institut national de recherche sur les eaux.
- Barua, M. 1995. *Projet Impact, Québec*. Laboratory Report. Direction de la restauration des écosystèmes aquatiques, Institut national de recherche sur les eaux.
- Bérubé, J. 1997. Dragage sélectif des hauts-fonds dans la voie navigable du Saint-Laurent entre Montréal et le Cap à la Roche. Montreal: Environment Canada Quebec and Ontario regions, Environmental Protection Branch, Technology Development Section.
- Bérubé, J. 1994. *Environmental Impacts of Dredging and Sediment Disposal*. Montreal: Environment Canada Quebec and Ontario regions, Environmental Protection Branch, Technology Development Section.
- Bruce, J.P., O.W. Brown, C. Pellegrin, S. Williams, and T.O. Kolberg. 1973. *Shore Erosion on the Great Lakes–St. Lawrence System*. Government of Canada.
- Bureau, J. and H. Sloterdijk. 1992. Bioaccumulation de certains contaminants chez les poissons juvéniles de la région de Cornwall-Saint-Régis-Lac Saint-François et ses principaux affluents. Scientific Report. Montreal: Environment Canada Quebec Region, St. Lawrence Centre.

- Carignan, R. 1990. Étude sur l'utilisation des radio-isotopes et autres marqueurs chronologiques pour déterminer la dynamique et le temps de résidence des sédiments du lac Saint-François. INRS-Eau, for Environment Canada Quebec Region, Conservation and Protection, St. Lawrence Centre, Montreal.
- Carignan, R. and S. Lorrain. 2000. Sediment dynamics in the fluvial lakes of the St. Lawrence River: Accumulation rates and characterization of the mixed sediment layer. *Can. J. Fish. Aquat. Sci.* 57(suppl. 1): 63–77.
- Carignan, R., S. Lorrain, and K. Lum. 1994. A 50-yr record of pollution by nutrients, trace metals, and organic chemicals in the St. Lawrence River. *Can. J. Fish. Aquat. Sci.* 51: 1088–1100.
- Carignan, R., S. Lorrain, and K. Lum. 1993. Sediment dynamics in fluvial lakes of the St. Lawrence River: Accumulation rates and residence time of mobile sediments. Unpublished.
- CENTREAU. 1973. Fleuve Saint-Laurent, Aspects physiques et sédimentologiques entre Cornwall et Varennes. For Environment Canada, Transport Canada, and Régie des eaux du Québec, Ministère des Richesses naturelles, Québec.
- Chan, C.H. 1980. *St. Lawrence River Water Quality Surveys, 1977.* Report No. 113. Burlington, Ontario: Environment Canada, National Water Research Institute, Canada Centre for Inland Waters.
- Coakley, J.P., J.-C. Dionne, and D. Brodeur. 1989. Revue de la littérature et bibliographie des processus géologiques et des sédiments du Saint-Laurent. Report No. 89-07F. Burlington, Ontario: Environment Canada, National Water Research Institute, Canada Centre for Inland Waters.
- Corbeil, P. 1984. Géologie du quaternaire de la région de Rigaud/Rivière-Beaudette : quelques applications pour l'environnement. Master's thesis. Département des sciences de la terre, Université du Québec à Montréal.
- Cornwall Economic Development. 2001. Cornwall, Ontario, Canada History Update March 5 2001. Available from World Wide Web: http://www.city.cornwall.on.ca/hist01.html.
- Crémer, M. 1979. Influence de l'histoire géologique du Saint-Laurent sur ses aspects morphosédimentaires actuels. *Bull. Inst. Géol. Bassin d'Aquitaine* 26: 5–41.
- Dauphin, D. and D. Lehoux. 2000. Érosion des rives du Saint-Laurent dans le tronçon Cornwall-Montmagny: influence de la navigation commerciale et de la navigation de plaisance sur l'état des rives et approches proposées pour réduire l'érosion au niveau des rives les plus sévèrement menacées. Preliminary Report. Ministère des Transports du Québec.

- Désilets, L. and C. Langlois. 1989. *Variation spatiale et saisonnière de la qualité de l'eau du fleuve Saint-Laurent*. Montreal: Environment Canada, Conservation and Protection Quebec Region, St. Lawrence Centre.
- Duncan, G.A. and G.G. Lahaie. 1979. *Size Analysis Procedures Used in the Sedimentology Laboratory*. Hydraulics Division Manual. Burlington, Ontario: Environment Canada, National Water Research Institute, Canada Centre for Inland Waters.
- Environment Canada. 1979. *Analytical Methods Manual*. Environment Canada Ontario Region, Inland Waters Directorate, Water Quality Division.
- Fortin, G. and D. Desrochers. 1990. Échantillonnage et caractérisation des sédiments du lac Saint-François, 1989. Environnement Illimité Inc., for Environment Canada, Conservation and Protection, Quebec Region, St. Lawrence Centre. 42 pp. + appendices.
- Fortin, G., D. Leclair, and A. Sylvestre. 1994. Synthèse des connaissances sur les aspects physiques et chimiques de l'eau et des sédiments du lac Saint-François. Technical Report on Priority Intervention Zones 1 and 2. Environment Canada Quebec Region, St. Lawrence Centre.
- Frame, G.M., J.W. Cohran, and S.S. Bowadt. 1996. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRDC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Resol. Chromatogr.* 19: 657–668.
- Frenette, M., C. Barbeau, and J.L. Verrette. 1989. *Aspects quantitatifs, dynamiques et qualitatifs des sédiments du Saint-Laurent*. Montreal: Hydrotech Inc., for Environment Canada, Quebec Region, Conservation and Protection, St. Lawrence Centre.
- Germain, A. and M. Jason. 1984. *Qualité des eaux du fleuve Saint-Laurent de Cornwall à Québec (1977–1981)*. Environment Canada Quebec Region, Inland Waters Directorate.
- Kauss, P.B., Y.S. Hamdy, and B.S. Hamma. 1988. St. Lawrence River Environmental Investigations Vol. 1–Background: Assessment of Water, Sediment and Biota in the Cornwall, Ontario and Massena, New York Section of the St. Lawrence River, 1979–1982. Toronto: Ontario Ministry of the Environment, Water Resources Branch.
- Laliberté, D. 1992. Évolution des teneurs en mercure et en BPC dans la chair des poissons du fleuve Saint-Laurent et au lac Saint-François entre 1976 et 1988. Report no. QE-91-15. Ministère de l'Environnement du Québec, Direction de la qualité de l'eau.
- Landry, B. and M. Mercier. 1992. *Notions de géologie, 3^e édition*. Ville Mont-Royal: Modulo Éditeur.
- Lepage, S. 1999. Contamination of Suspended Solids in Lake Saint-François and in the Cornwall-Massena Sector. Scientific and Technical Report ST-171E. Environment Canada Quebec Region, Environmental Conservation, St. Lawrence Centre.

- Lepage, S., B. Rondeau, L.F. Richard, and Y. Lafleur. 2002. Influence des niveaux d'eau sur l'érosion et la remise en suspension des sédiments dans le secteur Verchères-Contrecoeur du fleuve Saint-Laurent. Environment Canada Quebec Region, St. Lawrence Centre. Unpublished.
- Lepage, S., B. Rondeau, G. Létourneau, and L.F. Richard. 2001. État d'avancement des projets CARCOIS et Érosion. Noon seminar series, St. Lawrence Centre, Environment Canada – Quebec Region, Montreal, March 23, 2001.
- Lepage, S., J. Biberhofer, and S. Lorrain. 2000. Sediment dynamics and the transport of suspended matter in the upstream area of Lake St. Francis. *Can. J. Fish. Aquat. Sci.* 57 (Suppl. 1): 52–62.
- Loiselle, C., G. R. Fortin, S. Lorrain, and M. Pelletier. 1997. *Dynamics and Contamination of St. Lawrence River Sediments*. Environment Canada Quebec Region, St. Lawrence Centre.
- Lorrain, S. and R. Carignan 1992. Évolution temporelle de la contamination par les métaux traces dans les sédiments fluvio-lacustres du Saint-Laurent. Summary of the 61st. ACFAS Conference, Rimouski, May 1992.
- Lorrain, S. and V. Jarry. 1993. Évolution spatiale des métaux traces, pesticides organochlorés, chlorobenzènes et hydrocarbures aromatiques polycycliques dans les sédiments du lac Saint-François: 1989. Montreal: Environment Canada Quebec Region, Conservation and Protection, St. Lawrence Centre.
- Lorrain, S., V. Jarry, and K. Guertin. 1993. Répartition spatiale et évolution temporelle des biphényles polychlorés et du mercure dans les sédiments du lac Saint-François; 1979-1989. Environment Canada Quebec Region, Conservation and Protection, St. Lawrence Centre. 63 pp.
- MacPherson, J.B. 1967. Raised shorelines and drainage evolution in the Montreal Lowland. *Cahiers de géographie du Québec* 23: 343–360.
- Manchester-Neesvig, J.B. and A.W. Andren. 1989. Seasonal variation in the atmospheric concentration of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* 23: 1138–1148.
- Morin, J. and M. Leclerc. 1998 From pristine to present state: Hydrology evolution of Lake Saint-François, St. Lawrence River. *Can. J. Civ. Eng.* 25: 864–879.
- Morin, J., P. Fortin, P. Boudreau, Y. Secretan, and M. Leclerc. 2001. *Atlas des courants du Saint-Laurent: Lac Saint-François*. Scientific Report RS-101. Montreal: Environment Canada Quebec Region, Canadian Meteorological Service. 30 pp. + maps.

- Morin, J., P. Boudreau, and M. Leclerc. 1994. *Réhabilitation de l'écosystème du Saint-Laurent, Lac Saint-François: Les bases de la modélisation hydrodynamique*. Research Report No. R-412. INRS-Eau. 65 pp.
- NYPA New York Power Authority. 1992. *The St. Lawrence-FDR Power Project*. The New York Power Authority. 20 pp.
- Occhietti, S. 1989. "Quaternary Geology of St. Lawrence Valley and Adjacent Appalachian Sub-region". In *Quaternary Geology of Canada and Greenland*, R.J. Fulton (ed.). Ottawa: Geological Survey of Canada.
- Oliver, B.G., M.N. Charlton, and R.W. Durham. 1989. Distribution, redistribution, and geochronology of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in Lake Ontario sediments. *Environ. Sci. Technol.* 23: 200–208.
- Parent, M. and S. Occhietti. 1988. Late Wisconsinian deglaciation and Champlain Sea invasion in the St. Lawrence Valley. *Géographie Physique et Quaternaire* 42: 215–246.
- Planas, D., M. Sylvestre, and C. Vanier. 1992. *Bioaccumulation and Biotransformation of PCBs by Periphyton. Preliminary Report on Bottom Sediment PCB Concentrations in Lake St. Francis and Plans for 1992-1993*. Montreal: GEOTOP and INRS-Eau.
- Prest, K.V. 1972. "Géologie du Quaternaire au Canada". In *Géologie et Ressources minérales du Canada*, Geological Survey of Canada.
- Prichonnet, G. 1977. La déglaciation de la vallée du Saint-Laurent et l'invasion marine contemporaine. Géographie Physique et Quaternaire 31: 323–345.
- Reavie, E.D., J.P. Smol, R. Carignan, and S. Lorrain. 1998. Diatom paleolimnology of two fluvial lakes in the St. Lawrence River: A reconstruction of environmental changes during the last century. *J. Phycol.* 34: 446–456.
- Reineck, H.E. and I.B. Singh. 1986. Depositional Sedimentary Environments with Reference to Terrigenous Clastics. New York: Springer-Verlag.
- Richard, M.R., M.E. Fox, and F.R. Pick. 1997. PCB concentrations and congener composition in macrophytes and sediments in the St. Lawrence River near Cornwall, Ontario. *J. Great Lakes Res.* 23(3): 297–306.
- Rondeau, B., D. Cossa, P. Gagnon, and L. Bilodeau. 2000. Budget and sources of suspended sediment transported in the St. Lawrence River, Canada. *Hydrological Processes* 14: 21–36.
- Rukavina, N.A. 2000. Sedimentology of Contaminated St. Lawrence River Sediments at Cornwall, Ontario. Contribution No. 00-052. Environment Canada, National Water Research Institute.

- Saulnier, I. and C. Gagnon (in preparation). Background levels of contaminants in St. Lawrence River sediments: Implications for sediment quality criteria and environmental management.
- Schulz, D.E., G. Petrick, and J.C. Duinker. 1989. Complete characterization of polychlorinated biphenyl congeners in commercial aroclor and clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.* 23(7): 852–859.
- Shepard, F.P. 1954. Nomenclature based on sand-silt-clay ratios. *Jour. Sed. Petrology* 24(3): 151–158.
- SLC St. Lawrence Centre. 1997. *The River at a Glance*. Info-flash on the State of the St. Lawrence River, St. Lawrence UPDATE series. Montreal: Environment Canada Quebec Region, Conservation and Protection.
- SLC and MENVIQ St. Lawrence Centre and Ministère de l'Environnement du Québec. 1992. Interim Criteria for Quality Assessment of St. Lawrence River Sediment. Montreal: Environment Canada, Conservation and Protection, Quebec Region.
- Sloterdijk, H. 1991. Mercury and organochlorinated hydrocarbons in surficial sediments of the St. Lawrence River (Lake St. Francis). *Water Poll. Res. J. Canada* 26(1): 41–60.
- Sloterdijk, H. 1985. Substances toxiques dans les sédiments du lac Saint-François. Environment Canada, Inland Waters Directorate, Quebec Region.
- Sylvestre, A. 1987. Organochlorines and Polyaromatic Hydrocarbons in the St. Lawrence River at Wolfe Island 1982-84. Technical Bulletin No. 144. Burlington, Ontario: Environment Canada, Inland Waters / Lands Directorate Ontario Region, Water Quality Branch.
- Sylvestre, A., K.W. Kuntz, and J. Biberhofer. 1987. *Contributions to Appendix B: Toxic Substances St Lawrence River, Wolfe Island Station*. Burlington, Ontario: Environment Canada, Inland Waters / Lands Directorate Ontario Region, Water Quality Branch.
- Transport Canada. 1996. *Les transports au Canada 1996* Annual Report. Available on the World Wide Web: http://www.tc.gc.ca/pol/fr/anre1996/tc96_table_des_matieres.htm.
- Tremblay, A. 1997. Caractérisation géochimique de la matière en suspension des principaux tributaires du Saint-Laurent entre Cornwall (Ontario) et Québec. Master's thesis, Université du Québec, INRS-Géoressources.
- Vanier, C., M. Sylvestre, and D. Planas. 1996. Persistence and fate of PCBs in sediments of the St. Lawrence River. *Sci. Tot. Environ.* 192: 229–244.
- Verrette, J.-L. 1990. *Délimitation des principales masses d'eau du Saint-Laurent (Beauharnois à Québec)*. Montreal: Les consultants Hydriques, for Environment Canada, Conservation and Protection Quebec Region, St. Lawrence Centre.

Appendices