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A historical reconstruction of organic and inorganic contamination events in the Saguenay Fjord/St. Lawrence system from preindustrial times to the present

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Abstract

Based on published chronologies of Hg contamination to the Saguenay/St. Lawrence system as well as sedimentary profiles for this heavy metal in the Lower St. Lawrence Estuary, we have established a 100–200 year chronology in the studied sediments and reassessed sedimentation rates for the estuarine system. Our results suggest that sedimentation rates might be higher, by a factor of 1.5–2, than previously assumed for the Lower Estuary. This chronology in parallel with concentrations of Hg and lignin, the latter an unambiguous marker of terrigenous organic matter, were used successfully to describe natural conditions prevailing prior to the late 19th to early 20th century and the changes due to industrial activities (chlor-alkali, pulp and paper mills) that occurred in the first half of the 20th century. In contrast to earlier studies, no significant relationship was found between Hg and lignin in ancient and recent sedimentary intervals contradicting the hypothesis of a particulate lignin-rich carrier-phase controlling the transport and distribution of Hg within the system. Such a correlation between Hg and lignin was only observed in sediments deposited during a discrete period of high Hg contamination (1940–1975). However, the covariation of Hg and lignin in sediments deposited in this period results from simultaneous loadings of these two compounds following production growth of chlor-alkali and pulp and paper industries, respectively, and conservative dispersal of sediments from the Upper Saguenay Fjord down to the Lower St. Lawrence Estuary.

Keywords: Mercury; Lignin; Saguenay Fjord; Lower St. Lawrence Estuary

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1. Introduction

Local industrial inputs and long-range atmospheric transport of mercury (Hg) are the two major processes responsible for the contamination of pristine aquatic ecosystems by this heavy metal (Loring, 1975; Loring and Bewers, 1978; Iverfeldt, 1991; Johansson et al., 1991; Swain et al., 1992; Lucotte et al., 1995). In the case of long-range atmospheric transport, it has been shown that high Hg burdens in sediments from remote natural lakes are directly proportional to the relative size of the drainage basin (Swain et al., 1992; Tremblay et al., 1995). However, this relationship seems to be independent of the nature of catchment soils showing that total inputs of organic matter, directly related to the relative size of the drainage basin, control Hg burdens within lake sediments (Swain et al., 1992; Lucotte et al., 1995; Tremblay et al., 1995). It is well documented that Hg forms stable complexes with organic matter (Wallace, 1982; Wallace et al., 1982; Lindqvist, 1991), and that within soil profiles as well as lake and coastal marine sediments Hg is preferentially associated to organic matter (Smith and Loring, 1981; Schafer et al., 1990; Louchouarn et al., 1993; Dmytriw et al., 1995; Grondin et al., 1995; Lucotte et al., 1995; Tremblay et al., 1995, 1996; Bono, 1997). In light of these observations, it has become common practice to relate the transport and fate of Hg to that of organic matter in diverse aquatic environments (Loring, 1975; Pocklington, 1976; Schafer et al., 1980; Smith and Loring, 1981; Louchouarn et al., 1993; Lucotte et al., 1995; Tremblay et al., 1995; Grondin et al., 1995; Bono, 1997; Quémerais et al., 1997).

Within the Saguenay/St. Lawrence system (Fig. 1), positive correlations between surface sediment concentrations of Hg and lignin-derived materials, a specific kind of particulate terrigenous organic matter, have led to the generally accepted conclusion that scavenging, transport, and sediment distribution of Hg in this system are mainly controlled by lignin (Loring, 1975; Pocklington, 1976; Schafer et al., 1980). Particulate lignin materials are still considered, to this day, a major carrier-phase of Hg in this coastal environment (Gobeil and Cossa, 1993). Mass balance calculations and geochronologies of anthropogenic fluxes of Hg within the Saguenay/St. Lawrence have shown that the high contamination of the system by this heavy metal in the recent past has been directly related to the waste inputs of a chlor-alkali plant active in the upstream region of the Saguenay from 1947 to 1976 (Loring and Bewers, 1978; Barbeau et al., 1981; Smith and Loring, 1981). Significant industrial inputs of ligneous materials have similarly been shown in last decades within the whole system (Pocklington and MacGregor, 1973; Pocklington, 1976; Louchouarn et al., 1996, 1997). However, little is known about the evolution of lignin and Hg concentrations in sediments through recent times.

In this study, we present new data for Hg and lignin concentrations and association in diverse sediments from the system and analyze the evolution of inputs of these two compounds through discrete time intervals which were determined using a Hg-derived 100–200 year chronology. This chronology was further used as an independent measure to reassess ^{210}Pb-derived sedimentation rates estimated for the estuarine system. Mercury and lignin content were thus used successfully to describe natural conditions prevailing in the Saguenay/St–Lawrence system prior to the late 19th to early 20th century and the changes due to industrial activities (pulp and paper mills, chlor-alkali) that occurred during the first half of the 20th century.

2. Methodology

Five undisturbed sediment cores were collected in August 1994, in the Saguenay/St. Lawrence system (stations St-Fulg, Sag05B, Sag15B, G2B, and 23B, Fig. 1) using an Ocean Instrument MarkII box-corer. Gravity cores, covering longer time intervals, were recovered in May of 1995 [stations Sag05(95), C. Étern(95), and 23(95), Fig. 1]. Additional box-core samples collected in 1992 in the Estuary and 1993 in the Gulf of St. Lawrence (stations 22 and G1, respectively. Fig. 1) were made available to us by Drs C. Gobeil (IML) and A. Mucci (McGill University). Box-cores collected at each station were sectioned in

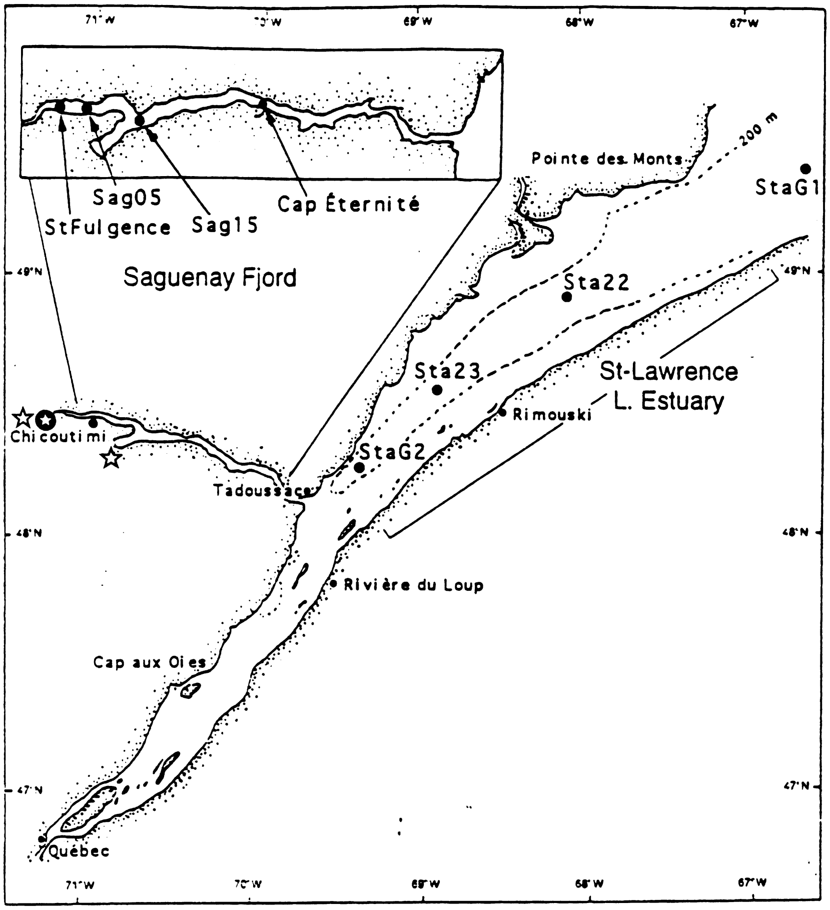

Fig. 1. Saguenay Fjord and St. Lawrence Estuary showing the location of sampling stations (●) as well as industrial installations (chlor-alkali plant: *; Pulp and paper mills: ☆).

0.5 cm thick layers near the sediment–water interface and then thicker layers (1 cm) at progressively wider intervals of 1, 2, and 5 cm along core depth. Gravity cores were subsampled in 1-cm thick layers at 1 cm interval in the top 10 cm and then progressively wider intervals of 2, 3, and 5 cm down to the bottom of the core. Only the top 1 cm section of core G1 (Gulf of St. Lawrence) was analysed and presented here. Sediments were stored frozen until later chemical analyses.

Total Hg and lignin concentrations were determined on freeze-dried sediments and all values were corrected for salt content. Total Hg was analysed by atomic fluorescence after digestion of the sediment samples in a nitric/hydrochloric acid solution for 6 h (Bloom, 1989; Louchouarn et al., 1993). Lignin-derived oxidation products (LOP) were obtained following an alkaline CuO oxidation for 3 h in a closed vessel in absence of oxygen (Goñi and Hedges, 1992; Louchouarn et al., 1997). The retention times and quantification of all eight lignin-derived monomers used in this study were determined by gas chromatography on a non-polar capillary column (DB-1) from their FID responses relative to authentic phenolic standards (Aldrich) and using ethyl vanillin (3-ethoxy, 4-methoxybenzaldehyde) as an internal standard.

3. Results

Sediment profiles of total mercury (Hg) and the sum of all eight lignin-derived monomers ($\Sigma 8$) in the solid phase at all stations are presented in Fig. 2. Surface Hg concentrations vary widely from site to site ranging 100–600 ng/g and ≈ 200 ng/g for the Saguenay Fjord and the Lower Estuary, respectively. The most notable features in sediment concentrations for Hg are the depth

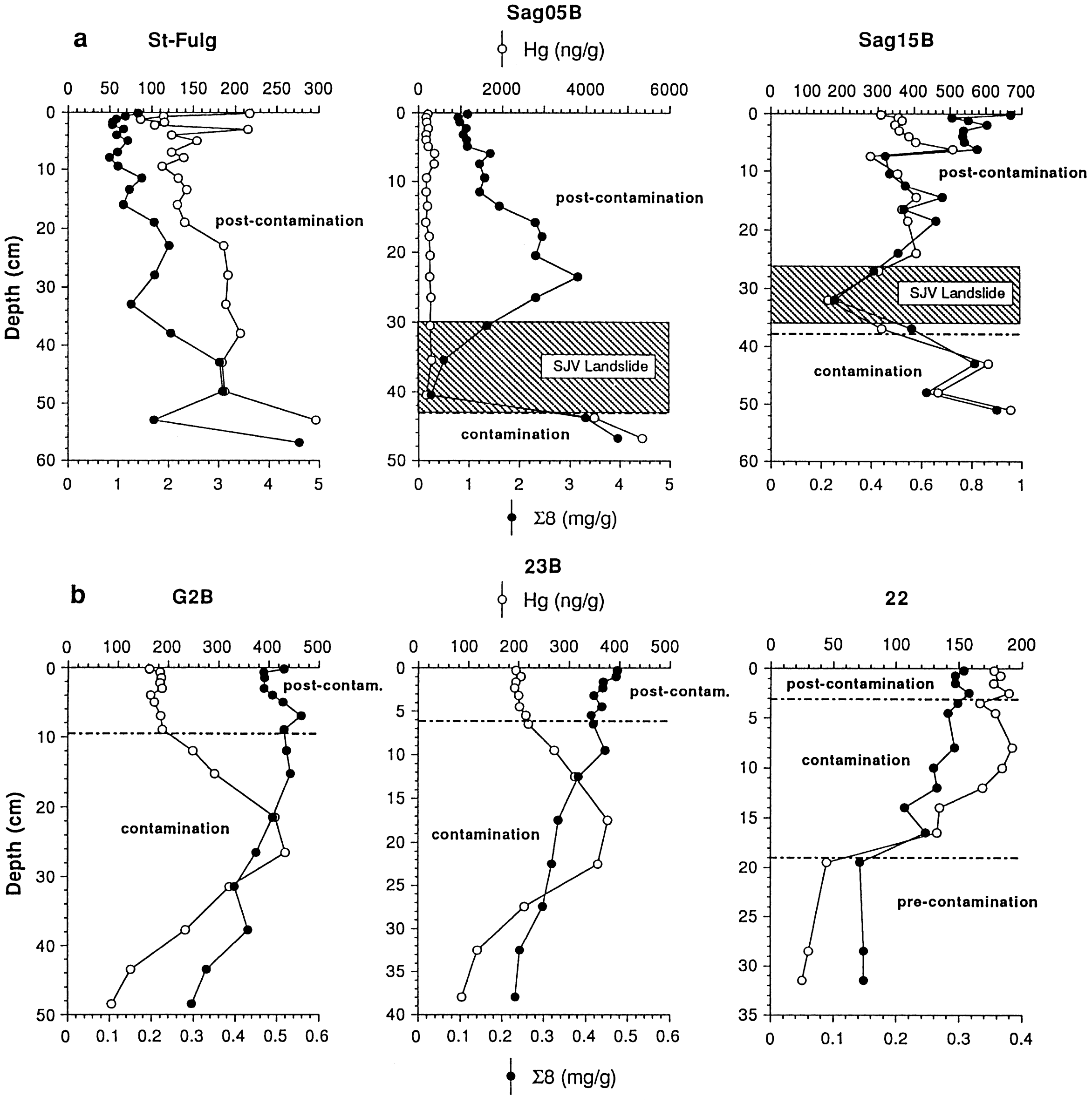

Fig. 2. Vertical profiles of total mercury (Hg: ○, in ng/g dry) and the sum of all eight lignin-derived monomers (Σ8: ●, in mg/g dry) in sediments of (a) the Saguenay Fjord (Aug. 1994); (b) the Lower St. Lawrence Estuary (Aug. 1994); and (c) the Saguenay Fjord and the Lower St. Lawrence Estuary in gravity cores (May 1995). Approximate chronological marks were determined according to the Hg profiles for each core and indicated as: pre-contamination period (prior to ≈ 1940), contamination period (from ≈ 1950 to late 1970s), post-contamination period (≈ 1980 to the present). When observed, the Saint-Jean Vianney landslide layer (SJV, see text) is indicated within cores from upstream Saguenay Fjord locations.

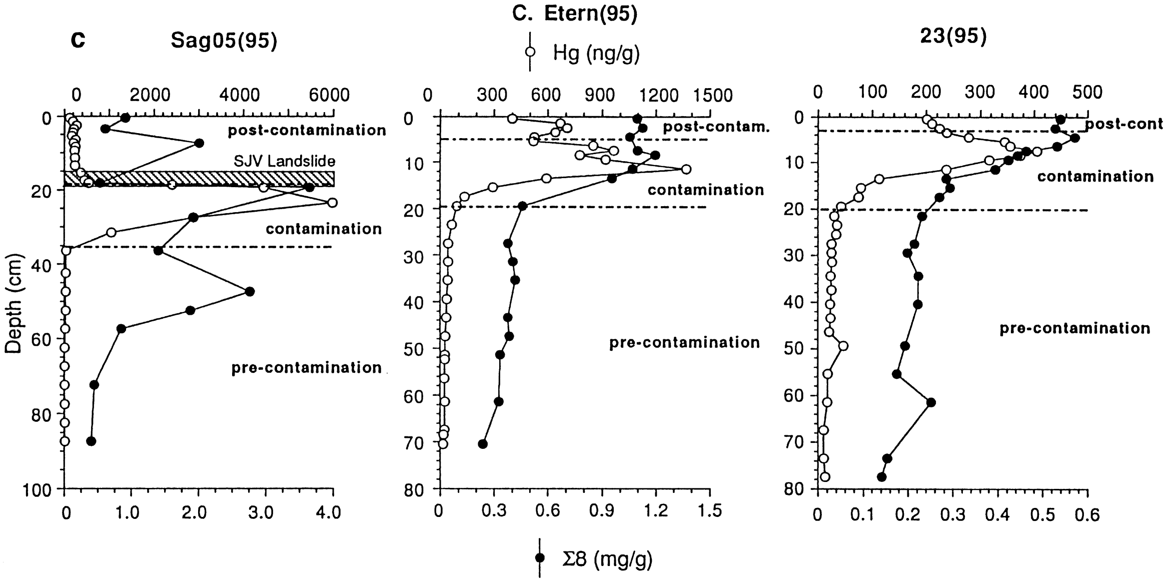

Fig. 2. (*Continued*)

variations attesting to the historical variations of anthropogenic Hg inputs to the Saguenay River from the late-1940s to early-1970s. Subsurface maxima in both the Fjord and the Estuary sediments correspond to the period of maximum Hg discharges from a chlor-alkali plant operating in the Upper Saguenay before abatement of its effluent discharges and complete halt of its activities in the early- to mid-1970s (Barbeau et al., 1981; Smith and Loring, 1981). The Hg peaks in sediments reach highest values in the upstream Saguenay station close to the original industrial point-source (Sag05: ≈ 6000 ng/g; Fig. 2a,b), and decrease in the seaward direction (Cap Éternité: ≈ 1500 ng/g; Fig. 2c), to reach lowest values within the estuarine sediments of the deep Laurentian Trough (450, 400, 200 ng/g for stations G2, 23, and 22, respectively; Fig. 2b,c). Pre-anthropogenic Hg levels are observed only in cores with slow sedimentation rates (i.e. station 22, Silverberg et al., 1986) or within gravity cores which recovered sediments deposited in late-19th to early-20th century [cores Sag05(95), C. Étern(95), and 23(95)]. These levels remain stable at ≈ 25 ± 10 ng/g (Fig. 2b,c), a value which is quite comparable to the constant background value (30 ng/g) proposed by Gobeil and Cossa (1993) for the system. The sediment columns in the Upper Saguenay Fjord stations (Sag05 and Sag15), are further characterized by the presence of an organic-poor clay deposit (SJV: Fig. 2a,c) originating from a major landslide which occurred at St-Jean Vianney in May 1971 (Schafer et al., 1990). This landslide layer is not observed in the St-Fulgence core since rapid sedimentation rates characteristic of the upper parts of the Fjord (≈ 7.0 cm/year; (Smith and Walton, 1980; Perret et al., 1995)) have favored the burial of the slumped layer in deeper sediments.

Organic matter distribution within the Saguenay/St. Lawrence system shows that sediments of the Saguenay Fjord are not only richer in organic materials (organic carbon, C_{org}: 3–5% dry weight) than those from the Lower Estuary (C_{org}: 1–2%; Louchouarn et al., 1997), but also receive highest proportions of terrigenous materials (Pocklington and Leonard, 1979; Louchouarn et al., 1996, 1997). Sediment distributions of lignin oxidation products (LOP), a suite of lignin-derived phenolic biomarkers exclusive to land plants, attest to this difference with surface concentrations within the Fjord (8–10 mg/g; Fig. 2a,c) that are twice those observed within the Lower Estuary (3–5 mg/g; Fig. 2b). Moreover, whereas vertical sediment concentrations of organic matter, including LOP, within the Lower Estuary seem to be controlled by diagenesis (Louchouarn et al., 1997), LOP fluctuations within sediments of the Saguenay Fjord depict, in a large part, input variations through time (Schafer et al., 1980, 1990; Louchouarn et al., 1997). The presence of identifiable wood fibers within discrete core intervals at the head of the Fjord and concomitant high concentrations of organic matter and lignin-derived compounds (Pocklington, 1976; Schafer et al., 1980; Louchouarn et al., 1997) have been related to increased discharges of pulp and paper industries following their expansion during the 1920s–1940s (Schafer et al., 1980). In some organic-rich layers at station Sag05, LOP can reach as high as 30–40 mg/g (Fig. 2c) which represent up to 10–14% of total particulate C_{org} (Louchouarn, 1997; Louchouarn et al., 1997), a proportion similar to that found in pure wood (Goñi and Hedges, 1992). Previous studies have shown that much of the lignin-derived materials within these sedimentary deposits originate from woody residues released from pulp and paper industries and sawmill outfalls (Pocklington and Leonard, 1979; Louchouarn et al., 1996, 1997). The influence of industrial LOP inputs is not limited to these layers, however, since within surface sediments about 70% of LOP in the Lower Estuary and up to 90–100% in the Saguenay Fjord are industrially-derived (Louchouarn, 1997), indicating that recent industrial discharges of LOP to the sediments completely mask natural inputs of ligneous compounds leached from soils of the drainage basin.

4. Discussion

4.1. Reevaluation of sedimentation rates in the Lower St. Lawrence Estuary

In order to reconstruct precisely the historical evolution of Hg and lignin inputs throughout the last decades, we needed to establish a 100–200 year chronology for the sediments of the Saguenay/St. Lawrence system. This has been done for each core using their Hg profiles (Fig. 2) and by applying the known chronology of Hg pollution within this system (Loring and Bewers, 1978; Smith and Loring, 1981; Barbeau et al., 1981). Smith and Loring (1981) and Barbeau et al. (1981) have shown that maximal inputs of Hg occurred in the Fjord around 1962–1966 as a result of increased effluent discharges of this heavy metal, during the 1950s and early '60s, from the chlor-alkali plant operating in Arvida about 24 km upstream of the head of the Saguenay Fjord since 1947. Government implementations on reduction of Hg discharges after 1970, and the final closing of the chlor-alkali plant in 1976, have led to a sharp fall in inputs and concentrations of this element in the sediments (Loring and Bewers, 1978; Barbeau et al., 1981). Since at least 10% of the total industrial load of Hg discharged into the Saguenay have reached the Lower St. Lawrence Estuary (Loring and Bewers, 1978), subsurface Hg maxima within the deep Laurentian Trough sediments (Gobeil and Cossa, 1993; Gagnon et al., 1996) provide chronological marks comparable to those of the Saguenay.

Because Hg shows low diagenetic mobility in the sediments of the Saguenay and the Lower Estuary (Smith and Loring, 1981; Gobeil and Cossa, 1993; Bono, 1997; Gagnon et al., 1997), Hg profiles thus reflect mainly the temporal changes in the rate of supply of this heavy metal to the sediments (Gobeil and Cossa, 1993). Moreover, the good agreement between core dating results obtained from ^{137}Cs and Hg profiles in the Saguenay Fjord (Barbeau et al., 1981), suggest that Hg can be used in a similar fashion to that of the radiogenic Cs isotope for sedimentation rate determination and core dating. Sedimentary Hg profiles were thus used for establishing a chronology of post-1940 sediments from the region. Core dating of earlier intervals (deep sediments) covered by some gravity cores, was extrapolated from post-1940 sedimentation rates (cm/year) since it has been shown that this type of sediment sampling involves a linear shortening which is independent of porosity gradients within the sediments (Lebel et al., 1982). The good agreement between chronologies obtained from both box- and gravity-cores (Fig. 3) attest to the

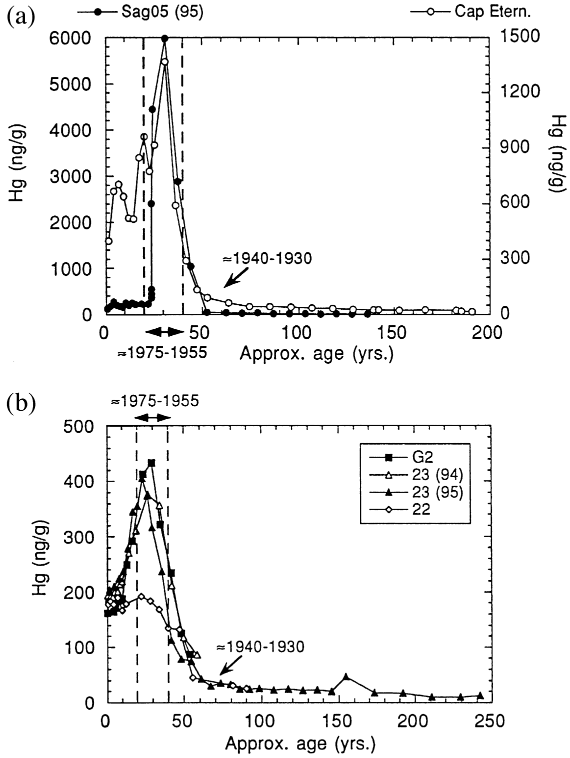

Fig. 3. Sediment dating established using previously reported chronology of industrial Hg inputs to the Saguenay/St. Laurent system (Barbeau et al., 1981; Smith and Loring, 1981). Sediment dating at the head of the Saguenay Fjord (station Sag05) was also estimated using the previously dated St. Jean Vianney landslide layer (1971; Mucci and Edenborn, 1992). See Fig. 1 for geographic location of each station.

appropriateness of this method for assigning approximate dates to the recent sediments of the system.

A recent assessment of sedimentation rates within sediments of the Lower Estuary, using Hg profiles (station 23: ≈ 0.6–0.8 cm/year; Gobeil and Cossa, 1993) showed greater estimates, by up to a factor of two, than those previously estimated from radiogenic ^{210}Pb at the same location (≈ 0.3 cm/year; Silverberg et al., 1986). Gobeil and Cossa (1993) attributed this ‘discrepancy’ to the natural variability associated to bioturbation activities in surface sediments which involved transport and burial of the Hg maximum below the predicted value. However, total Hg profiles at the same station for a core sampled 7 years later (Gagnon et al., 1996), also suggest higher accumulation rates (≈ 0.5–0.6 cm/year).

In this study, the subsurface maximum Hg concentrations at station 23 (≈ 1965–1970; Barbeau et al., 1981; Fig. 2b) yield sedimentation rates (≈ 0.6–0.7 cm/year; Fig. 3b) that fall in the same range as those of Gobeil and Cossa (1993) for a sediment core collected 10 years later. Moreover, the depth at which the ≈ 1940s Hg levels appear (≈ 100 ng/g; Barbeau et al., 1981; Fig. 2b), produce very similar results (≈ 0.7 cm/year), suggesting that sedimentation rates have remained close to constant for the last 50–60 years at this location. Finally, the ‘burial’ rate of (1) the post-contamination stabilization in Hg concentrations (≈ 0.5 cm in 1985; Gobeil and Cossa, 1993, and ≈ 5–6 cm in 1994, Fig. 2b), and (2) the Hg maximum (10–15 cm in 1985; Gobeil and Cossa, 1993, and 15–21 cm in 1994, Fig. 2b) again yield comparable sedimentation rates (0.5–0.6 cm/year). It seems very unlikely that bioturbation activity in these sediments could be responsible for the burial of the Hg profile at such a depth and in such a uniform fashion without major distortion to its shape and absolute quantities. Using the Hg profiles (Fig. 2b), we have estimated the sedimentation rates for the other two estuarine stations. Our estimated values for the upstream station (G2: 0.8–1.0 cm/year) are close to the values derived from ^{210}Pb profiles (≈ 1.6 cm/year; Silverberg et al., 1986) whereas they are slightly higher at the downstream station (22: 0.3 cm/year vs. 0.2 cm/year; Silverberg et al., 1986). Although the sedimentation rates determined here for the Laurentian Trough are within the order of magnitude of those presented in the literature, they might be higher by a factor of 1.5 (station 22) to 2 (station 23) relative to previously published estimates (Silverberg et al., 1986) and seem to have remained close to constant during the last decades.

4.2. Historical reconstruction of contamination events in the Saguenay / St. Lawrence system

A strong correlation has been reported between the distribution of particulate organic matter and

Hg within sediments of the Saguenay/St. Lawrence system (Loring, 1975; Loring and Bewers, 1978; Schafer et al., 1980; Smith and Loring, 1981; Pelletier and Canuel, 1988; Mucci and Edenborn, 1992). Further correlations of this heavy metal with both high C/N ratios and particulate lignin-derived materials (Loring, 1975; Pocklington, 1976; Schafer et al., 1980), have led to the general and accepted conclusion that particulate lignin, a rather refractory vascular plant biopolymer, is the main scavenger and carrier phase of Hg in the Saguenay/St. Lawrence system (Loring, 1975; Pocklington, 1976; Schafer et al., 1980; Smith and Loring, 1981; Schafer et al., 1990; Gobeil and Cossa, 1993). This conclusion has been reached through the analyses of surface sediments along longitudinal transects from upstream sections of the Fjord and into the Estuary seawards (Loring, 1975; Pocklington, 1976). It is thus tempting to investigate, on a first approach, the recent distribution and transport mechanisms of Hg in this system by comparing surface concentrations of this heavy metal and lignin-derived oxidation products in sediments from the head of the Fjord down to the mouth of the Estuary. However, these sediments represent environments with very different sedimentation rates ranging from 2–7 cm year^{-1} in the upper basin of the Fjord (Smith and Walton, 1980; Perret et al., 1995) to a few millimeters per year in the Lower Estuary and about 1 mm year^{-1} in the Gulf of St. Lawrence (Silverberg et al., 1986). Because surface concentrations in these widely different sedimentary environments represent seasonal to decadal inputs of material, they may not be readily comparable.

We have solved this problem by comparing three different time intervals which are all clearly characterized by specific input events. These three periods were identified using the chronology of Hg contamination presented in the previous section (Fig. 3) and representing pre-contamination (prior to ≈ 1940), contamination (from ≈ 1950 to mid-1970s), and post-contamination times (≈ 1980 to the present; Fig. 2). Fig. 2c, which covers the longest sedimentary record (gravity cores) in Hg and lignin concentrations through time, shows that Hg concentrations have remained consistently low, up to the early 20th century (≈ 1930–1940), and increase rapidly to reach maxima in the early 1970s. This rapid increase in concentrations is similarly observed for LOP within sediments of the Fjord's deep basin [station C. Étern(95); Fig. 2c] and in the Lower Estuary [stations 22 and 23(95); Fig. 2b,c]. Deep sediments from the Upper Saguenay Fjord [Sag05(95)], however, show an additional and unique peak in LOP content prior to the 1940s increase recorded in all other cores (Fig. 2c). An early peak in lignin-derived materials and total organic matter in upstream Fjord sediments has previously been reported by Schafer et al. (1990) who observed an increase in these compounds within one year of the introduction of the first large pulp machines to the pulp mills at Kenogami and Alma (Saguenay River) in the early 1920s. The bankruptcy of these pulp mills during the recession years of the 1930s was followed by severe production abatements and associated declines in anthropogenic organic matter concentrations within sediments of the Upper Saguenay Fjord (Schafer et al., 1990). In the mid-1940s, a renewed expansion and wide-range industrialization of the forest and pulping industry led again to increased inputs of organic materials to the whole Fjord/Lower Estuary system and are responsible for the recorded increasing concentrations in lignin-derived compounds within sediments of the whole systems (Smith and Loring, 1981; Schafer et al., 1990; Louchouarn, 1997; Louchouarn et al., 1997). However, the coincidental increase of Hg and LOP does not necessarily mean they are linked through a causal relationship such as a chemical or physical bond.

The division of Hg vs. lignin-derived compounds into the three above-mentioned periods is presented in Fig. 4. This figure, shows that during the pre- and post-contamination period these two compounds behave quite distinctly throughout the system. In contrast to earlier conclusions cited in the literature (Loring, 1975; Schafer et al., 1980; Pelletier and Canuel, 1988), the lack of significant correlation between Hg and lignin during these two time intervals ($r^2 = 0.07$ and $r^2 = 0$, respectively) suggests that the transport of Hg and LOP to the sediments are not necessarily related. The

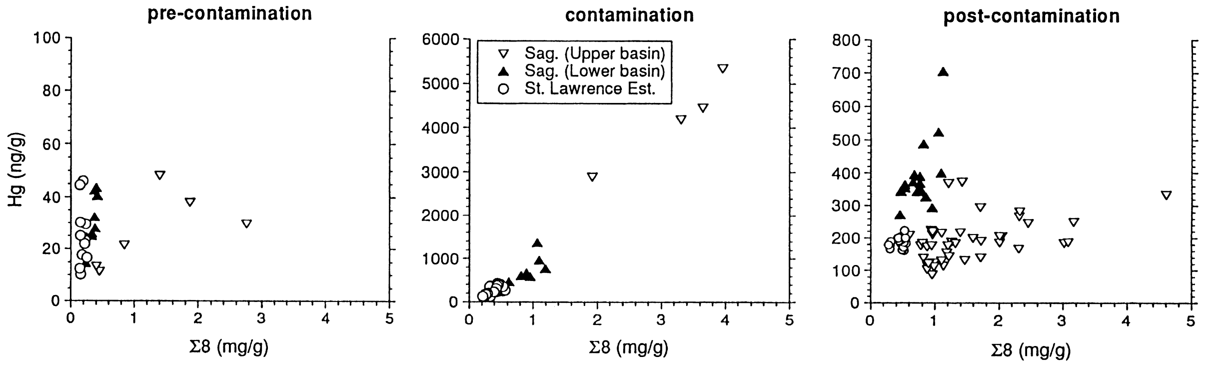

Fig. 4. Relationships between total mercury (Hg) and lignin oxidation products (Σ8) in sediments of the Saguenay Fjord (▽: Upper basin; ▲: Lower basin) and the Lower St. Lawrence Estuary (○) during specific time-intervals: pre-contamination period (prior to ≈ 1940); contamination period (from ≈ 1950 to late 1970s); and post-contamination period (≈ 1980 to the present).

pre-1940 local inputs of industrially-derived organic matter may in part be responsible for the significant gradient in LOP concentrations observed from the upper reaches of the Fjord (≈ 2.800 mg/g) to the Lower Estuary (≈ 0.150–0.200 mg/g; Fig. 3a). However, despite the introduction of large quantities of anthropogenic lignin materials to the upstream region of the Fjord, Hg concentrations do not increase concomitantly and remain close to the background value (≈ 25 ± 10 ng/g; Fig. 3a) throughout the whole system.

During the late 1940s and early 1950s, increased production of sodium hydroxide from the chlor-alkali plant and paper products from the pulp and paper mills, led to a concomitant high loading of Hg and lignin-rich materials to the aquatic system (Loring and Bewers, 1978; Smith and Walton, 1980; Schafer et al., 1980; Barbeau et al., 1981; Schafer et al., 1990; Louchouarn et al., 1997). This simultaneous large scale contamination is illustrated by rapid increases in concentrations of Hg and lignin-derived material in sediments of the whole system (Fig. 2c) reaching extremely high levels (Hg > 5000 ng/g and lignin > 4 mg/g) in sediments of the Upper Saguenay Fjord (Fig. 4). These gradients in Hg and lignin concentrations in sediments deposited during the contamination period (≈ 1950s to late 1970s), produce a very strong correlation between Hg and LOP ($r^2 = 0.98$; Fig. 4) similar to the one found by Loring (1975) in surface sediments collected from 1961 to 1974. However, one can see from Fig. 4 that both these parameters are equally correlated to distance away from the mouth of the Saguenay River suggesting that a conservative dilution could equally be responsible for the observed Hg and lignin distributions. One could argue that anthropogenic lignin material selectively scavenged Hg as it discharged simultaneously from the mouth of the Saguenay River and deposited rapidly in the Fjord's delta. However, the distinct evolution of these two sources of contaminants in the late 1970s to early 1980s (significant decline in Hg inputs whereas lignin inputs have not abated; Fig. 2b,c) shows that while this association between Hg and lignin is possible during the contamination period, it is not apparent in recent sediments. In fact particulate lignin materials, mostly present in wood fiber residues derived from pulping processes, may not be the most reactive organic materials to favor chemical or physical adsorption of Hg. Because LOP found in the Fjord/Estuary system are derived almost exclusively from anthropogenic industrial inputs (up to 80–90% of sedimentary lignin in the water column and sediments of the Lower Estuary as far downstream as station 22; Louchouarn, 1997; Louchouarn et al., 1997), this material masks almost completely more mature humified lignin material leached from soil organic matter and which may act as a significant carrier phase for Hg. A similar lack of correlation between Hg and 3,5-dihydroxybenzoic acid, a marker of soil particulate organic matter (Prahl et al., 1994; Louchouarn, 1997), in all three periods ($r^2 = 0.1–0.2$, unpublished data) further indicates that Hg is not carried in the system by either anthropogenic or soil-derived particulate organic matter. The covariation of Hg and lignin in sediments deposited during the 1940s to 1970s might just be fortuitous. Most probably it indicates two simultaneous contamination events and the conservative dispersal of sediments from the Upper Saguenay Fjord to the Lower St. Lawrence Estuary.

However, despite this lack of significant association between Hg and particulate lignin-derived components and other refractory soils components, a recent study (Bono, 1997) indicates that most (typically 50–85%) of the Hg found in the Saguenay Fjord and Lower Estuary sediments is associated with organic matter extractable by a dilute cold NaOH solution. Extraction of sediment samples with dilute NaOH solution is known to remove easily soluble, usually labile organic matter leaving more recalcitrant insoluble components, such as lignin, in the solid-phase (Opsahl and Benner, 1993). Indeed, Bono (1997) has extracted up to 76% of the total organic matter with this technique leaving behind, in the solid-phase, more recalcitrant organic materials. Because LOP-associated C_{org} contributes from 5–15% of total particulate organic carbon within recent sediments of the Saguenay Fjord and up to 20–30% in older organic-rich contaminated layers (Louchouarn, 1997; Louchouarn et al., 1997), the proportion of insoluble organic materials (25–30%) proposed by Bono (1997) is rather consistent with our lignin data. Therefore, the predominant association of Hg with a reactive, easily soluble organic phase seems more coherent than that proposed between Hg and recalcitrant lignin-derived materials. These results are consistent with earlier works in temperate coastal waters which suggest that the organic ligands responsible for the binding of Hg are not represented by humic material isolated from seawater (Mantoura and Riley, 1975) but may instead be of a labile mainly colloidal non-humic nature (Wallace, 1982; Wallace et al., 1982). A recent work has indeed shown a positive association between Hg and dissolved organic carbon but only a weak association between Hg and particulate organic matter in suspension within the St. Lawrence River (Quémerais et al., 1997). Although the distribution and partition of Hg in the water and sediments of the St. Lawrence system seem to be related to those of the organic matter, the question still remains as to the type and quality of organic ligands that bind Hg. These, however, are not among the recalcitrant particulate materials which comprise lignins.

5. Conclusions

Total Hg analyses in multiple cores from the Saguenay/St. Lawrence system show that the preindustrial level of Hg in these sediments is rather uniform for the region and averages ≈ 25 ng/g. The present anthropogenic sediment enrichment factors for this heavy metal range from 5–30 in the Saguenay Fjord and 6–8 in the Lower St. Lawrence Estuary. This level of contamination is, however, lower than what can be observed from sediments deposited during 1940–1975 in which surface enrichment factors reach as high as ≈ 200 in the Fjord and ≈ 20 in the Estuary.

While it has been demonstrated that this heavy pollution of Hg is almost entirely due to the activity of the chlor-alkali plant in the Upper Saguenay, it has been assumed that Hg distribution in these sediments was dependent upon a terrigenous organic matter carrier phase, namely lignin (Loring, 1975; Pocklington, 1976). However, pre- or post-contamination sedimentary intervals presented in this study do not show a significant relationship between these two compounds. The strong correlation between Hg and lignin in sediments deposited during the contamination period (1940–1975) can be explained by a simultaneous increase in production in both the chlor-alkali and pulp and paper industries in the Saguenay drainage basin in the early 40s and 50s contributing to an increased load in lignin material as well as Hg to the system. The lack of significant correlation between Hg and lignin does not, however, dismiss Hg-organic associations, but these probably reside in reactive easily soluble pools of organics rather than within refractory materials comprising lignins.

The increases in Hg and lignin in the mid-20th century illustrate the rapid impact and consequences of post-World War II expansion of industrial activities in the region. Although we observed a significant drop in Hg inputs following the closing of the plant in 1976, the return to pre-anthropogenic concentrations in the system seems to be hampered by still significant inputs of this heavy metal from more diffusive sources via the atmosphere and industrial effluents (Loring and Bewers, 1978; Gobeil and Cossa, 1993). On the other hand, lignin inputs have remained high in the whole system since the expansion of the pulp and paper industry in the Saguenay/St. Lawrence drainage basins. Nevertheless, due to its high rates of sedimentation (2–7 cm/year; Smith and Walton, 1980; Perret et al., 1995), the Upper Saguenay Fjord does show some signs of recovery through lower LOP concentrations and changes of signature towards those of natural soil materials since compliance, by the paper industry in the late 1980s to early 1990s, to government regulations on effluent discharges (Louchouarn, 1997; Louchouarn et al., 1997). Because of much less dynamic sedimentary fluxes in the Lower Fjord basin and St. Lawrence Estuary (Smith and Walton, 1980; Silverberg et al., 1986; Perret et al., 1995), it is doubtful that on a short time-scale, any significant change will be observed in sedimentary concentrations of anthropogenic lignin.

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