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# Mercury transfer from watersheds to aquatic environments following the erosion of agrarian soils: A molecular biomarker approach

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Caron, S., Lucotte, M. and Teisserenc, R. 2008. **Mercury transfer from watersheds to aquatic environments following the erosion of agrarian soils: A molecular biomarker approach.** *Can. J. Soil Sci.* **88**: 801–811. Lake St. Pierre, an important freshwater location for sports and commercial fisheries in Canada, is composed of a 120 km<sup>2</sup> stretch of the St. Lawrence River, located at the center of the St. Lawrence Lowlands. Receiving its waters from the St. François, Yamaska, Ottawa, and St. Lawrence Rivers, it is subjected to important inputs of mercury (Hg) and suspended particles eroded from its watershed. This study aims at tracing back the origin of terrigenous Hg loadings to Lake St. Pierre. The specific phenol signatures yielded by a mild oxidation of the terrestrial organic matter (TOM) carried in the water column was used as a tracer to identify the different sources of terrigenous Hg to the lake. Our results demonstrate that most of the Hg bound to suspended particulate matter (SPM-bound Hg) found in Lake St. Pierre is associated with TOM. We were also able to distinguish the relative influence that forested soils, mainly drained by the Ottawa River, and agrarian soils, located on nearby watersheds, exert on the lake's Hg burden. Our data strongly suggest that the erosion of vast areas of agrarian soils, drained by the Yamaska and St. François rivers to Lake St. Pierre, greatly facilitates the transfer of Hg from the watersheds to the lake. This study stresses the need to improve the management of agrarian soils and protect them from extensive erosion in order to preserve the integrity of the fish resources harvested in Lake St. Pierre.

**Key words:** Mercury, soil erosion, Lake St. Pierre, lignin biomarkers

Caron, S., Lucotte, M. et Teisserenc, R. 2008. **Transfert du mercure des bassins versants vers les milieux aquatiques suite à l'érosion de sols agricoles: une approche par biomarqueurs moléculaires.** *Can. J. Soil Sci.* **88**: 801–811. Le lac Saint-Pierre, un site important pour la pêche commerciale et sportive au Canada, est un élargissement du fleuve Saint-Laurent de 120 kilomètres carrés au cœur des basses-terres du Saint-Laurent. Outre le fleuve, le lac Saint-Pierre est alimenté par les rivières Saint-François, Yamaska et des Outaouais. Il reçoit une quantité importante de mercure (Hg) et de particules en suspension provenant de l'érosion de son bassin versant. L'objectif de cette étude est de retracer l'origine des apports de Hg terrigène dans le lac. Les signatures phénoliques spécifiques de la matière organique terrigène (MOT), obtenues après une oxydation alcaline par l'oxyde de cuivre, ont été utilisées comme traceurs des différentes sources de Hg terrigène retrouvées dans la colonne d'eau. Nos résultats démontrent que la plus grande partie du Hg liée à la matière particulaire en suspension (MPS) retrouvée dans le lac Saint-Pierre est associée à la MOT. Nous avons également mis en évidence l'influence relative que les sols forestiers, essentiellement drainés par la rivière des Outaouais, et les sols agricoles, présents dans les bassins versants voisins, exercent sur la quantité de Hg apporté dans le lac. Les résultats obtenus suggèrent fortement que l'érosion des sols des grandes zones agricoles, drainés par les rivières Yamaska et Saint-François vers le lac Saint-Pierre, facilite grandement le transfert de Hg depuis les bassins versants vers le lac. Cette étude met en évidence la nécessité d'améliorer la gestion des sols agricoles et l'importance de les protéger de l'érosion extensive dans le but de préserver l'intégrité des ressources halieutiques exploitées dans le lac Saint-Pierre.

**Mots clés:** Mercure, érosion des sols, lac Saint-Pierre, Biomarqueurs de la lignine

The removal of the vegetation cover of soils following intensive agricultural practices exerts significant impacts on both terrestrial and aquatic environments. Mono-culture practices and excessive soil reworking weaken soil aggregates, which become vulnerable to lixiviation and wind erosion. Worldwide, as much as 10<sup>6</sup> ha of arable soils disappear each year following erosion (Mathieu 2001). In the province of Québec (Canada),

the agricultural lands are located for the most part along the shore of the St. Lawrence River and its main tributaries, and are characterized by a scarcity of trees on the shorelines. The area impacted by corn mono-culture covered 350 000 ha in 1997. Most of these lands are located in the St. Lawrence Lowlands, between

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**Abbreviations:** TOM, terrestrial organic matter; LB, lignin biomarkers; SPM, suspended particulate matter; C, Cinnamyls; S, Syringyls; V, Vanillyls; λ, lambda indicator

Montréal and Québec City (Pedneault 1997). Midway between these two urban centers lies an important stretch of the St. Lawrence River called Lake St. Pierre. This ecosystem sustains extensive commercial and sports fisheries.

Mercury (Hg) is naturally present in soils. In the St. Lawrence Lowlands, the background Hg levels range around 0.2 ppm (MDDEP 2006). Human activities such as metal extraction and the combustion of fossil fuels have greatly contributed to the global atmospheric Hg burden since the beginning of the industrial era (Fitzgerald et al. 1998). Mercury is usually readily volatilized and can be transported over long distances in the atmosphere. It can be deposited on soils, vegetation and lakes through dry and wet precipitation (Lucotte et al. 1995; Engstrom and Swain 1997; Munthe et al. 2007). More than 90% of the continental deposition of Hg occurs on soils (Lindqvist et al. 1991; Fitzgerald 1995). Once it enters the soils, Hg binds to terrestrial organic matter (TOM) (Louchouart et al. 1993; Lucotte et al. 1995). These Hg-TOM complexes can then be transported from watersheds to lakes through surface runoff or lixiviation of deeper soil horizons (Mierle and Ingram 1991; Meili 1997; Wiener et al. 2006; Pickhardt and Fisher 2007). The TOM thus represents an important transportation vector for the Hg contained in soils to lakes and rivers.

Although TOM is ubiquitous in aquatic environments, its nature remains poorly described. This is partly a consequence of the low concentrations and high heterogeneity of TOM in the water column, and its mixing with the autochthonous organic matter (algae, aquatic plants, etc.) produced in lakes and rivers. Moreover, TOM is subjected to different degrees of degradation once it has reached aquatic environments, which complicates its identification through conventional methods such as isotopic signature, which fails to differentiate between the allochthonous vs. terrigenous origins of the OM found in the water column (Fry 1991; Kendall et al. 2001).

Lignin, made up of polymer macromolecules that bind the fibrous tissues of plants, is rather refractory to degradation (Hedges and Mann 1979) and is unambiguously from terrigenous origins. It can be used to trace back the proportion of TOM present in lakes. A mild oxidation of lignin using cupric oxide under controlled laboratory conditions yields a series of phenol compounds, called here lignin biomarkers (LB), that can become powerful tools to study the TOM dynamics (Hedges and Mann 1979; Houel et al. 2006). The quantification of the relative proportion of the different types of phenols yielded by the mild oxidation – using coupled gas chromatography-mass spectrometry – enables us to identify the origin and state of degradation of TOM (Hedges and Mann 1979; Goñi and Hedges 1992; Goñi and Montgomery 2000; Houel 2003). Teisserenc et al. (2008) proposed that LB can be used to distinguish between the different types of soils present on the

watersheds of lakes. This approach will be used here to distinguish between the exports of Hg-TOM complexes to Lake St. Pierre from forested vs. agricultural soils.

This study follows a previous estimate from Caron and Lucotte (2008) of the seasonal variations marking inputs of Hg into Lake St. Pierre. We will first characterize the imports of TOM coming to Lake St. Pierre from the Yamaska, St. François and St. Lawrence Rivers, and then relate them with the Hg loadings from these three different sources.

## METHODS

### Pedology of the St. Lawrence Lowlands

Lake St. Pierre (lat. 46°11'33"N, long. 72°51'02"W) is composed of a 120-km<sup>2</sup> stretch of the St. Lawrence River, located at the center of the St. Lawrence Lowlands (Fig. 1). The geology of the Lowlands is characterized by glacial and marine deposits covering a sequence of Ordovician sandstones and shales. The area is enclosed by the Canadian Shield to the North and the Orogenic Appalachian Belt to the South (Landry and Mercier 1992). The soils of the Lowlands are mainly composed of podzols with local influences, such as drainage efficiency, leading to the local formation of peatlands or clayey podzols (Landry and Mercier 1992). The agrarian soils are generally composed of homogeneous silty brownish sands, with compaction increasing with depth. We could not distinguish any distinct horizons in agrarian soil profiles. The forested soils are mainly podzols with an organic horizon of about 10 cm thickness overlying an Ae horizon of about 10 cm thickness. The mineral horizons of these soils are composed of fine to medium grain brownish sands enriched with OM.

### Sampling Sites, Sample Collection and Treatment

#### Soil Samples

Soils from the watersheds of the St. François and Yamaska Rivers were collected for the purpose of this study. Typical soil samples from mature forests and agrarian soils were collected on the two watersheds. The location and characteristics of the soil sampling sites are presented in Fig. 1 and Table 1, along with the different types of vegetation coverage we could observe. Spatial distribution of samples has been based on land use maps and samples have been taken in the two major land uses of the region, i.e., agrarian lands (generally maize fields) and forested lands. The eight soil cores, two per sampling stations, were retrieved by driving a 15-cm-diameter PVC corer to a depth varying between 24 and 40 cm, depending on the soil compaction level. Sub-samples were then cut into 1-cm layers with a Teflon<sup>®</sup> spatula and frozen in Ziploc<sup>®</sup> bags. Back in the laboratory, they were then freeze-dried, crushed using a percussion grinder and homogenized prior to analyses.

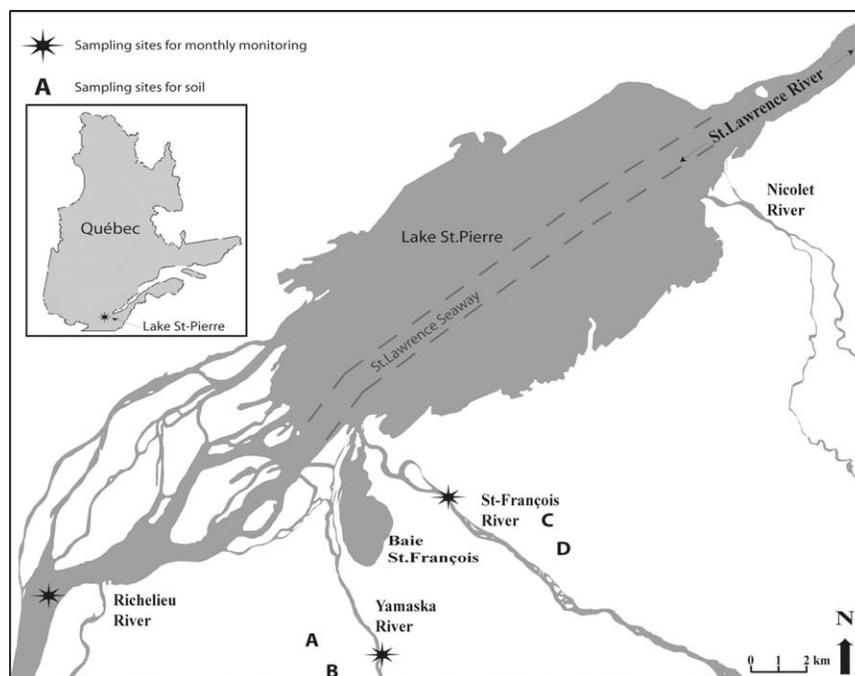


Fig. 1. Location of the sampling sites.

### Suspended Particulate Matter

In order to estimate the seasonal aquatic inputs of Hg into Lake St. Pierre, three major entry points for Hg (St. Lawrence River, Yamaska and St. François rivers) were selected for a monitoring program of the suspended particulate matter (SPM) found in the water column (Fig. 1). The sampling program lasted 2 yr (from April 2002 to April 2004) and sampling was realized on a monthly basis whenever possible. For the St. Lawrence River, the results comprise SPM values from two sampling stations, located in each of the two parallel water masses that can be distinguished in the river: The Northern (brownish waters from the Ottawa River) and the Southern (greenish waters from the Great Lakes) waters (Rondeau 1993).

Water for determination of SPM-bound Hg was sampled in one or two 50-L Nalgene<sup>®</sup> carboys, using an electric pump equipped with a 210- $\mu$ m filter followed by a 64- $\mu$ m filter. The pre-filtered water was then treated

by tangential flow ultra-filtration system using a Pelli-con filter system by Millipore<sup>®</sup> with a Durapore membrane of 0.45  $\mu$ m. The particles from 0.45 to 64  $\mu$ m making up the SPM were collected and concentrated down to a volume of 1 L. The ultra-filtered water was then transferred to four 250-mL Nalgene<sup>®</sup> bottles and frozen until analysis.

### Laboratory Analyses

Determination of mercury concentrations in SPM was performed using atomic fluorescence spectrophotometry. A detailed description of the analysis procedure is presented in Pichet et al. (1999).

The protocol we used for the production of phenol derivatives from ligneous TOM following the mild cupric oxide oxidation was first developed by Hedges and Ertel (1982), and adapted by Goñi and Montgomery (2000). Briefly, sediment samples were weighed to include 2–5 mg of organic carbon in the Teflon-lined

Table 1. Description of the soil sampling sites

Sample name	Location (lat/long)	Watershed	Vegetation coverage
A	45°59'06"N 72°54'32"W	Yamaska River	Corn crop
B	45°58'26"N 72°54'57"W	Yamaska River	Coniferous forest
C	46°03'52"N 72°46'45"W	St-François River	Corn crop
D	46°03'52"N 72°46'47"W	St-François River	Maple grove with patches of white birch and white pine

vessels of an analytical microwave oven (CEM MDS 200). Samples were digested with CuO in the absence of oxygen at 1508°C for 90 min. The quantification of oxidation sub-products was performed using a coupled gas chromatograph (VARIAN 3800) mass spectrometer (VARIAN Saturn 2000). Replicate analyses of two "standard" sediment samples ( $n=2-11$ ) showed that the analytical variability of the major CuO-oxidation products and related parameters ranged from 2 to 19% and averaged  $10\% \pm 7\%$ . We proceeded to the determinations of a series specific phenols grouped into three distinct categories: Cinnamyls (C), Syringyls (S) and Vanillyls (V). Phenols of the C, S and V families are solely derived from the oxidation of TOM produced by vascular terrestrial plants (Hedges and Ertel 1982). The Lambda indicator ( $\lambda$ ) used here refers to the sum of C, S and V compounds produced by the oxidation of 100 mg organic carbon. This indicator represents the relative proportion of TOM collected in the samples.

The relative proportion of C, S and V phenols yielded by the mild oxidation also informs us about the different types of vascular plants at the origin of the TOM (angiosperm vs. gymnosperm; woody vs. non-woody) (Hedges and Mann 1979; Ertel and Hedges 1985; Goñi and Hedges 1995; Opsahl and Benner 1995; Louchouart et al. 1997, 1999). For example, phenols from the S family are solely derived from lignin produced by angiosperms, those of the C family are derived from non-woody tissues, while phenols of the V family are derived from all types of vascular plants (Hedges and Mann 1979; Opsahl and Benner 1995).

The relative abundance of C, S and V molecules also brings other information on the origin of the TOM. While gymnosperms solely produce V derivatives, angiosperms can yield both S and V phenols (Hedges and Mann 1979). Therefore, an elevated S:V ratio is characteristic of vegetation dominated by angiosperms. The C:V ratios are rather used to distinguish between woody vs. non-woody vegetal compounds, since C phenols are only yielded by non-woody plant tissues (Hedges and Mann 1979). Such information between the abundance and ratios of phenol compounds yielded by the oxidation of OM has increasingly been used to trace the occurrence and origins of TOM in sediments (Louchouart et al. 1997, 1999; Farella et al. 2001; Houel 2003), SPM (Montgomery 2000; Farella et al. 2001) and dissolved organic carbon (Ertel and Hedges 1984; Ertel et al. 1986).

### Calculation of Mercury and Lambda Fluxes to Lake St. Pierre

The fluxes of Hg and  $\lambda$  entering Lake St. Pierre carried by the SPM from the Yamaska, St. François and St. Lawrence rivers were calculated using the Hg and  $\lambda$  contents of SPM measured on a monthly basis between August 2002 and April 2004, and water discharge values

provided by governmental agencies. The discharge values for the Yamaska River (hydrometric station #30345 – daily measurements) and St. François River (hydrometric station #30208 – daily measurements) were provided by the Québec Ministry of the Environment, while the discharge values for the St. Lawrence River were retrieved from the *Cornwall Report – Environment Canada* – monthly measurements.

### Statistical Analyses

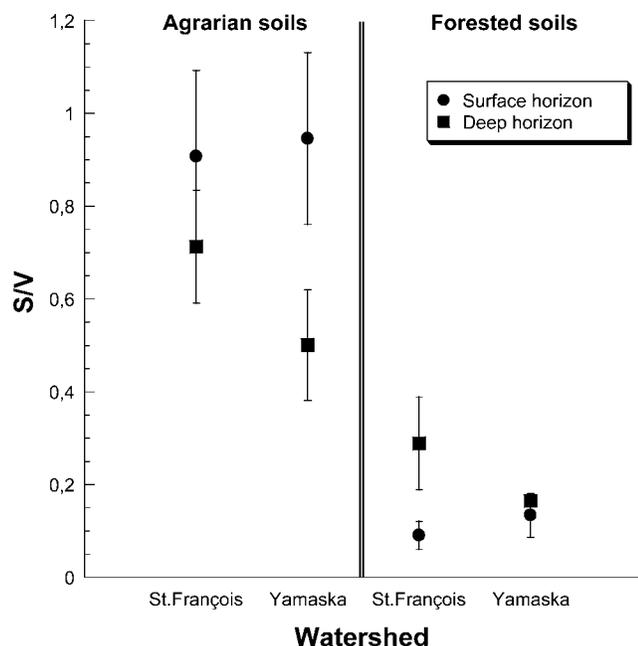
The statistical treatments of our data were performed using the Statistical Analysis Software (SAS Institute, Inc. 2003). Statistical tests were applied to distinguish between the LB contents of the different types of soils (agrarian vs. forested), and between the surface vs. deeper soil horizons. The values for LB in the soil cores used for calculations were segregated according to the following criteria: (1) The samples from forested soils were split into two groups according to the carbon contents of the different horizons. The surface (organic) horizon corresponds to organic carbon content greater than 25% and the deep (mineral) horizon corresponds to organic carbon content inferior to 25%. (2) The samples from agrarian soils were also split into two groups. The first 15 cm of agrarian soils are usually perturbed by plowing. Therefore this depth was selected to discriminate between the surface and the deep horizons.

For each horizon (surface vs. deep) of the soil cores, the specific distributions of S:V or C:V ratios vs. depth were modeled: (1) If the relationship between the indicator vs. depth in the horizon group was best described using a polynomial or a linear model, this model was used to estimate the ratios at mid-depth with 95% confidence interval; (2) if there was no significant polynomial, or linear, relationship between the ratios vs. depth, the mean of all ratio values for the soil horizon group was used (and 95% CI). When 95% confidence interval error bars were not overlapping, there was a significant difference between soils or horizons. Between 4 and 20 ratios, according to the depth of the horizon groups, were used for calculations. The statistical treatment of our data was performed using the JMP Software (SAS Institute, Inc. 2003).

## RESULTS

### Lignin Biomarkers in Soils

The modeled S:V ratios were significantly higher ( $P < 0.05$ ) in the agrarian soils than in the forested soils, except for the deep soil horizons from the Yamaska River watershed (Fig. 2). For the agrarian soils, the S:V ratios range between 0.38 and 1.13, whereas for the forested soils, the ratios range between 0.19 and 0.40. The S:V ratios in these soils are higher in the reworked surface horizons than in the deeper horizons. However the difference between the ratios of surface and deeper

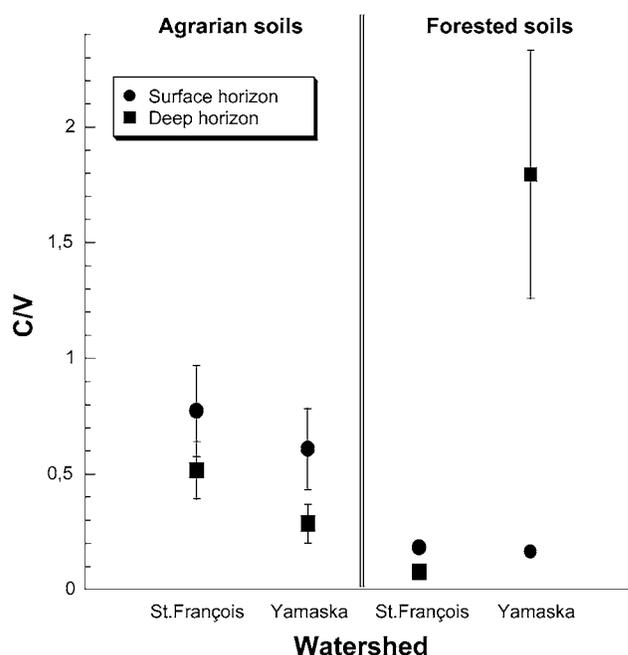


**Fig. 2.** Ratio between S:V ratios in agrarian and forested soils of the St. François and Yamaska Rivers watersheds. For the agrarian soils, the surface horizon corresponds to depths between 0 and 15 cm and the deep horizon corresponds to depths of >15 cm; for forested soils, the surface horizon corresponds to the organic layer of soils and the deep horizon corresponds to the inorganic layers.

horizons in the Yamaska River watershed are not statistically different.

On the contrary, the S:V ratios in the surface organic horizons of forested soils are lower than in the deeper mineral horizon. The difference between S:V values for organic and inorganic horizons is not statistically different for the St. François River watershed. For the Yamaska River watershed, both the S:V and C:V ratios of the reworked surface horizon are statistically higher ( $P < 0.05$ ) than those of the deeper horizon.

The C:V ratios for the two watersheds are significantly higher in agrarian soils than in forested soils ( $P < 0.05$ ) (Fig. 3). The C:V ratios in agrarian soils range between 0.43 and 0.97, whereas they range between 0.05 and 0.19 in the forested soils. In the agrarian soils, the difference between C:V ratios in the reworked surface horizon is statistically different ( $p < 0.05$ ) from those found in deeper horizons only for the Yamaska River watershed. This difference between surface and deeper horizons is statistically significant for both watersheds in the case of forested soils ( $P < 0.05$ ). However, the C:V ratio in the deeper inorganic horizon of the forested soils of the Yamaska River watershed is considerably higher than the one found in the surface organic horizon (1.80).



**Fig. 3.** Ratio between C:V ratios in agrarian and forested soils of the St. François and Yamaska Rivers watersheds. For the agrarian soils, the surface horizon corresponds to depths between 0 and 15 cm and the deep horizon corresponds to depths of >15 cm; for forested soils, the surface horizon corresponds to the organic layer of soils and the deep horizon corresponds to the inorganic layers.

### Relationship Between the TOM Molecular Signature of SPM and that of Soils

It is possible to trace back the origin of TOM by relating the S:V vs. C:V signatures of soils, SPM and that of the dominant crop growing in the watershed, in this case corn, the latter being considered as the end-member signature on Figs. 4–7.

The S:V vs. C:V ratios were determined in the different parts of corn plants and appear to decrease from the leaves to the stems to the roots, reflecting their different vegetal structures. The S:V vs. C:V ratios in reworked horizons of agrarian soils range close to those of corn stems and roots in the dilution diagrams presented in Figs. 4–7. The deep horizons of agrarian soils show S:V vs. C:V values lower than surface horizons. The S:V vs. C:V values for all the agrarian soils we sampled fall between, to the lower left of the diagrams, the S:V vs. C:V values for SPM of the studied river draining the soils, and, to the higher right of the diagrams, the S:V vs. C:V endpoint values of corn. In the case of the St. Lawrence River South and the Yamaska River diagrams, the S:V vs. C:V values for forested soils are isolated from the other points in the lower part of the diagrams with lower S:V ratios.

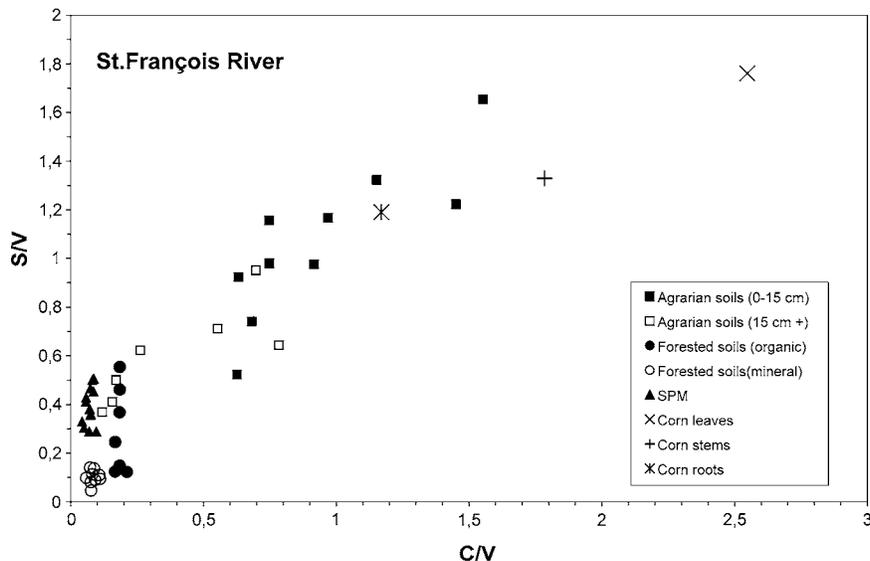


Fig. 4. Relationship between S:V and C:V ratios in soils and SPM; St. François River; the end-point signal corresponding to corn plants are marked by an (X) for leaves, a (+) for stems and a (X) for roots.

**Relationship Between Mercury Inputs and Lambda Inputs**

Fig. 8 presents the relationship between SPM-Hg and SPM-λ fluxes for the different tributaries of Lake St. Pierre. There is a strong relationship between SPM-Hg and SPM-λ fluxes entering Lake St. Pierre from the Yamaska ( $r^2=0.86$ ) and St. François ( $r^2=0.95$ ) rivers as well as from the northern section of the St. Lawrence River brownish waters from the Ottawa River ( $r^2=0.76$ ). This relationship is weaker in the waters flowing

from the Great Lakes and entering Lake St. Pierre through the southern part of the St. Lawrence River ( $r^2=0.47$ ).

**DISCUSSION**

**Lignin Biomarkers in Soils**

The S:V and C:V ratios enable us to clearly distinguish between TOM originating from agrarian vs. forested soils. These two ratios are significantly higher in agrarian soils than in forested soils, with the exception

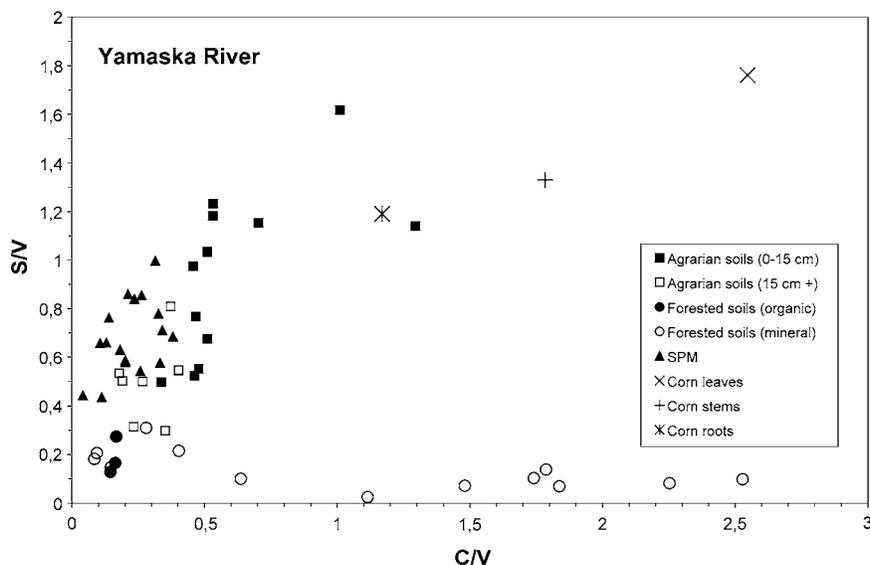


Fig. 5. Relationship between S:V and C:V ratios in soils and SPM; Yamaska River; the end-point signal corresponding to corn plants are marked by an (X) for leaves, a (+) for stems and a (X) for roots.

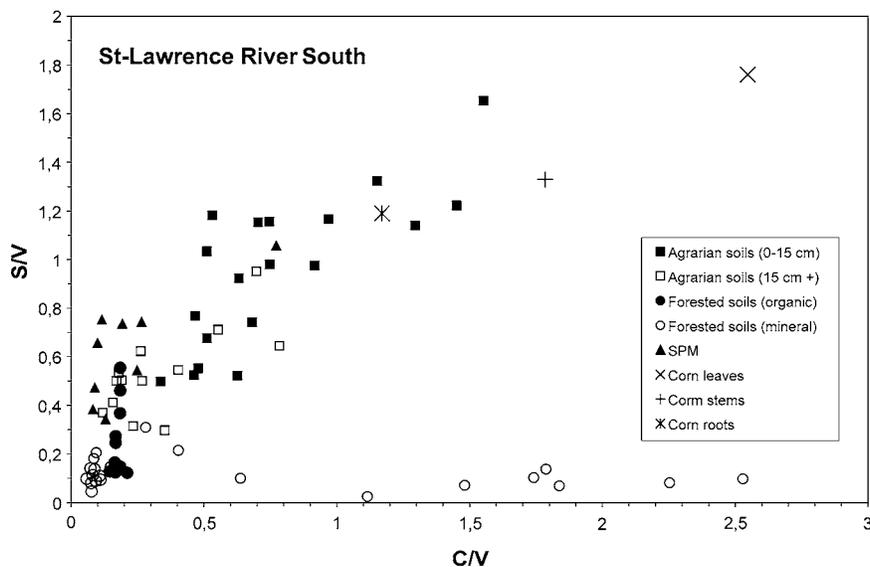


Fig. 6. Relationship between S:V and C:V ratios in soils of the Yamaska and St. François Rivers, and SPM from the St. Lawrence River–southern water mass; the end-point signal corresponding to corn plants are marked by an (X) for leaves, a (+) for stems and a (⌘) for roots.

of the high C:V ratio (1.80) measured in the deeper inorganic horizons of forested soils from the Yamaska River watershed. The presence of dense patches of coniferous trees nearby the Yamaska River sampling site might partly explain this discrepancy. Teisserenc et al. (2008) also observed elevated C:V values in the inorganic horizons of boreal forests mainly populated by black spruce. The C family is mainly composed of ferulic and *p*-coumaric acids. In forested soils, the

transition between the organic and inorganic horizons is marked by a sharp drop of the ferulic acid and V contents following active demethylation processes (Vane 2003). However, the *p*-coumaric acid is not affected by demethylation, and remains high in inorganic horizons. It is thus plausible that the preservation of the *p*-coumaric content in inorganic soils in conjunction with a decrease of the V content leads to higher C:V ratios in the deep inorganic soils. This hypothesis is

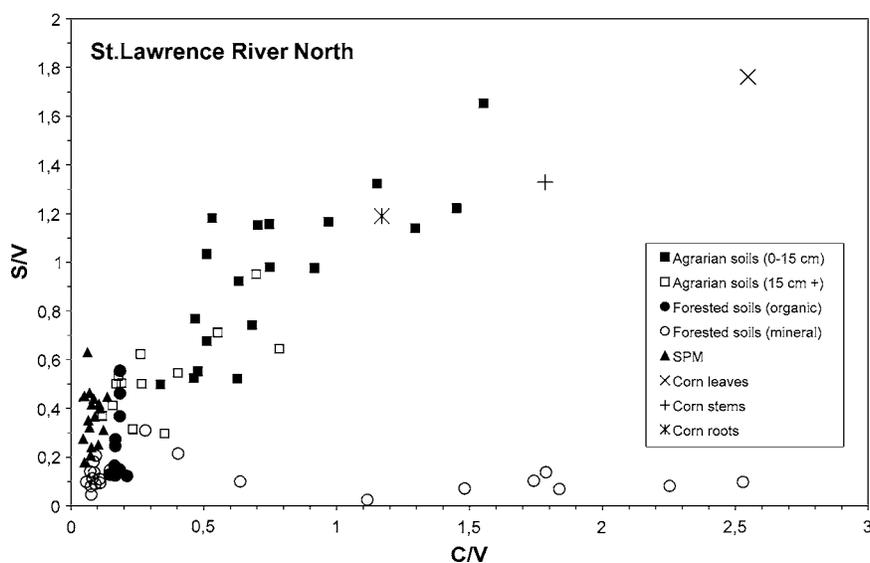


Fig. 7. Relationship between S:V and C:V ratios in soils of the Yamaska and St. François Rivers, and SPM from the St. Lawrence River–northern water mass; the end-point signal corresponding to corn plants are marked by an (X) for leaves, a (+) for stems and a (⌘) for roots.

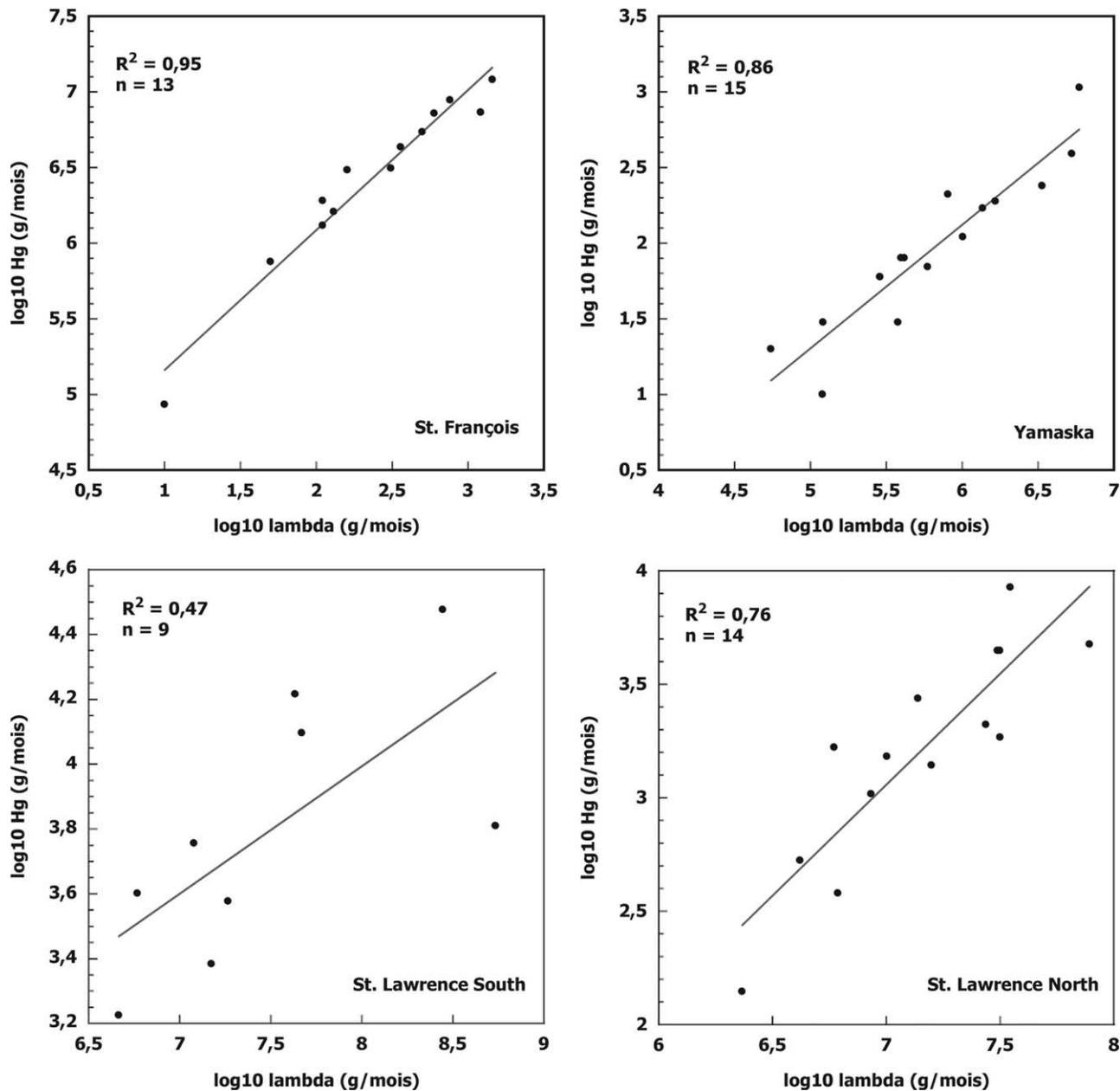


Fig. 8. Relationship between inputs of Hg associated to SPM ( $\text{g month}^{-1}$ ) and inputs of TOM expressed as lambda ( $\lambda$ ) ( $\text{g month}^{-1}$ ) to lake St. Pierre from the Yamaska River and St. François River – sampling stations located near the mouth of the rivers – and from the St. Lawrence River – sampling stations located upstream of Lake St. Pierre – August 2002 to April 2004.

confirmed by the absolute values of V and C concentrations we measured for the forested soil profiles (data not shown).

The C:V ratio is generally used to distinguish between the woody (branches, trunks) and non-woody (leaves) tissues of plants. Corn and other herbaceous plants also produce significant amounts of C. The S:V ratio gives indications to the deciduous (angiosperms) vs. conifer-

ous (gymnosperms) origins of TOM originating from higher ranking plants. Most of the studies dealing with LB use ratios obtained from fresh plant tissues as end-point signals. However, these ratios often evolve greatly during the transfer of TOM from the end-point source up to aquatic ecosystems, essentially following pedogenesis (Opsahl and Benner 1995; Houel et al. 2006; Teisserenc et al. 2008). The LB signature of TOM thus

represents an integrated indicator of TOM genesis, reflecting the vegetation diversity at the watershed scale, and of all processes affecting its nature during its transit to aquatic ecosystems.

### Sources of TOM in Lake St. Pierre

Similar LB signatures of the SPM organic matter found in the Yamaska River and the TOM found in the deep horizons of the agrarian soils present in its watershed clearly demonstrate the close relationship between these two pools of organic matter. The pedogenetic processes occurring in soils have the effect of decreasing the concentrations of LB from the surface to the deeper parts of soil profiles. Furthermore, the TOM aggregates present at the surface of eroded soils and carried to aquatic environments are altered by photochemical processes during their transit. Consequently, the TOM found in aquatic environments often exhibits an organic composition expressed by its LB signatures, similar to the one found in the deeper horizons of soils from the surrounding watershed (Houel 2003).

Although the influence of agrarian soils is also clearly distinguishable in the LB signature of the SPM collected in the St. François River, the organic composition of the SPM in this river is also influenced by the organic horizons of forested soils from the watershed, with lower S:V ratios. Indeed, the watershed of the St. François River consists of 66% of forested land (compared with 42% for the Yamaska River) and 23% of agrarian lands (compared with 54% for the Yamaska River) (COGEBY 2006; COGESAF 2006).

The LB signature characterizing the SPM collected in the southern part of the St. Lawrence River is similar to the SPM collected in the St-François River. In these two cases, the mixed influence of the agrarian soils and the organic layer of forested soils can be observed. However, the LB signature of the TOM fraction of the SPM in the northern part of the St. Lawrence River is more closely related to the organic horizons of forested soils. The northern water mass of the St. Lawrence River drains the waters issuing from the more densely forested watershed of the Ottawa River. Furthermore, the S:V ratio reported here for the SPM collected at the St. Lawrence River North sampling station is similar to the one observed by Teisserenc et al. (2008) in forested soil samples collected in the Ottawa region. It thus seems that the LB can also be used to track back the origin of TOM even in wide-scale aquatic ecosystems such as the St. Lawrence River.

### Source of Hg loadings in Lake St. Pierre

More than 86% of the variability observed in the Hg loadings from the SPM carried by the Yamaska River to Lake St. Pierre is explained by variations of TOM loading, evaluated using the  $\lambda$  indicator. This proportion of the explained variability rises to 95% in the case of the

St. François River. Furthermore, the LB signature of TOM found in the SPM of these two rivers is closely related to the signature of agrarian soils from their respective watersheds, which puts the emphasis on the role of soil erosion as a vector of Hg transport. This strong relationship between Hg and TOM loading is certainly attributable to the relatively small size of these watersheds (Yamaska: 4784 km<sup>2</sup>; St-François: 10 230 km<sup>2</sup>). Such characteristics of the watershed limit the importance of other Hg loading processes compared with soil erosion, and shorten the ecosystem response time considering its limited capacity to buffer the Hg inputs.

A strong relationship also exists between SPM-Hg and TOM loading (expressed as  $\lambda$  values) from the northern part of the St. Lawrence River, but this relation is slightly weaker than for the two other rivers with 76% of the variability explained. It is likely that the strength of the relationship is buffered by the distance between the source of the TOM (assumed to be the forested soils along the Ottawa River) and Lake St. Pierre, more than 100 km downstream. Other factors such as the presence of the water treatment plant of the city of Montréal, located about 50 km northwest of Lake St. Pierre can dilute the SPM-Hg vs.  $\lambda$  relation.

Finally, the TOM loadings (expressed as  $\lambda$  fluxes) from the southern water mass of the St. Lawrence River only explains about half of the variability of SPM-Hg loading in Lake St. Pierre. This observation is probably explained by the huge watershed drained by the St. Lawrence River, all the way upstream to the Great Lakes. It is likely that the TOM signature observed at the St. Lawrence River-South sampling station represents the integration of a series of regional TOM sources rather than the portrait of local loading.

## CONCLUSIONS

In this study, we successfully used the LB signatures of TOM to differentiate between agrarian vs. forested soils and between the surface and deeper horizons of these soils. We were able to demonstrate that most of the Hg associated with the SPM found in the tributaries of Lake St. Pierre is associated with TOM and was transported to aquatic environments following the erosion of agrarian soils. Furthermore, the amount of Hg brought to Lake St. Pierre in the form of Hg-TOM complexes today surpasses the inputs of Hg to LPS from local industries (which has decreased significantly since the enforcement of the St. Lawrence Action Plan in 1993, imposing a drastic lowering of the pollutant inputs from local industries) or from the remobilisation of bottom sediments through the dredging of the St. Lawrence waterway or commercial navigation. These findings stress the need to take action to limit the erosion of agrarian soils in order to preserve the integrity of Lake St. Pierre and the quality of its important fish resource.

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