Terrestrial organic matter biomarkers as tracers of Hg sources in lake sediments

Roman Teisserenc · Marc Lucotte · Stéphane Houel

Abstract Terrestrial organic matter (TOM) plays a key role in mercury (Hg) dynamics between watersheds and lakes. In this study we attempts to determine the role of TOM source and quality and not only quantity, in the fate and transport of total Hg (T-Hg) to boreal lakes. Integrating the watershed complexity is a daunting task. Within the scope of this project, we characterized this organic matter at a molecular level in order to determine Hg transfer conditions to the sediments. We sampled ten lakes in the Quebec boreal forest. In each lake, we took a sediment core at the deepest point in addition to analyzing T-Hg and a set of terrigenous biomarkers in recent sediments. Our results show no relationship between TOM quantity and T-Hg concentration in lake sediments. However, [T-Hg] variation is well explained by the increase of 3,5Bd/V ratios ($R^2 = 0.84$; $p < 0.0002$) and the decrease of C/V ratios ($R^2 = 0.5$; $p < 0.0227$). Our study shows that TOM source and quality are determinant for Hg loadings in lake sediments. More precisely, increasing TOM derived from humified soil horizons explains most of Hg level variation within sediments.

Keywords Mercury · Lignin biomarker · Boreal forest lakes · Terrigenous organic matter · Sediment

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Introduction

Mercury (Hg) deposition in boreal lakes has increased significantly over the last century (Jackson 1997; Lindberg et al. 2007). There is a consensus among the scientific community that this increase can be attributed to the anthropogenic emission of gaseous Hg that has been taking place since the beginning of the industrial era, primarily due to the combustion of fossils fuels (Pacyna et al. 2006). This anthropogenic Hg adds to Hg naturally present in ecosystems. Even in remote areas, high Hg levels in boreal ecosystems are observed. Indeed, Hg (anthropogenic, natural) can be carried over long distances far from point sources via atmospheric transport (Fitzgerald et al. 1998; Pacyna et al. 2006). Atmospheric Hg is then transferred to the

environment by dry and wet depositions. Hg then tends to accumulate in lake sediments where increases in T-Hg are well recorded (Lucotte et al. 1995; Rognerud and Fjeld 2001). Previous studies measuring T-Hg concentrations [T-Hg] in recent boreal lake sediments reported values that vary between 50 and 500 ppb (Lucotte et al. 1995; Kainz and Lucotte 2006). The role of TOM dynamics on the fate of Hg in these environments has often been proposed to explain [T-Hg] differences among lake sediments (Kolka et al. 1999). Indeed, organic matter is composed of a complex mixture of various compounds that bind heavy metals including Hg. Several studies have observed that the levels of T-Hg transported to lakes are related to TOM concentration (Driscoll et al. 1995; Kolka et al. 1999; Kainz et al. 2003; Sanei and Goodarzi 2006). More precisely, some studies raised the issue that TOM quality (source, composition), more than the sole quantity of TOM entering the lake, plays a key role in the fate of Hg in the environment (Lucotte et al. 1995; Kainz and Lucotte 2006; Sanei and Goodarzi 2006; Caron et al. 2008; Ouellet et al. 2009). The regime of atmospheric Hg deposition on soil also varies according to vegetation (Schroeder and Munthe 1998; Demers et al. 2007). Furthermore, the hydrologic regime of forested watersheds will be modified by its vegetation composition, leading to differential Hg and TOM leaching into lakes.

Lignin phenol derivatives, obtained after a mild cupric oxidation (CuO), yield interesting information on TOM source and composition. Applicable in several environments, they have been broadly used to describe the TOM composition of sediments from various watersheds in addition to reconstructing past vegetation changes (Hu et al. 1999; Dalzell et al. 2007). Recent studies have used these biomarkers for environmental issues (Louchouarn et al. 1999; Houel et al. 2006) such as the fate of contaminants in the environment (Louchouarn and Lucotte 1998; Caron et al. 2008; Ouellet et al. 2009). Earlier studies validated the use of CuO derived biomarkers to describe TOM composition variation due to watershed characteristics (Teisserenc 2009). Here, we propose to follow the influence of TOM composition, revealed by CuO derived biomarkers, as a predictive variable on [T-Hg] in recently deposited lake sediments. By tracing TOM coming from deciduous and coniferous species as well as describing its state of degradation, we aim at determining the importance of TOM on Hg dynamics. This integration of watershed characteristics through molecular analysis should improve our understanding of [T-Hg] variation among lakes from the same region.

Materials and methods

Sampling sites

Ten oligotrophic lakes situated in the boreal forest were sampled. These lakes are located in two distinct administrative regions of North-eastern Canada: Outaouais and Temiscamingue (Fig. 1, Table 1). All lakes studied are part of the boreal forest ecosystem dominated by black spruce (*Picea mariana*), balsam fir (*Abies balsamea*), and grey pine (*Pinus sabineana*) for gymnosperm species and by white and yellow birch (*Betula papyrifera*, *Betula alleghaniensis*), maple (*Acer* spp.) and aspen (*Populus* sp.) for angiosperm species. Watersheds are covered by mixed wood forest dominated by deciduous species for the ten lakes and are located on the Grenville geological province (Fig. 1). These lakes lie on gneiss bedrock covered by thin glacial deposits. The soils are mainly podzolic, and overlay till or sand deposits.

Sampling

Sediment cores were sampled using a pneumatic Mackereth corer (Mackereth 1958) at maximum depth of each lake. The top 5 cm were subsampled at each centimeter in order to study the recent TOM and Hg deposition in these lakes. To avoid cross contamination, the contour in contact with the corer was removed. The samples were then freeze-dried prior to analysis.

Chemical analysis

Sediment samples were homogenized with a glass rod prior to total carbon and nitrogen analysis on a Carlo Erba (NA-1500) elemental analyzer with a reproducibility of 5%. Analyses of molecular biomarkers were performed based on the copper oxidation (CuO) method initially developed by Hedges and Ertel (1982) and modified by Goñi and Montgomery (2000). Extraction products were analyzed on a

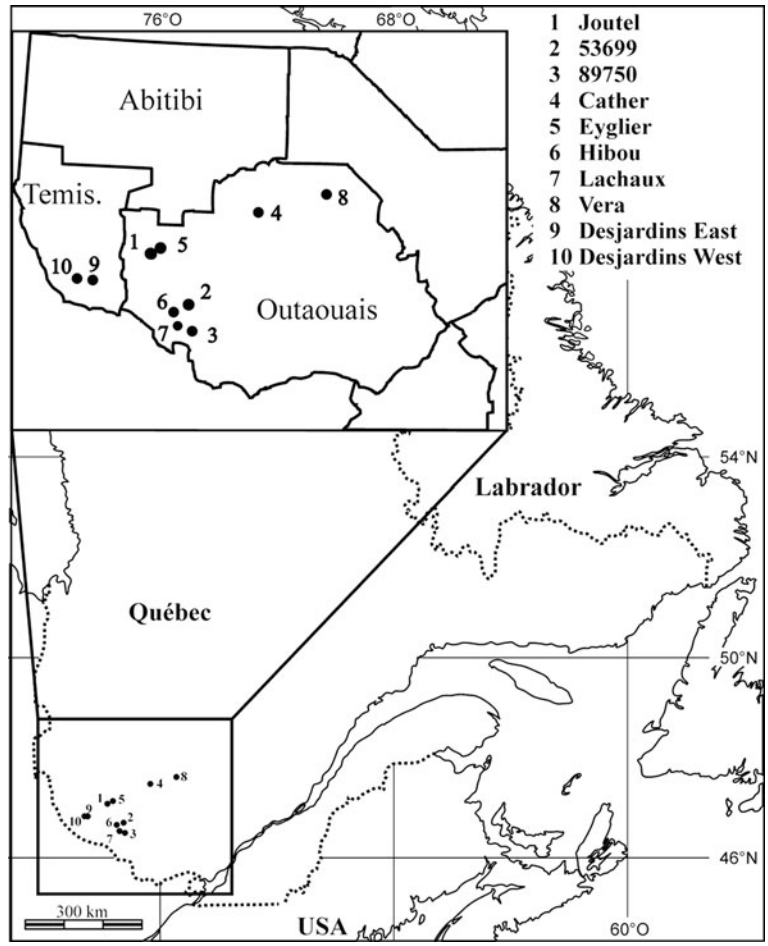

Fig. 1 Map of studied lakes

Table 1 Localization of the ten study lakes and morphometric properties of their watersheds

Lakes	Region	Lake area (km^2)	Drainage area (km^2)	DA/LA
Joutel	Outaouais	0.66	4.72	7.15
53699	Outaouais	0.30	4.18	13.93
89750	Outaouais	0.44	1.63	3.70
Cather	Outaouais	0.29	1.33	4.59
Eygliers	Outaouais	0.38	3.49	9.18
Hibou	Outaouais	0.40	1.50	3.75
Lachaux	Outaouais	0.34	1.78	5.24
Vera	Outaouais	0.36	4.60	12.78
Desjardins east	Temiscamingue	10.26	38.84	3.79
Desjardins west	Temiscamingue	8.88	46.95	5.29

GC/MS system (VARIAN 3800/Saturn 2000) fitted with a fused capillary column (Varian FactorFour VF-1 ms 60 m, 0.32 mm). The most common CuO derivatives used in recent literature and analyzed for the purpose of our study are three lignin derived phenols families: Vanillyls (V: ubiquitous in all terrestrial plants), Cinnamyls (C: produced by non-woody tissues) and Syringyls (S: specific for angiosperm plants) (Hedges and Mann 1979). These three families are used to determine the source of TOM along

with its relative abundance (Σ8 normalized according to 10 g of sample: sum of V, C and S). *p*-Hydroxyl phenols and an aromatic carboxylic acid (3,5-dihydroxybenzoic acid) are also combined with V and S to describe the state of degradation and humification of TOM (Houel et al. 2006; Dickens et al. 2007).

Analyses of T-Hg concentrations were performed by cold vapour atomic fluorescence spectrometry detection (CVA-FS) following the protocol developed by Bloom and Fitzgerald (1988) and adapted by Pichet et al. (1999). Briefly, a combination of acid HNO_3:HCl (16:6 N) (10:1 ml) is added to approximately 250 mg of freeze dried, ground sediment and then heated to 120°C for 6 h. The remaining solution is brought back to a volume of 30 ml with NANOpure® water and analyzed by atomic fluorescence.

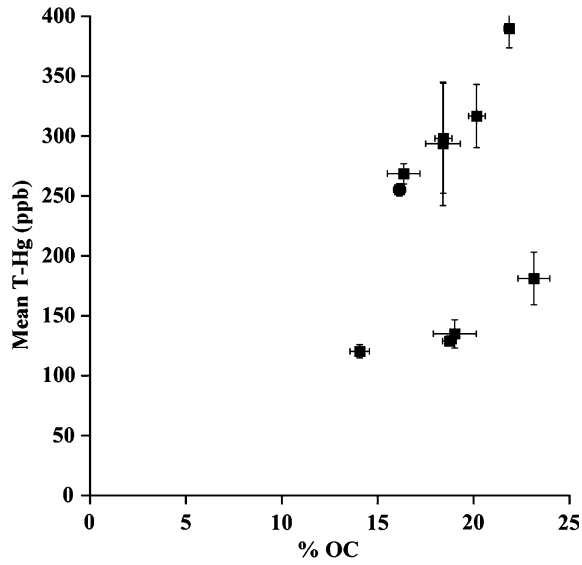

Fig. 2 Relationship between [T-Hg] and %OC in recent lake sediments

Results

In the following results we present the average values and standard deviation for the top 5 cm of each sediment core. Indeed, in order to integrate TOM dynamics between a lake and its surrounding watershed, we chose to analyze the first 5 cm of each sediment core. The first 5 cm represent between 20 and 30 years of sedimentation, estimated according to sedimentation rates measured in this region (sedimentation rate: 0.22 ± 0.06 cm year^{-1} $n = 4$) by Lucotte et al. (1995). In order to evaluate potential changes due to early diagenesis in this 5 cm sediment layers, we plotted each indicator measured in the first centimeter against the mean value of 2–5 cm. For each indicator, the relationships are linear with regression coefficients varying between 0.83 and 0.96 and slopes close to 1 (0.76–0.96). The C/V, P/(V + S) and 3,5Bd/V ratios are less affected by early diagenesis than S/V ratio. However these changes—deduced from lower slopes of the regression diverging from 1—are limited and confirm that once reaching subaqueous condition, lignin macromolecules undergo limited degradation over a period of a few decades (Opsahl and Benner 1995). Kastner and Goñi (2003) also found high stability of lignin biomarkers measured in sediment cores. Ligneous compound accumulation in sediments thus appears well suited to hold long-term records of TOM sources (Louchouarn et al. 1997; Hernes et al. 2007).

Figure 2 presents the relationship between [T-Hg] and percentage of organic carbon (%OC) in recently deposited sediments of the ten lakes. We observe a variation of %OC from 14 to 24% and a range of [T-Hg] from 120 to 390 ppb. No relationship is observed between these two variables. Figure 3 presents sedimentary [T-Hg] plotted against Σ8, which is the sum of C, V and S for 10 g of sample. This sum is used to estimate total lignin concentration and has been commonly used as indicator of TOM contribution to sediments (Hedges and Parker 1976; Hedges and Ertel 1982; Onstad et al. 2000). Σ8 values ranging from 24.5 to 43.1 mg/10 g of dw are recorded in these lakes. We do not observe any significant relationship between this variable and [T-Hg] variation.

In Figs. 4, 5, 6 and 7, T-Hg values are normalized according to Σ8. This normalization is driven by the fact Hg affinity for organic matter is well known and has been extensively described (e.g. Swain et al. 1992; Lucotte et al. 1995; Kolka et al. 1999; Kainz and Lucotte, 2006). Changes in organic matter quantity can carry important implications for Hg recruitment to sediments. To examine what influence the quality of terrigenous organic matter may play in the transport of Hg to lake sediments, normalization of Hg concentrations to organic matter concentrations allows for absolute comparisons of the influence of

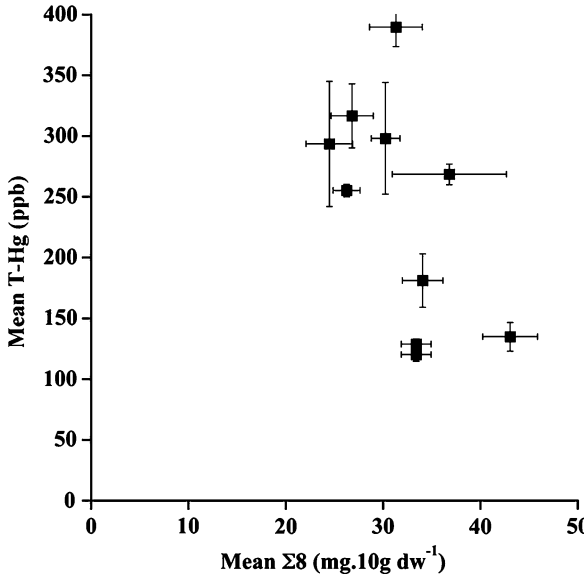

Fig. 3 Relationship between [T-Hg] and Σ8 in recent lake sediments

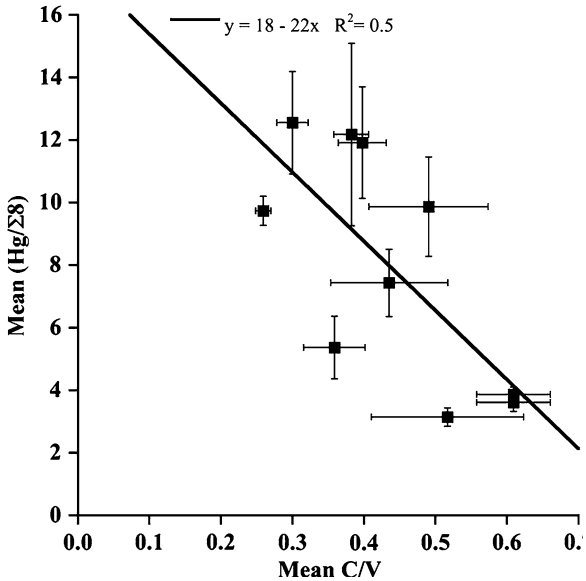

Fig. 5 Relationship between [T-Hg]/Σ8 and C/V ratios in recent lake sediments

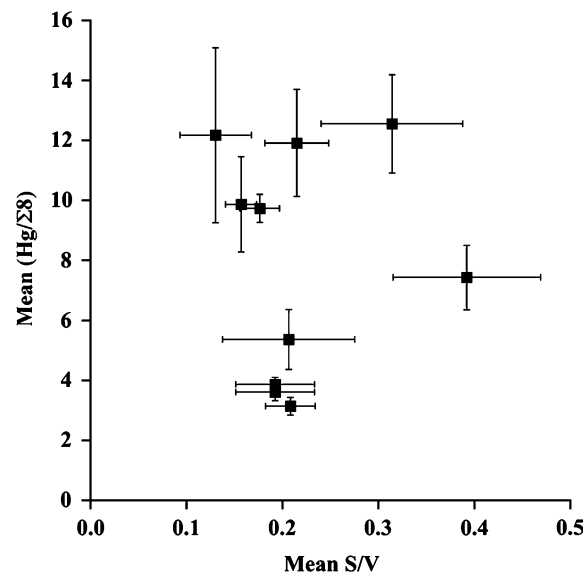

Fig. 4 Relationship between [T-Hg]/Σ8 and S/V ratios in recent lake sediments

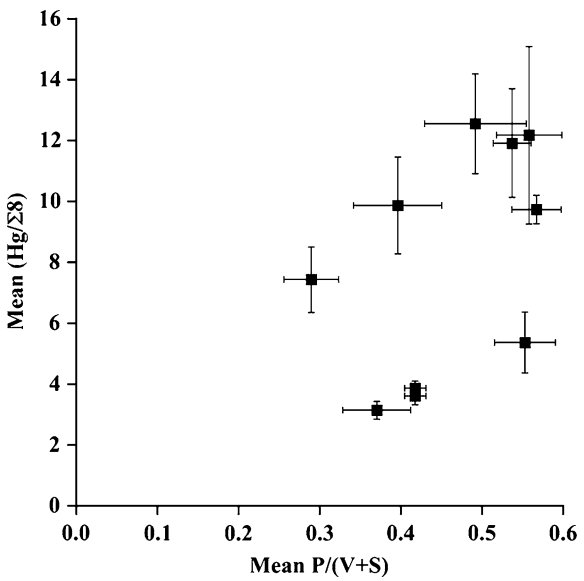

Fig. 6 Relationship between [T-Hg]/Σ8 and P/(V + S) ratios in recent lake sediments

specific TOM compounds as preferential vectors of the contaminant from the watershed to the aquatic system. Figure 4 presents the variation of [T-Hg]/Σ8 and S/V ratios in recent sediments. S/V ratio is an indicator of angiosperm-derived lignin in sediments (Hedges and Mann 1979; Tesi et al. 2008). We observe variation of [T-Hg]/Σ8 ratios between 3 and 12 and S/V ratios between 0.13 and 0.39. No relationship is observed between the Hg associated with organic matter and angiosperm derived lignin compounds. C/V ratios vary between 0.25 and 0.65 (Fig. 5). This variation of non-woody and coniferous

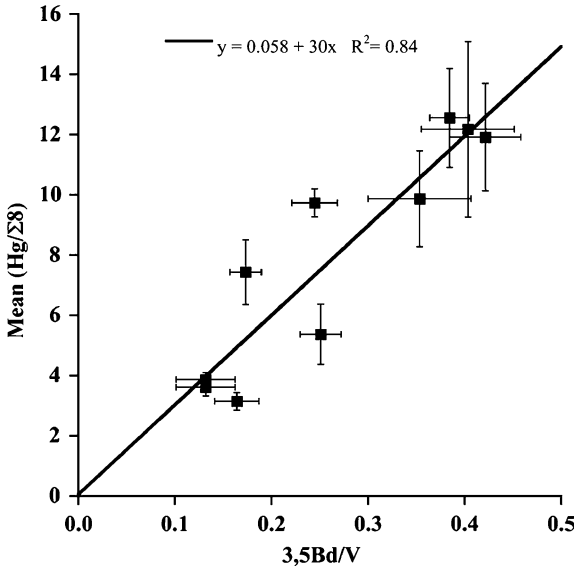

Fig. 7 Relationship between [T-Hg]/Σ8 and 3,5Bd/V ratios in recent lake sediments

derived lignin in sediments (Hedges and Mann 1979; Hu et al. 1999) explains up to 50% of the observed variation of [T-Hg]/Σ8. Figure 6 presents [T-Hg]/Σ8 ratios plotted against P/(V + S) which is an indicator of TOM state of degradation (Dittmar and Lara 2001; Farella et al. 2001; Tesi et al. 2008). The range of P/(V + S) values is limited, as sedimentary records of this indicator for the ten lakes is comprised between 0.29 and 0.57. No significant relationship is observed between [T-Hg]/Σ8 and P/(V + S) ratios in these lakes. Finally, Fig. 7 presents [T-Hg]/Σ8 ratios plotted against 3,5Bd/V ratios, which is an indicator of TOM maturation in soils. Variation of this ratios explain much of observed values of [T-Hg]/Σ8 in lakes sediments ($R^2 = 0.84$; $p < 0.0002$).

Discussion

Hg and TOM in recent sediments

Percentages of organic carbon measured in recent lake sediments in this study (Fig. 2) are relatively high and correspond to the upper range of values measured in the same area by previous studies (2–18 %OC) (El Bilali et al. 2002; Kainz and Lucotte 2006; Sanei and Goodarzi 2006). In oligotrophic lakes, %OC is often referred as an indicator of TOM inputs. We observe here that the variation of %OC does not influence [T-Hg] in recent sediment among lakes under study. TOM loadings from watershed to lakes were also estimated thanks to Σ8 measurement in recent sediments. This indicator plotted against [T-Hg] allows highlighting that no variation of Hg is related to an increase of TOM in recent sediments. Indeed, we do observe elevated fluctuations of [T-Hg] in lake sediments but rather constant Σ8 values (Fig. 3). In these small headwater lakes, estimation of TOM inputs is not sufficient to understand the [T-Hg] variation in sediments. This result may be surprising as several studies have observed that the levels of T-Hg transported to lakes are related to TOM concentration in stream (Kolka et al. 1999), water column (Meili et al. 1991; Driscoll et al. 1995; Selvendiran et al. 2009) and sediments (Rasmussen et al. 1998). However this absence of relationship, within the range of organic carbon concentration observed, has been reported in recent studies (Sanei and Goodarzi 2006; Kainz and Lucotte 2006). These authors raised the importance of the quality and particularly the source of TOM on Hg dynamics (Kainz and Lucotte 2006) instead of solely bulk estimation of TOM inputs (Sanei and Goodarzi 2006; Ouellet et al. 2009).

Hg and TOM sources

Lignin derived biomarkers hold precious information on the composition of TOM. S/V ratios trace the increasing influence of angiosperm stands in a given watershed on TOM found in lake sediments (Hu et al. 1999). C/V ratios are commonly used to trace grassland along with coniferous dominated watersheds in boreal ecosystems (Hu et al. 1999; Castañeda et al. 2009). Our results indicate that variations in the presence of angiosperms on the watershed do not explain variations in sedimentary Hg levels from one lake to the next (Fig. 4). However the increasing presence of a non-woody or coniferous source in the watershed seems to lower the inputs of Hg to the lake (Fig. 5). These results tend to confirm that the increasing presence of open scrubland and coniferous forests corresponds to lower amounts of Hg leached out to lakes (Demers et al. 2007). Two main reasons may explain these observations. First, the incorporation of Hg to litter and soils are lower in coniferous stands than in deciduous one because of differences in litter dynamics (rate of foliage renewal between

evergreen and deciduous trees, rate of organic matter degradation and accumulation, humification processes) (Sheehan et al. 2006; Demers et al. 2007). Moreover fluxes of T-Hg in forest floor leachates are lower in coniferous stands than in deciduous stand, with a difference in annual T-Hg fluxes estimated at 23% with respect to vegetation composition for lakes in the Adirondak region (Demers et al. 2007). Several studies have also shown that open forest areas, grasslands and scrublands are sites of lower Hg deposition leading to reduced [T-Hg] in litterfall as in addition to lower Hg fluxes in soils (Sheehan et al. 2006; Poulain et al. 2007; Nelson et al. 2007; Witt et al. 2008). Second, in these studied watersheds, a previous study revealed that coniferous and open areas are mainly found in very low slope and ill-drained areas that act as buffer zones for TOM transfer to the lake (Teisserenc 2009). These results are particularly significant as the role of vegetation on Hg uptake and transfer in a watershed is a key parameter to understand Hg cycle in the boreal ecosystem (Grigal 2003; Sheehan et al. 2006; Demers et al. 2007; Poulain et al. 2007; Witt et al. 2008).

Hg and TOM quality

The ratio of *p*-hydroxy phenols over the sum of vanillyls and syringyls [P/(V + S)] represents an indicator of lignin demethylation. Indeed, demethylation (e.g. by brown rot fungi) leads to the selective loss of vanillyl and syringyl phenol methoxylated groups, but does not affect the yield of phenols without methoxyl groups such as the *p*-hydroxyl phenols (Ertel et al. 1986; Dittmar and Lara 2001). This process has led to the use of P/(V + S) as an indicator of the state of TOM degradation. TOM freshness, estimated through P/(V + S) ratios, does not influence Hg inputs to sediments of region A (Fig. 5). Yet we were expecting a relationship between this indicator and [T-Hg]/Σ8 as P/(V + S) ratios increase in soils horizons (Houel et al. 2006) where [T-Hg] are higher (Grondin et al. 1995; Obrist et al. 2009). However, since the range of P/(V + S) values is limited in these ten lakes, this ratio may not be appropriate for understanding the variation of [T-Hg] recorded in sediments. The variation of P/(V + S) ratios variation is related to the demethylation of V and S phenols by fungal pathway (brown, white rot fungi). The close relationship between these small lakes and their watershed may limit their variations. Furthermore, we observed little variation of P/(V + S) in angiosperm's soils between horizons, explaining the absence of relationship with Hg loadings in these southern lakes surrounded by deciduous vegetation (Teisserenc 2009).

Finally, 3,5Bd compound has been identified as a product of soil degradation (Ugolini et al. 1981). The precursors of this compound are tannins and other flavonoids (Goñi and Hedges 1995). These polyphenolic precursors tend to accumulate within plant senescence and decaying cells (de Leeuw and Largeau 1993). The relative increase of 3,5Bd phenols in soils has been linked to the increase of degradation and humification of fresh plant tissues (Houel et al. 2006) and a recent study has confirmed the potential use of 3,5Bd/V as a tracer of TOM input to aquatic systems (Dickens et al. 2007). Houel et al. (2006) also used this ratio as model end-member between surface soil litter and mineral horizons of soils. This latter application is relevant to the study of Hg dynamics, as it tends to present variable concentrations along soil profiles (Grigal 2003). The relationship between [T-Hg]/Σ8 and 3,5Bd/V is quite significant ($R^2 = 0.84$; Fig. 7). This strong relationship leads to the explanation that more Hg is transferred to lake sediments when it is associated with more humified TOM. This observation is in contradiction with results observed in the water column of lakes (Ouellet et al. 2009). However, in this study, anthropogenic activities (agriculture, forestry) drastically disturb the steady-state equilibrium of soil organic matter with selective erosion of soil humus and litter (Lal 2003). Thus, in unperturbed watersheds, the leaching of more humified horizons below the surface litter will increase the association between Hg and TOM. This result confirms that strong mobilization of Hg is achieved in lower soils horizons and supports the simulated mobilization of T-Hg in soil by the water flow studied by Lee et al. (1994). In a previous study, we observed that the mean slope of the watershed influences the 3,5Bd/V ratio in sediments (Teisserenc 2009). Indeed, when the mean slope of the watershed decreases, water percolates more efficiently and accesses deeper soil horizons where 3,5Bd/V are higher and Hg is strongly associated with TOM (Grigal 2002; Houel et al. 2006; Obrist et al. 2009). While major research initiatives have tried to understand Hg retention in

soils and its delayed release from watersheds (Hintelmann et al. 2002; Demers et al. 2007; Johnson et al. 2007; Graydon et al. 2008) none has achieve to assess the role of soils horizon on this dynamics.

The aim of this paper was to investigate whether variable TOM sources and quality could explain sedimentary [T-Hg] differences amongst nearby lakes in the boreal forest. TOM quality as defined by its humification state and its origin from various soil horizons plays a crucial role in Hg loadings towards lakes. The role of vegetation composition and soils on Hg dynamics has been addressed within several research project using extensive sampling and analytical efforts along with heavy logistic (Ericksen et al. 2003; Demers et al. 2007; Graydon et al. 2008). In our study, the unique analysis of lignin biomarkers in sediments allowed to conclude on the preponderant influence of both humification process and coniferous stands in the watershed and open areas on terrestrial Hg transfers to a lake. Along with the two previous paper published by Caron et al. (2008) and Ouellet et al. (2009), this study highlights the potential usage of lignin derived biomarkers to better understand the Hg cycle at the ecosystem level.

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