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Integrated transfers of terrigenous organic matter to lakes at their watershed level: A combined biomarker and GIS analysis

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Abstract

Terrigenous organic matter (TOM) transfer from a watershed to a lake plays a key role in contaminants fate and greenhouse gases emission in these aquatic ecosystems. In this study, we linked physiographic and vegetation characteristics of a watershed with TOM nature deposited in lake sediments. TOM was characterized using lignin biomarkers as indicators of TOM sources and state of degradation. Geographical information system (GIS) also allowed us to integrate and describe the landscape morpho-edaphic characteristics of a defined drainage basin. Combining these tools we found a significant and positive relationship ($R^2 = 0.65$, $p < 0.002$) between mean slope of the watershed and the terrigenous fraction estimated by $\Lambda 8$ in recent sediments. The mean slope also correlated with the composition of TOM in recent sediments as P/(V + S) and 3,5Bd/V ratios significantly decreased with the steepness of the watersheds ($R^2 = 0.57$, $p < 0.021$ and $R^2 = 0.71$, $p < 0.004$, respectively). More precisely, areas with slopes comprised between 4° and 10° have a major influence on TOM inputs to lakes. The vegetation composition of each watershed influenced the composition of recent sediments of the sampled lakes. The increasing presence of angiosperm trees in the watershed influenced the export of TOM to the lake as $\Lambda 8$ increased significantly with the presence of this type of vegetation ($R^2 = 0.44$, $p < 0.019$). A similar relationship was also observed with S/V ratios, an indicator of angiosperm sources for TOM. The type of vegetation also greatly influenced the degradation state of OM. In this study, we were able to determine that low-sloped areas ($0-2^\circ$) act as buffer zones for lignin inputs and by extension for TOM loading to sediments. The relative contribution of TOM from the soil organic horizons also increased in steeper watersheds. This study has significant implications in our understanding of the fate of TOM in lacustrine ecosystems.

1. INTRODUCTION

Lakes represent almost 2.8% of our planet's terrestrial surface area (Downing et al., 2006). Over the last decades, an increasing scientific interest has focused on organic mat-

ter (OM) dynamics within lake ecosystems. Two major environmental issues: the fate of contaminants and climate change, drive this scientific interest. First, the role of OM, particularly TOM, is crucial to the contribution of contaminants in lakes (Lindqvist et al., 1991; Coquery and Welbourn, 1995; Grigal, 2002; Ouellet et al., 2009). Second, OM dynamics is the central factor controlling carbon dioxide (CO_2) and methane (CH_4) production in these inland aquatic ecosystems. Since Cole et al.'s (1994) study on CO_2 supersaturation in lake surface waters, several authors have addressed the cycling of OM in lakes within the scope of carbon transfers to the atmosphere and oceans (Algesten

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et al., 2004; Cole et al., 2007; Jonsson et al., 2007). These issues increased the need to reinforce our understandings of terrestrial and aquatic ecosystems linkage (Chapin et al., 2006; Cole et al., 2007; Prairie, 2008).

Recently, increased attention has been given to the understanding of the parameters controlling the transfer of TOM from watersheds to lakes. At the watershed level, both physiographic and edaphic parameters influence TOM inputs to lakes. As such, the mean slope declination, the drainage area, the lake surface area, the type of soil, and the vegetation composition appear as dominant variables (Rasmussen et al., 1989; D'arcy and Carignan, 1997; Rantakari et al., 2004; Sobek et al., 2006). A particular emphasis has been placed on understanding the role of these variables on the composition of dissolved and particulate organic carbon (DOC and POC), however, few studies use sediment records to address the question (Müller et al., 1998). Compared to the water column, sediment records have the potential to integrate time variability. Sediments sampled in the maximal depositional zone (i.e. focal zone) also integrate spatial variation of overall lake–watershed organic matter (OM) dynamics (Håkanson and Jansson, 1983). Furthermore, organic matter buried in lake sediments represents a carbon sink that remains stable for millennia (Cole et al., 2007). Based on these specificities, we chose to determine the watershed influence on the composition of specific TOM biomarkers as recorded by recent lake sediments. In order to achieve this goal we used the combination of two promising tools for environmental and ecosystem studies: TOM biomarkers yielded by mild cupric oxide (CuO) oxidation and GIS.

TOM biomarkers, usually referred to as lignin-derived phenols biomarkers, have successfully been used to identify the abundance, source and relative state of degradation of terrestrially derived OM. In particular, lignin-derived phenols have been used in soils (Otto and Simpson, 2006; Nierop and Filley, 2007), water columns and sediments (Houel et al., 2006; Dalzell et al., 2007; Caron et al., 2008) to trace back and describe land-derived OM. In recent studies, lignin biomarkers have proven to be powerful tools to understand OM fluxes and fates at the watershed scale (Farella et al., 2001; Dalzell et al., 2005; Houel et al., 2006; Caron et al., 2008; Ouellet et al., 2009). Furthermore, there is strong evidence in recent literature that the lignin composition is also controlled by hydrologic and soils processes in watersheds (Dalzell et al., 2005; Houel et al., 2006; Duan et al., 2007; Hernes et al., 2007). Within the daunting task that is the characterization of a given drainage basin, the analysis of lignin biomarkers in sediments is an advantageous tool for predicting basin scale processes (Houel et al., 2006). GIS is a powerful tool for mapping and analyzing geo-reference data. It permits spatial linking of different types of data such as elevation, slope, vegetation and land-use of a defined area (Longley et al., 2005).

In this paper, we used GIS to describe the landscape morpho-edaphic characteristics of entire drainage basins. TOM signatures were analyzed in recent lake sediments and were compared to watershed property.

2. MATERIALS AND METHODS

2.1. Sampling sites

The 12 lakes sampled in this study are spread out over 51,000 km² within the Canadian Shield boreal forest ecosystem (Fig. 1). This area overlaps three administrative and ecological zones of the province of Québec (Canada): Abitibi, Témiscamingue and Outaouais regions. Preissac and Malartic lakes are the two northern-most and largest lakes of this study with surface areas of 129.25 and 122.32 km², respectively. They are located in the Lowland of the Abitibi geological province, which belongs to the Superior geological province. The bedrock is composed of igneous and metamorphic rocks. Their watersheds sustain agriculture, mining and small-scale urban areas on Quaternary deposits of sand and clay.

The 10 other lakes are located within the Southern Laurentides region in the Grenville geological province. Thin glacial deposits cover the gneiss bedrock of this region. The soils are mainly podzolic, and lay on till or sand. Lakes Desjardins East and Desjardins West (10.26 and 8.88 km², respectively) are located in the western part of our study area, the Témiscamingue region. Mature mixed wood forests cover their watersheds. Few perturbations exist in this area, with the exception of gravels roads and forest harvesting. The lake Desjardins East flows into lake Desjardins West. The last eight lakes are located in the Outaouais region, which is characterized by medium elevations with hilly to mountainous topological structure and scattered, small lakes that fill depressions. The vegetation is composed of mixed wood forests, predominantly deciduous forests in the southern region, and an increasing proportion of coniferous trees at higher latitude, altitude and drainage. The lake areas for this subset vary from 0.29 to 0.66 km². These lakes are all headwater lakes with no major perturbation on the watersheds over the last 30 years, with the exception of Lake Vera where large patches of post clear-cut regenerating forests were observed during sampling.

2.2. Sampling

Sediment cores were sampled using a pneumatic Mackereth corer (Mackereth, 1958) at the deepest point of the lake to obtain a representative record of overall watershed influence on lake sediments. Indeed, sediments sampled in the accumulation zone is the most suited zone to integrate spatial variation of overall lake–watershed OM dynamics (Håkanson and Jansson, 1983; Smol, 2008). In relation to the rest of the lake, accumulating-zone sediments represent a spatially homogeneous area (Shotbolt et al., 2005). Each core was sub-sampled at every centimeter. To avoid cross contamination between samples, the contour in contact with the corer was removed. Samples were frozen immediately after collection and then freeze-dried prior to analysis. In order to integrate TOM dynamics at the watershed scale over the last decades, we analyzed the first 5 cm of each sediment core. These first 5 cm are estimated to represent between 20 and 30 years of sedimentation, according to sedimentation rates previously reported for lakes of the

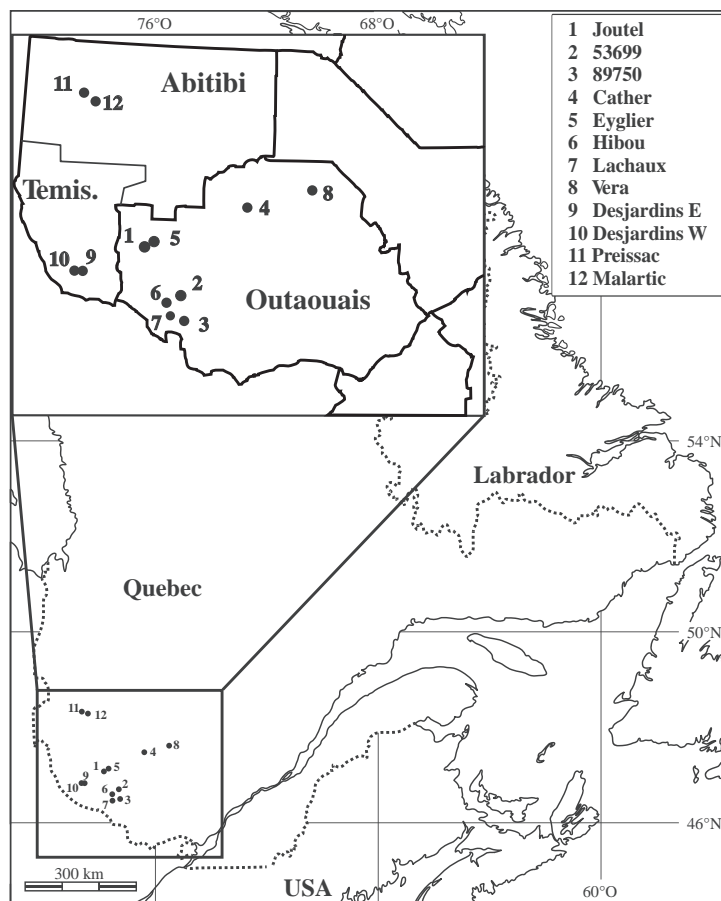


Fig. 1. Map of studied lakes.

studied region ($0.22 \pm 0.06 \text{ cm year}^{-1}$, Lucotte et al., 1995). Sediment data presented in this manuscript then represent the average values with their standard deviation for the combined top 5 cm in each core.

2.3. Chemical analysis

Sediment samples were first homogenized with a glass rod. Total carbon and nitrogen analyses were performed with a Carlo Erba (NA-1500) elemental analyzer, with a reproducibility of 5%. The analysis of molecular biomarkers was performed according to the CuO method initially developed by Hedges and Ertel (1982) and modified by Goñi and Montgomery (2000). A sediment aliquot providing 3–5 mg of organic carbon was oxidized under alkaline conditions with CuO at 150 °C for 3 h in 3.2 mL stainless steel mini-bombs. Right after reaction, quantitative amount of ethyl vanillin and cinnamic acid internal standard were added. The aqueous solution was then acidified to pH 1 with 6 N HCl and extracted with ethyl acetate ($3 \times 3 \text{ mL}$). Excess water was removed with Na_2SO_4 before evaporation of the solvent using a LabConco CentriVap[®] vacuum concentrator system. Extraction products were dissolved in 300 μL of pyridine and kept frozen until derivatization. Fifty microliters of this solution was diluted with 200 μL pyridine and derivatized with bis-trimethylsilyl

trifluoroacetamide (BSTFA) at 80 °C during 1 h. Separation and quantification of derivatives were performed on a GC/MS system (VARIAN 3800/Saturn 2000) fitted with a fused capillary column (Varian FactorFour VF-1ms 60 m, 0.32 mm). GC oven temperature program was as followed: from initial 100 °C to 300 °C at 4 °C min^{-1} . Final temperature was kept for 10 min. Each compound was identified according to its retention time and by comparing it to commercially available standards. Average standard deviation of replicate analysis is below 15% for the major CuO oxidation products. A “standard” lake sediment sample SAG05 was also regularly analyzed for comparison with previous study (Louchouart et al., 1997; Goñi and Montgomery, 2000; Houel et al., 2006). For the purpose of our study, we analyzed the most common CuO derivatives used in recent literature, three lignin-derived phenols families: vanillyls (V (VI, vanillin; Vn, acetovanillon; Vd, vanillic acid); ubiquitous in all terrestrial plants); cinnamyls (C (p-Cd, p-coumaric acid; Fd, ferulic acid); produced by non-woody tissues) and syringyls (S (SI, syringaldehyde; Sn, acetosyringone; Sd, syringic acid); specific of angiosperm plants) (Hedges and Mann, 1979). These three families are used to determine the source of TOM along with relative abundance ($\Delta 8$: sum of V, C and S). p-Hydroxyphenols (PI, p-hydroxybenzaldehyde; Pn, p-hydroxyacetophenone; Pd, p-hydroxybenzoic acid) and a benzene carboxylic acid (3,5-

dihydroxybenzoic acid) were also combined with V and S to describe the TOM state of degradation and humification (Houel et al., 2006; Dickens et al., 2007).

2.4. Landscape analysis

Landscape analysis was performed with raster satellite images from Landsat 7 satellite imagery at a 1/50,000 scale (Natural Resources Canada (<http://geogratis.cgdi.gc.ca/>). These images were processed using the Geographic Resources Analysis Support System (GRASS) software to determine both the morphology and the vegetation composition of the watersheds. We also analyzed the Canadian digital elevation data (scale: 1/50,000), extracted from the hypsographic and hydrographic elements of the National Topographic Data Base (NTDB, <http://geobase.ca/>). We delimited each watershed using GRASS and the watershed analysis tool. Watershed delimitation was limited to land area draining directly into a lake. Within each watershed, the slope of each individual pixel was computed in order to calculate the mean slope and to classify the different categories of slopes. These categories were regrouped in intervals of 2° (from 0–2° up to 18–20° and 20°+). The maximum likelihood classification method was used to determine seven classes of spectral reflectance based on the spectral signature information for land cover generated by clustering algorithm. This clustering was performed using the six image layers from Landsat 7. From these seven classes, we reclassified the data from on-site validation and ecoforestry maps (scale: 1/20,000—Quebec forestry ministry).

3. RESULTS

3.1. Lakes and watersheds

Results of the spatial analysis of lakes and watersheds are presented in Table 1. Ratios between drainage area

and lake area (DA/LA) vary between 3.70 and 13.93. Lakes 53699 and Vera have particularly large watersheds when compared to their surface area (DA/LA of 13.93 and 12.78, respectively), followed by lakes Eygliers and Joutel (DA/LA of 9.18 and 7.15, respectively). The eight remaining lakes have DA/LA varying between 3 and 5. The mean slopes are higher for lakes located in the Outaouais region (between 3.37 and 6.93), compared to lakes of the Abitibi and Témiscamingue regions (1.23 and 2.99). The proportion of low-slope area (between 0° and 2°) is the highest for Abitibi lakes (77% for Preissac and 81% for Malartic). Additionally, almost half of the watersheds of lakes Desjardins East and Desjardins West are composed of low-slope areas. For the eight Outaouais lakes, this proportion varies between 13% and 39%. The vegetation characterization obtained with GIS analysis reveals that the proportion of deciduous forest varies between 13% and 64%, while coniferous forests represent between 32% and 52% of the total watershed vegetation cover. Finally, the proportion of wetlands varies between 2% and 25% of the watershed.

3.2. Lignin biomarkers composition of sediments

Lignin biomarker measurements are presented in Fig. 2 (mass-normalized yields of individual lignin phenols are provided in Appendix Table A1). Fig. 2a presents the relationship between $\Lambda 8$ and N/C ratios in sediments. N/C ratios in sediments were between 0.057 ± 0.001 and 0.077 ± 0.003 . Like N/C, $\Lambda 8$ is an indicator of terrigenous fraction of OM. We observed a weak inverse relationship ($R^2 = 0.32$, $p < 0.0572$) between the two variables. The $\Lambda 8$ values differed greatly between lakes (from 0.81 ± 0.12 to 2.27 ± 0.24). Fig. 2b presents C/V ratios and S/V ratios observed in sediments. The C/V ratios ranged from 0.19 ± 0.05 to 0.63 ± 0.20 , while S/V ratios varied between 0.07 ± 0.06 and 0.39 ± 0.08 , with increasing S/V values corresponding with decreasing C/V ratios. The 3,5Bd/V and P/(V + S) ratios are presented in Fig. 2c. These two indicators

Table 1
Watershed geographic and topographic properties of the 12 study lakes.

Lakes	Localization lat.-long.	Altitude (m)	Lake area (km ²)	Drainage area (km ²)	DA/ LA	Mean slope (°)	0–2/ DA	4–10/ DA	Angiosperms/ DA	Gymnosperms/ DA	Wetlands/ DA
Joutel	47.12° –77.88°	343	0.66	4.72	7.15	3.60	0.32	0.30	0.45	0.37	0.18
53699	46.67° –77.31°	371	0.30	4.18	13.93	3.58	0.39	0.30	0.28	0.44	0.12
89750	46.45° –77.35°	308	0.44	1.63	3.70	4.87	0.22	0.45	0.28	0.45	0.09
Cather	47.56° –76.48°	370	0.29	1.33	4.59	3.83	0.28	0.34	0.61	0.32	0.06
Eygliers	47.11° –77.71°	331	0.38	3.49	9.18	3.37	0.38	0.24	0.43	0.44	0.14
Hibou	46.51° –77.47°	373	0.40	1.50	3.75	4.32	0.27	0.34	0.46	0.36	0.04
Lachaux	46.57° –77.46°	359	0.34	1.78	5.24	6.93	0.13	0.47	0.44	0.36	0.07
Vera	47.60° –75.56°	391	0.36	4.60	12.78	3.57	0.32	0.34	0.64	0.33	0.02
Desjardins E	46.63° –78.27°	319	10.26	38.84	3.79	2.99	0.46	0.21	0.31	0.46	0.07
Desjardins W	46.63° –78.32°	319	8.88	46.95	5.29	2.98	0.47	0.21	0.23	0.52	0.11
Preissac	48.31° –78.35°	300	129.25	512.91	3.97	1.54	0.77	0.08	0.13	0.50	0.25
Malartic	48.26° –78.11°	298	122.32	610.99	5.00	1.23	0.81	0.06	0.16	0.38	0.21

Lat., latitude; long., longitude; DA, drainage area; LA, lake area; 0–2 and 4–10, drainage area where slope are comprised between 0–2° and 4–10°.

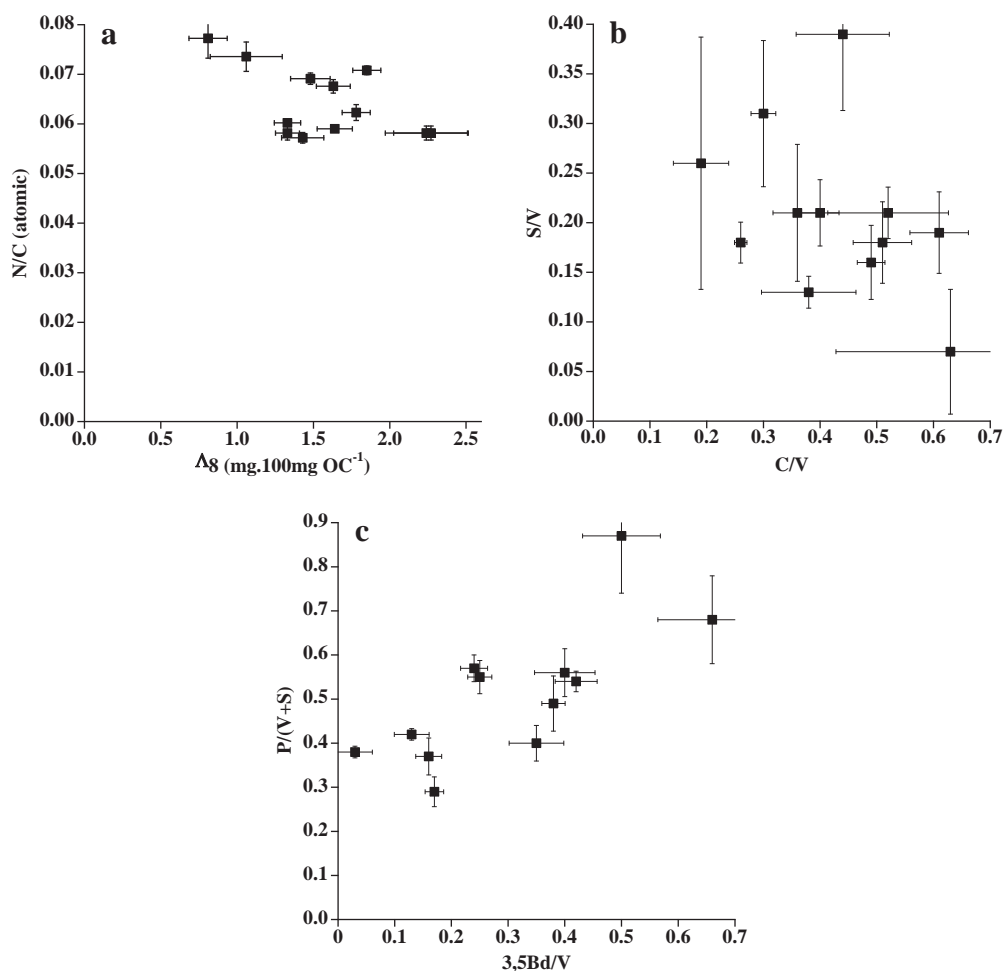


Fig. 2. TOM indicators measured in recent sediments of the 12 lakes. (a) N/C ratios vs. $\Delta 8$ (mg 100 mg OC^{-1}), (b) S/V vs. C/V, (c) P/(V + S) vs. 3,5Bd/V N/C, nitrogen/carbon atomic ratio; $\Delta 8$ sum of vanillyls (V), cinnamyls (C) and syringyls (S); P, p-hydroxyphenols; 3,5Bd, 3,5-dihydroxybenzoic acid.

were positively correlated (P/(V + S) with values between 0.29 ± 0.03 and 0.87 ± 0.13 , and 3,5Bd/V values between 0.03 ± 0.03 and 0.66 ± 0.09).

3.3. Principal component analysis

We applied a principal component analysis (PCA) to our dataset in order to highlight relationships between watershed parameters and biomarkers in sediments. The principal components 1 and 2 had Eigenvalue of 4.60 and 1.97, respectively, and accounted for 73% of the variance (Fig. 3). Thus, the PCA highlighted two major axes. The first axis (X) (51% of the variance) is explained by the variation of the slope, the angiosperm ratio, $\Delta 8$, P/(V + S), 3,5Bd/V and N/C ratios. The second axis (Y) (22% of the variance) is explained by the variation of the DA/LA and C/V. Four major groups of lakes were observed: (1) Preissac and Malartic with low-slope watersheds and highly degraded TOM; (2) Desjardins East and West, 53699, 89750 and Eyglies with median value on the two axes; (3) Cather, Lachaux, Hibou, Joutel, with steeper mean slopes, higher inputs of TOM and watersheds dominated by angiosperms; (4) Lake

Vera, which had a specific location on the Y-axis, with high influence of DA/LA.

3.4. Watershed characteristics and TOM composition in lakes

According to the results from the PCA, we tested all the potential relationships between sediment biomarker records and watershed characteristics. Figs. 4–6 present significant linear or polynomial relationships between molecular biomarkers and GIS data. Fig. 4a shows a significant and positive relationship ($R^2 = 0.65$, $p < 0.002$) between $\Delta 8$ in recent sediments and the mean slope of the watershed. The mean slope also correlated with the composition of TOM in recent sediments, as P/(V + S) and 3,5Bd/V ratios significantly decreased with the steepness of the watersheds ($R^2 = 0.57$, $p < 0.021$ and $R^2 = 0.71$, $p < 0.004$, respectively) (Fig. 5a). The ratio between DA/LA is often used to estimate terrigenous inputs to lakes (Wetzel, 2001; Xenopoulos et al., 2003). However, when plotted against $\Delta 8$, we did not observe significant relationships in sediments.

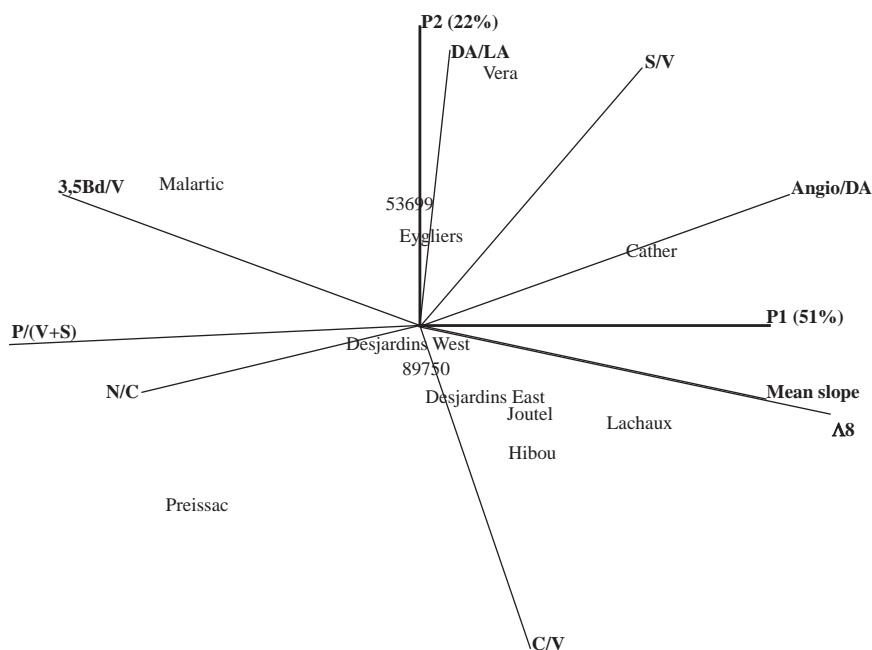


Fig. 3. Plot of the principal component analysis performed on CuO-derived biomarkers measured in recent sediments and watershed morpho-edaphic characteristics. DA/LA, drainage area/lake area ratio; angio/DA: angiosperm area/drainage area.

The GIS analysis allowed us to determine more precisely which parts of the watershed were important contributors of TOM exports to lakes. In this study, the increasing proportion of areas with slopes between 0° and 2° in a given watershed lowers the terrigenous inputs estimated by $\Delta 8$ (Fig. 4b; $R^2 = 0.69$, $p < 0.001$), and these inputs will be more degraded (higher $P/(V+S)$ and $3,5Bd/V$ ratios) in sediments (Fig. 5b). On the other hand, we observed inverse relationships with the increasing presence of areas with slopes comprised between 4° and 10° (cumulative area of classes $4-6^\circ$, $6-8^\circ$ and $8-10^\circ$) and the increasing presence of wetlands in the watershed (Figs. 4c and 6c).

The vegetation composition of each watershed influenced the composition of recent sediments of the sampled lakes (Fig. 6). The presence of angiosperm trees in the watershed influences the export of TOM to the lake, as $\Delta 8$ increases significantly with the abundance of this type of vegetation ($R^2 = 0.44$, $p < 0.019$) (Fig. 6a). A similar relationship is also observed with the S/V ratio ($R^2 = 0.51$, $p < 0.009$ for the 12 lakes and $R^2 = 0.77$, $p < 0.0004$ when Lake Malartic is removed from the dataset, outlier according to Jackknife distance) (Fig. 6c).

4. DISCUSSION

C/N ratios were commonly used in lakes to estimate allochthonous vs. autochthonous inputs of organic carbon (Meyers and Ishiwatari, 1993). However, Perdue and Koprivnjak (2007) have shown that a mixing line based on C/N ratios yields the fraction of terrestrially derived N. As TOM is generally depleted in nitrogen, terrestrial fraction of organic carbon appears to have been underestimated in previous studies (Perdue and Koprivnjak, 2007). N/C ratios are then used in this study to estimate the

fraction of terrestrially derived organic carbon along with $\Delta 8$. There is little variation for the N/C signal between lakes. However, the range of values observed (0.057 ± 0.001 and 0.077 ± 0.003) indicates that the OM found in sediments is primarily derived from allochthonous sources. Indeed terrestrial N/C endmembers range from 0.02 to 0.05 (Goñi et al., 2003). These results are also in accordance with the oligotrophic status of these headwater lakes, as reported by Dufour (2005). $\Delta 8$ is also used as a proxy for the relative contribution of allochthonous OM in sediments, considering that lignin-derived compounds are specific to terrestrial plants (Hedges and Mann, 1979). However, the relationship between N/C ratios and $\Delta 8$ is weak. Whereas, the variations of the N/C ratios are induced by shifts in the balance between in situ production and terrigenous inputs, $\Delta 8$ is influenced by vegetation type and soil processes (Houel, 2003). These two indicators also range in two different scales and it may be that the range of lakes studied here is not sufficient to yield high N/C variations. This result also shows that $\Delta 8$ is a more sensitive tool to assess TOM inputs in lake sediments. In fact, there exists significant variation of $\Delta 8$ values among lakes. For example, $\Delta 8$ in Lachaux Lake is 2.8-fold higher than in Malartic Lake. To our knowledge, it is the first time that such a wide range of $\Delta 8$ values in lake sediments has been reported, which is remarkable for lakes that are only 200 km apart. Previously, such a range of $\Delta 8$ values was only reported for time series variations in sedimentary records (Hu et al., 1999; Houel et al., 2006). These values are lower than those found in lake Washington by Goñi and Montgomery (2000) but are similar to values found by Houel et al. (2006) in the same region as this study. Values for the S/V and C/V ratios are also very variable in the studied lakes, suggesting that gradual changes in types of vegetation influence TOM

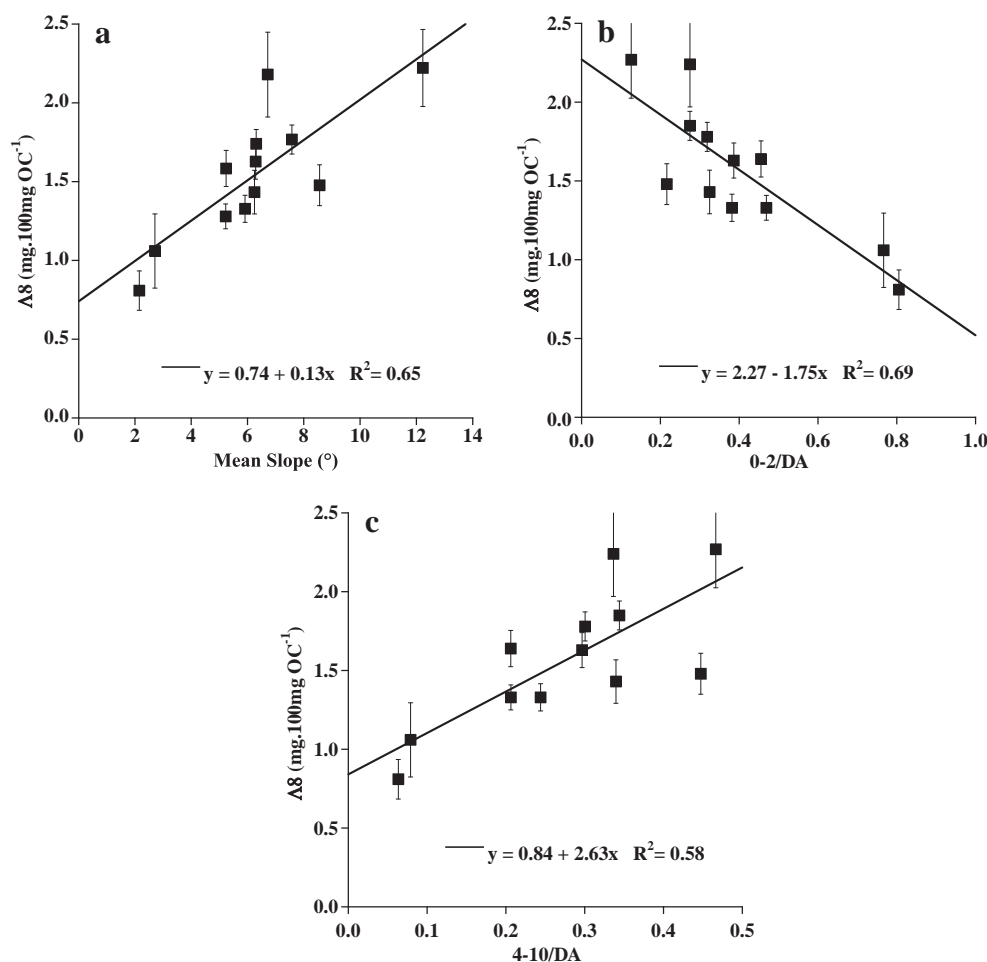


Fig. 4. Influence of watershed slope on TOM fraction estimated with $\Lambda 8$ (mg 100 mg OC⁻¹). (a) $\Lambda 8$ vs. mean slope of drainage area in degree, (b) $\Lambda 8$ vs. ratio of drainage area with 0–2° slope (0-2) to drainage area (DA), (c) $\Lambda 8$ vs. ratio of drainage area with 4–10° slope (4–10) to DA.

inputs. There is no concomitant variation between these two variables. This absence is related to the fact that these ratios are influenced both by the type of source vegetation (angiosperm vs. gymnosperm), type of tissues (woody vs. non-woody) and also differential rate of degradation and fractionation (Hernes et al., 2007; Benner and Kaiser, 2010). The range of values presented in Fig. 2b fits well with values measured in soils from watersheds in this region (Teisserenc, 2009). Soils signature measured previously reported very low value of S/V particularly in spruce and white birch forest (Teisserenc, 2009). This low value of S/V ratio in gymnosperm dominated forest is not surprising as gymnosperms plants do not produce syringyls. In a controlled laboratory study, Hedges et al. (1988) also showed that white-rot fungal degradation of birch wood tends to decrease the yield of total syringyls phenols much faster than total vanillyl phenols. Lake Malartic sediments have the lowest S/V ratios of the dataset and is also the lake draining a watershed dominated by gymnosperm forest and with the lowest proportion of angiosperm forest.

The P/(V + S) ratio is usually used as an indicator of OM degradation. In fact, demethylation leads to a selective loss of methoxylated phenol groups of the vanillyl and

syringyl phenol families. The p-hydroxyphenols are not affected by demethylation, thus, P/(V + S) ratios increase with higher states of degradation (Dittmar and Lara, 2001). The sources of p-hydroxyphenols are terrestrial plants and phytoplankton (Hedges et al., 1988). However, in oligotrophic lakes, the influence of autochthonous OM production on p-hydroxyphenols is limited (Houel et al., 2006). Furthermore, Pn is unequivocally derived from terrestrial plant and a constant Pn/P ratio enables one to determine the terrestrial origin of P phenols (Hedges et al., 1988). In our dataset, we observed a constant Pn/P ratio in the 5 cm of sediments considered. The mean value of Pn/P ratio was 0.12 ± 0.02 , close to the value found by Houel et al. (2006) in the same region. We then considered that most of p-hydroxyphenols were terrestrial derived.

The evolution of the maturation degree of TOM is also recorded with 3,5Bd/V ratios, which has become commonly used as a source indicator for TOM between soils horizons. In fact, 3,5Bd concentrations increase with the advance of plant cells decay. It has been suggested that tannins and other flavonoids are a source of 3,5Bd (Goñi and Hedges, 1995). Results observed in Fig. 2c show that the states of degradation of TOM found in lake sediments

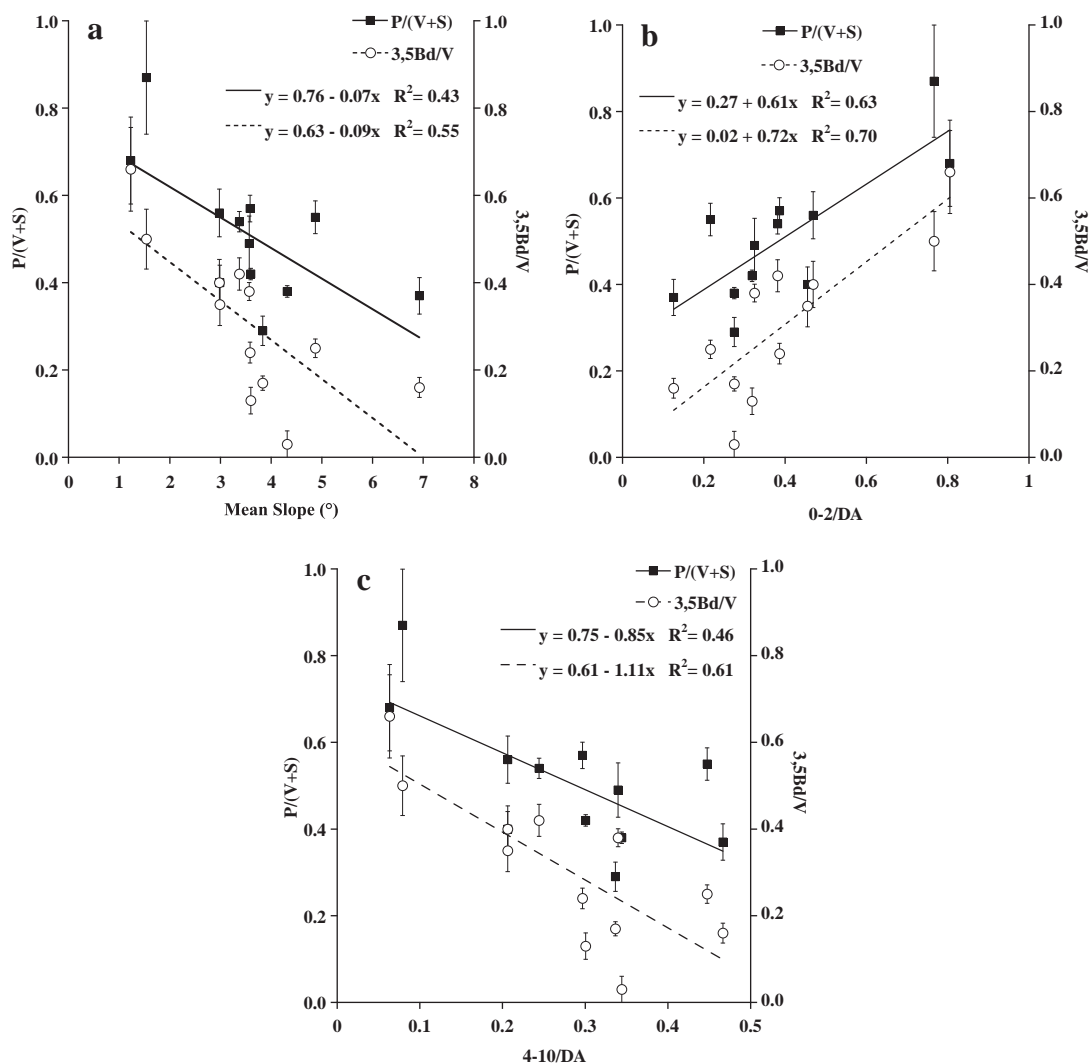


Fig. 5. Influence of watershed slope on TOM composition estimated with P/(V + S) and 3,5Bd/V ratios. (a) P/(V + S) and 3,5Bd/V vs. mean slope of drainage area in degree, (b) P/(V + S) and 3,5Bd/V vs. ratio of drainage area with 0–2° slope (0–2) to DA, (c) P/(V + S) and 3,5Bd/V vs. ratio of drainage area with 4–10° slope (4–10) to DA.

vary greatly between the studied lakes. As P/(V + S) and 3,5Bd/V ratios are related to organic matter degradation processes, we observed a positive relationship between these two indicators.

As previously mentioned, PCA has been used as an exploratory tool to highlight the link between the two matrices of data generated within this study: the watershed morpho-edaphic data and the sediment CuO-derived biomarkers. This analysis enables us to highlight the first principal axis that links topography and/or certain types of vegetation and the degree of OM alteration. The second highlighted axis has a lower relative explanatory weight but still stresses the importance of the DA/LA ratios as indicators of TOM loading. The mean slope of the watershed seems to play a key role in controlling the extent of TOM loading to lake sediments. Indeed, $\Lambda 8$ increases with the increasing steepness of watershed mean slope. The steepness influences the water seepage from soils

(Chang, 2006) and helps to regulate soil moisture conditions (Ogawa et al., 2006). In steep slopes, the runoff will occur mostly on topsoils, where the lignin content is high (Teisserenc, 2009). When the slope decreases, water percolates more efficiently and reaches deeper soil horizons where lignin content is lower (Houel et al., 2006; Hernes et al., 2007).

The decrease of lignin yield ($\Lambda 8$ or $\Lambda 6$) in DOC has also been related to biodegradation and photodegradation (Opsahl and Benner, 1998; Benner and Kaiser, 2010). In our study, we observe that the two largest lakes also exhibit the lowest $\Lambda 8$ values. One may argue that increasing the size of the lake may enhance photodegradation of lignin-derived compounds and then decrease the $\Lambda 8$ signal in sedimentary records. However, no relationship is observed between $\Lambda 8$ and DA/LA, which could be used as an indicator of water and OM residence time within the lake (Wetzel, 2001). To our knowledge, the photodegradation of lignin

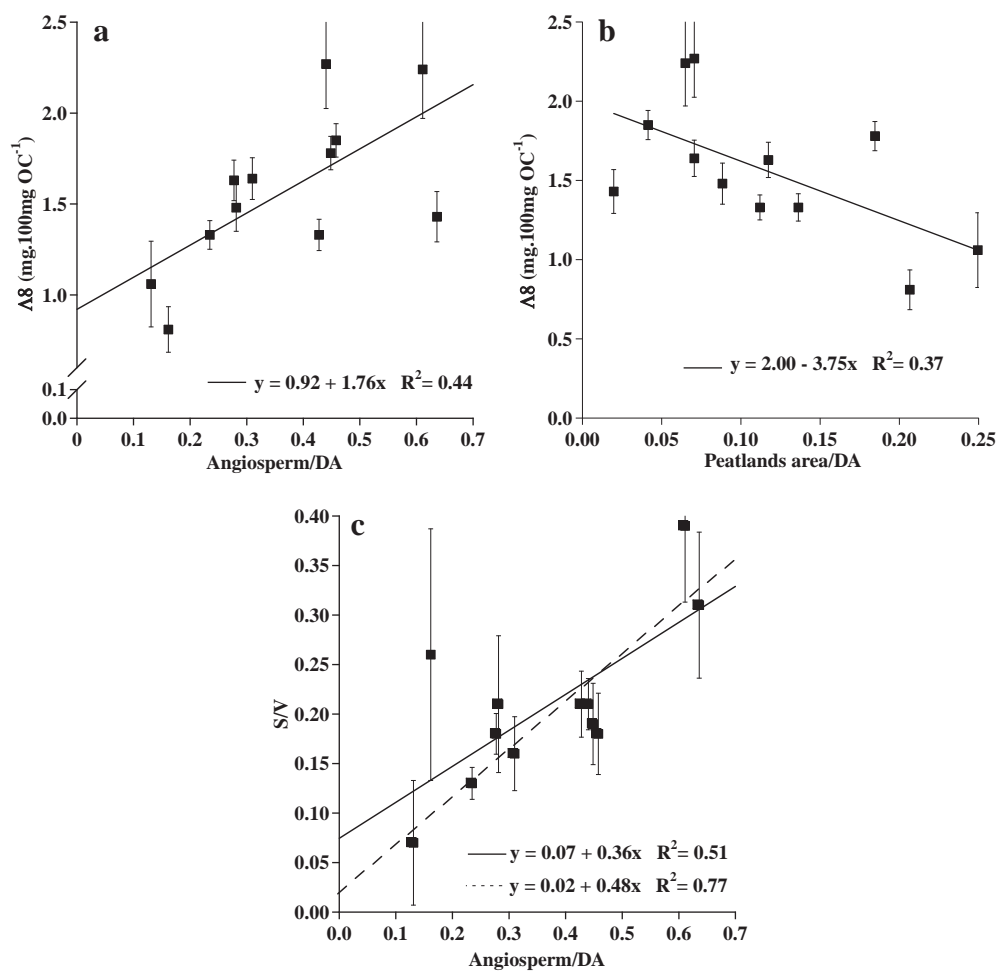


Fig. 6. Role of the type of vegetation cover on the drainage basin (angiosperms and peatlands) in TOM inputs to lake sediments. (a) $\Delta 8$ vs. ratio of angiosperm dominant cover to DA (angiosperm/DA), (b) $\Delta 8$ vs. ratio of peatlands area to DA (peatlands area/DA), (c) S/V vs. angiosperm/DA (dashed fit line: Lake Malartic excluded according to an outlier analysis (Jackknife distance)).

compounds in POC remains unknown, making it hard to conclude on the influence of photodegradation on lignin yields and ligneous compounds ratios in lake sediments.

The use of GIS allows us to determine the range of slopes that drive TOM transfer processes. By compiling slope data at 2° intervals, we were able to determine that low-slope areas (0–2°) act as buffer zones for lignin inputs and by extension for TOM loading to sediments. These zones are commonly referred to as depositional zones (Lal, 2003) and are mainly represented by “ill-drained” areas such as wetlands.

Although TOM in lake water columns is influenced by wetlands, as proposed by Xenopoulos et al. (2003) and Dillon and Molot (1997), the $\Delta 8$ values suggest that they act as a retention zone for TOM in sediments (Stallard, 1998). In fact, here we observed that the increasing presence of peatlands in the watershed lowers terrestrial inputs in lake sediments (Fig. 6b). The compilation of slopes between 4° and 10° (Fig. 4) suggests that these moderate slopes sustain more efficient TOM transfers to the lake.

Beyond these slope-related changes in $\Delta 8$ values, the watershed slope also influences the P/(V + S) and 3,5Bd/V ra-

tios measured in sediments. Watersheds with steep slopes bring “fresher” OM as indicated by the corresponding low P/(V + S) ratios. We also observed such a relationship with the 3,5Bd/V ratios, reinforcing the idea that the relative contribution of TOM from the soil organic horizons increases in steeper watershed.

The vegetation composition also drives the abundance of lignin biomarkers in studied sediments. With the increasing presence of angiosperm stands in the watershed, we observed an increase of TOM in sediments (Fig. 6a). This may be explained by two factors. First, angiosperm stands are found in upland well-drained areas of the boreal forest landscape (Grondin, 1996) and these well-drained areas correspond to steeper slopes where erosional processes are increased particularly for coarser particle. The second factor is that the flux of DOC is higher in deciduous forest than coniferous ones, which would have facilitated the transfer of TOM to lakes and ultimately to sediments (Michalzik et al., 2001). Lignin compositions of lake sediments are also useful for providing information regarding vegetation composition of the watershed. For example, the S/V ratios increase with the increasing presence of

angiosperm stands. Miltner and Emeis (2000) have already hypothesized this link in large-scale environment but without precisely describing the vegetation occupying the watersheds.

5. CONCLUSIONS

This study has significant implications in our understandings of TOM fate in lacustrine ecosystems. The first is that lignin biomarkers analyzed in sediments represent a good integration of watershed-scale processes of TOM and reflect the role of both topographic and edaphic properties of the drainage basin. They stress the role of both topographic and edaphic properties of the drainage basin. Secondly, the combined use of GIS and lignin biomarkers is promising as it allowed us to highlight the role of a specific area of the watershed (low-slope areas) or vegetation (angiosperms). The use of specific lignin biomarkers in continental aquatic ecosystems allows one to precisely describe the source and state of degradation of TOM. These results should help improve our understanding of OM cycling within these ecosystems.

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APPENDIX A

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Table A1

Elemental and molecular composition of recent lake sediments. OC, total organic carbon (mg 100 mg dw⁻¹); N/C, total organic nitrogen to total organic carbon atomic ratio; V, carbon normalized yields of the vanillyl phenols (Vl, vanillin; Vn, acetovanillone; Vd, vanillic acid); S, carbon normalized yields of the syringyl phenols (Sl, syringaldehyde; Sn, scetosyringone; Sd, syringic acid); C, carbon normalized yields of the cinnamyl phenols (p-Cd, p-coumaric acid; Fd: ferulic acid); P, carbon normalized yields of p-hydroxyphenols (Pl, p-hydroxybenzaldehyde; Pn, p-hydroxyacetophenone; Pd, p-hydroxybenzoic acid); 3,5Bd, 3,5-dihydroxybenzoic acid (mg 100 mg OC⁻¹).

Lakes	OC	N/C	V			S			C		P			3,5Bd
			Vl	Vn	Vd	Sl	Sn	Sd	p-Cd	Fd	Pl	Pn	Pd	
Joutel	18.75	0.06	0.27	0.22	0.50	0.09	0.06	0.04	0.58	0.02	0.25	0.06	0.19	0.13
53699	16.14	0.07	0.26	0.24	0.64	0.08	0.07	0.05	0.28	0.01	0.38	0.09	0.29	0.28
89750	23.14	0.07	0.25	0.20	0.49	0.08	0.07	0.05	0.33	0.01	0.35	0.06	0.22	0.24
Cather	16.36	0.06	0.52	0.23	0.49	0.25	0.09	0.14	0.43	0.09	0.20	0.07	0.23	0.21
Eyglie	20.17	0.06	0.18	0.18	0.46	0.05	0.06	0.06	0.31	0.02	0.27	0.07	0.19	0.35
Hibou	14.06	0.07	0.61	0.20	0.29	0.12	0.04	0.04	0.53	0.02	0.28	0.03	0.18	0.04
Lachaux	19.02	0.06	0.27	0.28	0.78	0.09	0.08	0.10	0.64	0.03	0.27	0.08	0.24	0.22
Vera	21.85	0.06	0.18	0.19	0.52	0.09	0.09	0.10	0.25	0.01	0.29	0.08	0.20	0.34
Desjardins East	18.43	0.06	0.42	0.18	0.41	0.10	0.04	0.02	0.48	0.00	0.20	0.04	0.21	0.35
Desjardins West	18.40	0.06	0.17	0.18	0.53	0.04	0.04	0.04	0.33	0.01	0.30	0.07	0.18	0.36
Preissac	2.26	0.07	0.11	0.12	0.39	0.01	0.01	0.03	0.39	0.00	0.26	0.06	0.25	0.31
Malartic	2.39	0.08	0.10	0.11	0.35	0.04	0.04	0.06	0.10	0.01	0.18	0.06	0.21	0.37

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